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Leather:

AN OVERVIEW OF MANUFACTURE

(Part 8)

Discussion

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Leather: AN OVERVIEW OF MANUFACTURE

Content and Structure:

This section includes a summary of hides and skins as raw materials.

Part 1: The removal of unwanted materials and extension of the structure.

Part 2: The introduction of new materials and extension of the structure.

Part 3: The removal of water and reconfiguration to a flat form.

Part 4: Application of the finish.

Part 5: Different types of bovine leathers.

Part 6: Small skins: hair sheep and goat: grain leathers.

Part 7: Small skins: wool bearing sheep: double face, shearling and rugs.

Part 8: Discussion.

Annex.

This Part serves as a review of the whole content of this study, and 30 issues are raised. These are mainly based on frequently asked questions raised by counterparts, and students within formal education. It is suggested that each is considered in turn, then compared with the response that follows.

Being a complex industry, often there is no single answer to any of the issues. Sometimes, the responses bring together information from several Parts, thus providing an expansion of technical detail.

It is clear that more can be said, but leather making is a technology, and not pure science.

The focus of "Overview" is self-study for technicians, but its design enables uses within formal education. If this Part is managed by a moderator with leather making experience, the various issues and responses can serve as base for group discussions.

1: Issue

Hides and skins from cattle, sheep and goat are the manufacturing base for leather. As raw materials, what are their main problems ?

1: Response

Hides and skins originate from animals raised and husbanded for milk and dairy products, wool and meat production.

These are very specific purposes, and do not take into account the needs of leather manufacture.

Various forms of damage can occur during the life of the animal, and at times of flaying and removal from the carcass.

Hides and skins are ultimately a waste product from the food industry.

They are subject to rapid deterioration and decay, unless they are processed very soon after removal from the carcass, or preserved in some way.

2: Issue

What advantages are offered by processing fresh hides and skins, rather than in a preserved state ?

2: Response

Managed correctly, fresh hides and skins can remain free from decay and, with the possible exclusion of ice for chilling purposes, avoid any chemical contamination.

For longer term preservation, salting is a highly effective option, but the salt requirement is high and raises issues of salinity in wastewater treatment. The use of salt in preservation assists the release of grease within the early stages of process too. The leathers may be slightly softer and more relaxed than fresh hides.

In dry salting, the low salt applications are sufficient to inhibit bacterial action in the early stages of preservation, then supported for long term preservation by air drying. This can provide better quality leathers than air drying alone.

Air drying provides excellent long term preservation. The reduction in moisture content of raw skins from around 65% to 12%, reduces weight in transport, hence costs. However, the skins are slow to rehydrate, tend to be slightly firmer than when freshly processed, and can suffer bacterial damage arising from within the drying phase.

Acid pickling options are also an excellent technique for small skins. Processing to the pickled state can be managed by small operations with basic equipment. Pickled skins can be kept for many months, especially if stored at a low temperature. For small skins, where the raw material supply is very spasmodic, this can be a more effective option than air drying or dry salting.

3: Issue

Why is it important to fully rehydrate hides and skins before chemical processing ?

3: Response

Full rehydration enables the most uniform penetration of chemicals during liming that is possible.

If parts of the structure are not soaked properly, then the swelling effects during liming are irregular, and this leads to distortions within the structure.

The reduction of growth marks in the neck areas, and draw or fine wrinkling in the belly parts is not as effective as otherwise possible.

However, if the soaking is too long *(oversoaking)* then there are dangers of the final leather being looser, especially in the belly parts.

4: Issue

Green fleshing – that is fleshing before liming – is often omitted.

What does this operation offer to leather making ?

4: Response

Even if the residual flesh is minimal, it forms a barrier that inhibits an even penetration of liming chemicals into the structure.

In turn, this creates irregularities in outcome that can affect subsequent processes.

Even in the best situations, the structure is not uniform due to variations in thickness, density and deposits of fats. The presence of flesh is yet another unwanted variation, but this can be eliminated.

There is also a reduction in the weight of the load entering liming, hence a saving in the chemicals, and subsequently a reduction in wastewater treatment.

If the recovered flesh is unswollen and in a non-alkaline state, it is more readily used for other purposes.

5: Issue

Hides and skins can be fleshed before liming, after liming, and for small skins even in the pickled state before tanning. The intent of these operations is to remove residual flesh, and to stretch and relax the structure.

What else occurs in limed fleshing that does not take place in the other two situations ?

5: Response

Considerable pressure is needed to hold the hides and skins securely between the transport and grip rollers as the cutting action takes place.

This compresses the structure, and squeezes water containing proteins that have degenerated in liming, fats, hair roots and pigmentation from the grain layer.

It is part of producing a cleaner grain surface.

6: Issue

What are the advantages of limed splitting ?

6: Response

Limed splitting provides a relatively thin grain split of reasonably level substance. This enables a fast and uniform release of residual products in deliming, and uniform penetration of chemicals in bating, pickle and tannage.

Only the grain layer is processed into the tanned state, and this means less weight for processing to this stage. This ensures a significant reduction in chemicals offered to process, and a reduced load for wastewater treatment.

It also means that the thinner grain section is more readily extended in processes and operations pre-shaving.

If the flesh split is trimmed for processing into leather, then the trimmings are uncontaminated by tanning materials. If the splits are not for tanning, then the untrimmed split is suitable for food manufacture, gelatine or bio-gas production.

7: Issue

Why should particular attention be given to the deliming process ?

7: Response

The deliming process is the major step between the change from a high alkali state into acidic conditions used for pickling.

This lowering of alkalinity to near neutral conditions is accompanied by a reduction in swelling, and water is released from within the structure. This water contains proteins that have been solubilised in the liming process. If they are not removed, at later stages they cause adhesions of the fibres and firming.

This process is usually monitored for full removal of alkali by spotting the section with phenol phthalein solution which reveals residual alkalinity as a pink colouration. However, there are two issues that need taking into account:

i] The cuttings need taking from the parts of the skin that are the most difficult to delime: that includes the thicker neck section, particularly where there are growth marks.

ii] Even if the indicators show complete deliming, more time is needed for complete release of the residual proteins from the centre parts.

The process also creates mildly alkaline conditions that suit good enzyme activity in bating. In this process part of the collagen structure is modified to cause a softening effect in the final leather. Both deliming and bating cause relaxation and help the release of pigmentation from the grain layer.

8: Issue

The acid / salt pickle is a major step in the preparation of hides and skins for tannage. Control of pH is essential to manage the penetration of the selected tanning agent into the collagen structure before fixation and tannage.

What is the role of salt in this operation ?

8: Response

If common salt is absent in the acid pickle, then acid swelling will occur. In the shift from neutral to high pH conditions in liming, soaked hides and skins swell by approximately 20% due to water uptake. Similarly, swelling occurs if the pH of delimed and bated pieces is shifted from around neutral towards low pH conditions.

Even if subjected to moderate acid conditions - pH 3.5 to 3.7 - the resulting leather will be firm with a hard grain structure.

The addition of common salt will reduce these effects, ensuring tannage in a relatively non-swollen state.

It is noted that other salts - such as sodium sulfate - can be used to suppress swelling, too, but they also change the properties of the leather.

9: Issue

Acid/salt pickle systems are used in preparation for tanning. They are also used as a method of preservation for sheepskins.

What are the differences ?

9: Response

The acidity of pickles used in preparation for tannage varies according to the tanning system. They are normally based on sulfuric acid with a small amount of formic acid, with added salt to prevent a swelling of the structure.

When pickles are used for preservation, the acidity is much greater *(a lower pH)* than used for tanning, and is based on sulfuric acid and salt. These skins can be kept for significant periods of time without significant change.

These skins normally need depickling as they are very acidic, followed by a conventional acid/salt pickle to suit the tanning technique.

The absence of a weak organic acid in the preservative pickle means it is less likely that mould is an issue for concern, and avoids a softening of the structure.

This softening can be exploited in rug manufacture where wool-retaining sheepskins can be piled for extended periods in the pickled state. The weak organic acid content *(formic, but may include lactic or glycolic acids)* helps compensate for the lack of opening/softening of the structure in liming.

10: Issue

There is no “best” tannage, as they all provide specific properties.

Wet blue leather is very versatile, stable, and has a high shrinkage temperature when fully saturated with water.

But what property makes it so different from other commercial tannages ?

10: Response

Chrome tannage is very cationic, that is, the collagen structure after tanning carries a strong positive charge.

This means that anionic products *(with negative charge)* - most retanning agents, fatliquors and dyestuffs - are fixed within the collagen structure by strong chemical bonds.

This favours a higher uptake of retanning, dyeing and fatliquoring products when compared to other systems.

Lower offers of these chemicals are therefore required, with less wastage as unused products at the end of the process.

This reduces costs in both chemical requirements and the environmental load within wastewater treatment.

11: Issue

The samming operation appears to be a simple means of removing water from saturated leathers after tanning.

It is a relatively slow operation, and unlike fleshing, splitting and shaving does not cut or slice the structure.

Why does it need particular attention ?

11: Response

The objective of samming is to produce a leather in the best state for offer to the shaving operation *(or splitting / shaving if full substance manufacture).*

The structure should be compact, with a consistent moisture content, to maintain good shape retention within splitting and shaving. It needs the correct balance between firmness and softness to optimise the outcome from these operations.

These requirements are controlled by a combination of a relatively slow and gentle compression of the fibre structure, and the final moisture content. Neither of these conditions can be measured accurately, and consistency is managed by frequent inspection.

As the leather is offered to the machine, the operatives should manually open and spread the shanks. This assists the action of the spread roller before application of the samming pressure. This helps to avoid the formation of creases and their compression in the peripheral parts of the hide or skin. If formed, these folds are sliced in either splitting or shaving, and need trimming away as waste.

Where hides have been limed split, the thinner substance can be extended quite substantially by the operatives.

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The feed is normally grain up, and if the out-feed employs a conveyor, this can incorporate quality selection, automatic substance measurement for thickness potential, and area.

In some situations, where hides are limed split, hides are offered grain side down. High pressure can be applied by the spread roller without damage to the grain, even allowing direct feed to the shaving operation.

The base for all chemical and water additions in neutralising, retanning, dyeing and fatliquoring is the weight of the damp leather.

If the moisture content varies, then the amounts of chemicals offered on the actual weight of the collagen will vary too.

12: Issue

Sorting operations usually occurs after samming.

However, it can take place in the wet tanned state too.

What advantage does this offer ?

12: Response

Many tanneries process hides to the wet blue state only, and quality selections may be made while the hides are still wet.

This is labour intensive, and each hide needs manipulation. However, defects such as vein indentations and small scratches are easier to observe in a non-compressed and saturated state, especially under good quality lighting.

The compression applied by samming often leaves a grain impression from the upper dewatering felt, and this effectively masks small grain defects. If the pressure is relatively heavy, then the dewatering causes a whitening of the grain surface, too, and this makes fault detection even more difficult.

This applies to all types of tannages, and is especially important for lighter weight leathers such as sheep and goat skins. After tannage, these are often drained thoroughly to avoid compression, then assessed for grain quality.

If they are to be sammed lightly or samm/set for shaving, inspection can take place at the time of machine offer by the operative. On outfeed, the skins can be stacked manually or automatically into packs according to grain quality.

13: Issue

The advantages of splitting in the limed state have been considered.

What can be gained by processing hides at full substance to the tanned state ?

13: Response

The main advantage is that the maximum options remain available at sorting pre-splitting/shaving for the substance of the final leathers.

This is very important when there is significant variation in substance requirements for a range of different leather types. For example, when making shoe upper leathers for a mix of, say, mens, ladies and children's footwear, which have different substance specifications.

In addition, the accuracy of splitting can be better in the tanned state than in the limed condition. This means that the splitting substance can be closer to the shaving substance, hence less waste in the form of shavings cut away from the hide.

14: Issue

Can splitting to substance be sufficiently accurate to avoid the shaving operation ?

14: Response

This is possible, but splitting is a delicate operation and may not provide the degree of accuracy required. Moreover, there are other issues to consider apart from uniformity of thickness.

The cutting action on the fibres during shaving provides an opening of the flesh side allowing a more even chemical uptake.

In addition, even if only a small amount of the substance is shaved from the flesh side of the hide or skin, the forces applied via the angled cutting blades stretches the whole structure.

Growth lines and wrinkles are extended at the time of cutting, and this results in a lessening of these defects. The grain layer is extended and flattened against the support roller too.

The outcome is permanent improvement with a smoother and finer grain surface.

15: Issue

Why is neutralising such an important process, and in particular for mineral tannages ?

15: Response

The tanned collagen structure carries a mix of negative and positive charges. Before neutralising, leathers are slightly acidic. A lowering of acidity by the addition of mild alkali in neutralising *(a rise in pH)* reduces the positive charge of the structure.

With a reduced positive charge, the less the attractions and slower the bonding with negative charged products – that is, most retanning agents, dyestuffs and fatliquors. This results in a slower uptake and greater penetration of these products into the structure before fixation.

If there is no neutralisation this uptake is too fast. This results in an irregular fixation of products that is limited to the surface of the structure.

If the neutralisation is 100% through the section, then, with a slow rate of fixation, very deep penetration of selected retanning agents can occur.

If the leather is only partly neutralised - say, with the middle of the leather section remaining at the original acidity - the penetration is limited to the neutralised outer layers.

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The neutralising process influences the rate of penetration, location and uptake of dyes, retanning and fatliquoring agents.

Accordingly, it affects the levelness of colour, the firmness, break characteristics, and filling throughout the structure.

16: Issue

Beside the neutralising, what other major factors affect dyeing, retanning and fatliquoring process ?

16: Response

There are six factors to take into account:

1. Management of the charge in neutralising – as discussed *(Issue 15)*.
2. The temperature of process. This affects the speed of the chemical reaction. The higher the temperature, the faster the uptake of chemicals.
3. The time of process. The longer the time, the greater the uptake.
4. The concentration of chemicals in the float. The higher the concentration, the better the uptake of products.
5. The float levels. A greater mechanical action increases the speed and depth of penetration of products into the structure.

However:

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If the float is too low:

i] This can cause poor distribution of chemicals in solution, and prevent uniform contact with the leather in process.

ii] The individual pieces of leather have an increased risk of tangling. Another cause of irregular chemical uptake and penetration.

6. The mechanical action provided by the processing vessel.

i] On rotation, the combination of speed and vessel design influence the stretching, flexing and compression of leather in process.

ii] These are important factors in determining the rate of penetration within the leather structure.

Neutralising, retanning, dyeing and fatliquoring processes are complex. There are numerous combinations of processing conditions, and products that are available.

17: Issue

Do these six factors apply to other parts of wet chemical processing ?

17: Response

All chemical processes are managed by controlling these six factors, although some factors are difficult to change.

For example, the action provided by processing vessels is fixed by design, so change is only possible by adjusting float levels, load weights, and sometimes the speed of rotation. In turn, these adjustments affect the concentration, distribution and penetration of chemicals.

It should be noted that process development takes theory into account. However, the final commercial process is dependent upon progressive trials. Success is dependent upon an understanding of the chemicals used, the way that the plant and equipment is used, and experience gained as the process is developed.

Fortunately, once a process is established, it can be readily controlled to provide a consistent production.

18: Issue

Processing vessels are clearly more than just reaction vessels.

How else do they affect leather manufacture ?

18: Response

Processing vessels apply very significant forces, often for many hours. The pieces are lifted and dropped on rotation, and subjected to continuous stretching, relaxation and compression actions.

These movements depend upon the vessel design, the speed of rotation, the load weight *(there are optimum load weights for all vessels)* and the float levels.

Each time the pieces are stretched and relaxed - from raw hides and skins to the end of chemical processing - a small part of this extension is retained.

This is important, as it is part of a flattening of the leather from the original rounded animal shape.

Defects - such as growth marks in the neck areas and draw lines in the belly section - can be extended and become less prominent.

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However, if the mechanical action is too high, there is a deterioration in quality.

For this reason, tri-compartmental vessels are widely used for retanning leathers shaved to lower substances. This reduces the risk of over-stressing - or even tearing - the structure.

In addition, whenever there is a firming or compacting of the structure during chemical processing, there is the danger of the formation of creases too.

For example, if the mechanical action is too great when the pieces are in a swollen state in liming, then growth marks and other natural fold lines will become more pronounced. It is a reason for pits being used for *(firm)* heavy vegetable tannages.

19: Issue

Stretching and relaxation cycles have an extending effect on hides and skins when applied over many hours at the time of chemical processing.

Does something similar occur in the short time of machine actions ?

19: Response

Every machine operation has this effect. From green fleshing to samm/setting in preparation for drying.

Every time the pieces are stretched, some of that extension is retained.

It is a key part of the gradual change from an irregular rounded shape to the flattened form.

20: Issue

The different processes and operations have significant effects on the final leather properties. How is the full process best managed ?

20: Response

This is the role of the leather technician. It requires an understanding of what is needed to control the chemical process, but also what is required from the various mechanical operations. Close attention to detail is necessary in both areas as changes can be subtle, and may develop over long periods of time.

It is also important to realise that change in any of the control parameters will have an effect. This may not appear significant at the time of change, but may be very apparent the end product.

Inspection, monitoring and attention to detail at each stage is crucial to ensure consistency.

21: Issue

How are chemical processes established ?

21: Response

There are two ways to establish a chemical process, such as a new retanning/fatliquoring combination:

i] A process is introduced by a chemical supplier. This is usually heavily dependent on use of their products. For success, this a “standard” process has to “work” with the existing plant and machinery. Although the process may prove a success in one tannery, it may fail in a second situation because of different conditions. It might be possible to amend the process, but this can be time consuming.

ii] The process is developed “In-house”. This takes into full consideration detailed knowledge of the plant and equipment. Also, a new product may be introduced, but used with selected products that provide known results.

This is the way to achieve the “best” results, but is often a slow process and rarely achieved in a single trial. It needs care and experience - and often time is short !

22: Issue

What are the guidelines for controlling the chemical process ?

22: Response

The detail is outside the scope of this overview. *(see Annex: Leather: THE TECHNOLOGY OF MANUFACTURE)*.

However, there are critical conditions that set limits to what is possible before pieces are tanned and stabilised.

In liming, high but safe alkali conditions at pH 12.4 are provided by lime, although slightly higher alkalinity *(higher pH conditions*) from use of sodium sulfide can be tolerated for relatively short periods of time.

On the acid side – during preparation for tanning – The pH may vary between pH 2.5 and pH 3.0. These are not extremely acidic conditions, but acid swelling must be supressed by the addition of salt to the process.

However, under both sets of conditions, the skin becomes very sensitive to temperature. Safe working conditions are generally taken as 25C: higher temperatures can be managed, but control is very sensitive.

Damage is guaranteed above 30C, starting with breakdown of the sensitive grain layer. And this applies too when warm water is used for washing limed goods, or added in preparation for deliming/bating.

Under mildly alkaline conditions – such as within soak (+/- pH 10.0), or after deliming (pH 7.5 to 8.5) the limits are probably best taken as 35C.

The other factor to take into account is the mechanical action *(Issue 18)*. In particular, when the hides/skins are firm and inflexible in the soaking process, when swollen in liming, during lime washes, and commencing deliming. Movement should be sufficient to move goods in the centre of the pack, but minimise folding/creasing and possible abrasions to the grain layer.

23: Issue

How does the samm/setting operation affect the outcome from drying ?

23: Response

This operation is a combination of samming actions to remove water, and setting actions to extend the leather. The degree that the leather is extended on setting *(the strain)* varies according the moisture content:

i] The wetter the leather from the samming action, the greater the strain that can be developed. However, as the leather relaxes before drying, there is a loss of this strain.

ii] The lower the moisture content after the samming action, the less the strain from a given load, but the longer this strain is retained.

Pressure affects quality too. If the samming pressure is too high, the structure becomes compressed. The leather becomes firmer, and the break may deteriorate.

For this reason, small skins for very soft leathers are often piled to drain to avoid compression.

High pressures from samming pre-shaving can cause problems too. Although thoroughly wetted in subsequent wet chemical processing, compression effects tend to persist.

24: Issue

Pressure is needed in samm/setting for best presentation to drying operations.

This makes the structure more compact and causes fibre adhesions.

Is it possible to minimise achieve the objectives of samm/setting, but with reduced fibre compression ?

24: Response

Wet stretching or wet staking can provide a loosening of a compacted structure, and if used correctly, without causing a deterioration in grain break. This technique can be used after samm/setting and before drying to causes a fibre separation and relaxation throughout the fibre structure. It is also accompanied with a stretching action for area increase.

Similarly, it can be used after a short vacuum drying to overcome the effects of fibre compression.

This loosening is coupled with a softening, and appears to improve the release of water during evaporation drying too.

The operation is not limited to drying areas.

It is used to open the flanks and extend vein marks pre-shaving, and also for softening within finishing. It is widely used in automotive leather production where it can be readily incorporated into machine linkages.

25: Issue

What are the effects of strain and compression within drying operations ?

25: Response

If a particular leather is:

i] Dried without any compression or extension, this will provide the softest result that is possible. The break will be fine, but the leather will be rounded in the flanks parts and not lay flat. It will be plump and provide the lowest area yield.

ii] Heavily strained throughout drying - such as in toggling - the leather will be harder, have a coarser break, and be flatter. The area will be greater, but coupled with a lower substance.

iii] Subjected to moderate strain and compression - such as when part dried in vacuum drying - followed by tension free hanging, produces effects between [i] and [ii]. The vacuum drying phase will provide flatness that is retained through tension free drying.

However, if the compression is too great on vacuum drying, coupled with a high temperature, then the grain can be over-compressed resulting in a poor and splintery break.

26: Issue

What is the role of temperature in drying operations ?

26: Response

The compressions and strain developed in preparation for drying, and within drying, influence the leather characteristics as discussed.

Regardless of the drying method used:

i] If low temperatures are applied throughout drying, the resulting leathers will tend to be softer and have a finer break.

ii] If higher temperature are used, the leathers will be harder, and have a coarser break and handle.

With the exclusion of vacuum drying, water removal by evaporation is strongly affected by the air temperature. However, if the temperature is low, with good circulation, and removal of air from the system, a rapid drying can be achieved by managing the relative humidity.

An equilibrium between water retained throughout the leather structure, and the moisture levels in the air (relative humidity) develops, and this prevents over drying.

27: Issue

Can softness be controlled by staking operations alone ?

27: Response

Considerable softening can be achieved by vibration staking at an optimum moisture content. However, the properties of the leather are strongly influenced by the procedures used before staking.

If too much mechanical force is applied, the leather may soften, but this is at the expense of the break characteristics.

For the best results, all of the processes and operations within leather making should be in balance.

28: Issue

The objective of finishing is to enhance and protect the leather surface to customer requirements.

Why do the properties of leather change so much within finishing ?

28: Response

There are many reasons for change, and the combined effects can be considerable.

As finish is applied, the grain structure is wetted and penetrated for surface bonding. This results in grain swelling and a coarsening of the surface.

Both the grain layer and finish films needs plating/rolling to provide a smooth surface. This requires a combination of heat and pressure, but this causes a compression and hardening of the leather structure too.

The properties of the final leather are influenced by the properties of the finishes applied. Most finishes are continuous films which are different in terms of elasticity/plasticity to crust leathers.

As water is introduced as various wet finish applications are made, drying operations are required. However, water removal is not just limited to the finish film. The leather is dried, too, and this loss of moisture from within the leather causes a hardening of the structure.

Additional:

The objective of "Overview" is to:

i] provide a broad technical study for a complex industry.

ii] establish factors common across an array of different leather types.

iii] highlight specialisation demanded by different raw materials and end-uses.

There are two important areas that lay outside these matters. These are acknowledged as issues 29 and 30.

29: Issue:

Health and Safety matters

The photographs set down in "Overview" were taken between 2000 and 2022. They were mainly selected for insight into certain technical aspects of leather making. However, some of the earlier images do not reflect current good practice in matters of health and safety.

In particular, full protective equipment for operatives should be provided and used, with all issues of health and safety considered of prime importance. Considerable information, expertise and equipment is available to address these issues.

30: Issue:

Recycling and regeneration of residual chemicals from manufacture, the treatment of solid and liquid wastes, energy and water savings.

Matters associated with sustainability are of high importance, and in particular, need addressing as part of chemical processing. This involves careful selection and best use of chemicals, reuse of residual chemicals if possible, and responsible treatment of solid and liquid waste.

These are major innovations, and the leather sector is at the front in these particular issues. A considerable amount of literature is already available for study.

It is noted that as "Overview" was finalised, a more detailed study was started. This is entitled "Leather: THE TECHNOLOGY OF MANUFACTURE" *(see Part 9: Annex),* and is intended for leather technologists.

One objective is to address these issues of sustainability within leather making practicalities.

Continues as:

<u>Leather:</u>

AN OVERVIEW OF MANUFACTURE

(Part 9)

<u>Annex</u>

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