

Unique wet end technologies offer sustainable competitive advantages in automotive leather

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New schemes and technologies increasingly promise to give the car-less majority vehicle access and increase usage overall that will subject leather to higher wear. Key innovative wet end products and processes are covered from soaking to crusting to show how performance can be improved together with increased sustainability. A “critical mass” point has been reached where these products, combined together across wet end processing, are able to offer automotive leather producers not only individual solutions to technical challenges but coherent sustainable competitive advantages, already proven and adopted by leading tanneries, helping to keep leather relevant and supporting the future of our industry.

Leather, the present and future material for mass transport applications

The average car is composed of ~28,000 parts made from thousands of raw materials⁽¹⁾. With a long successful history supplying multiple performance materials to the global automotive industry, Lanxess has a profound understanding of this sector.

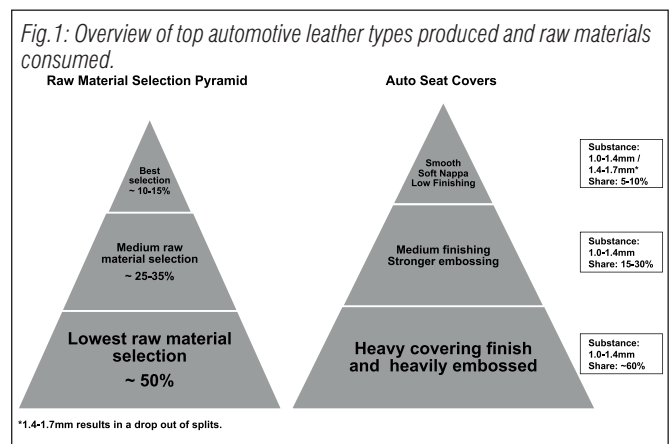
Today, increasingly common vehicle ownership schemes e.g., car share, are giving access to cars beyond those that cannot afford their own car (> 80% of the population). A top desire after housing has traditionally been a car, but however, for many younger people living in cities today this priority was either reduced or taken off the list. Shared cars are a new growing transportation segment which needs to be understood and considered. The consequences of covid-19 on the balance of public transport utilisation, the traditional segments of owned or leased cars versus the new growing one of shared cars must be seen. The utilisation rates of shared vehicles are expected to be high; they will not be sitting idle on driveways that most people do not have; thus, the seating and other internal contact components will be subjected to higher wear. Similar to even budget airlines, trains and shipping, etc., that choose leather because of its durability, economy and safety etc., so too will the growing car share businesses come to exactly the same conclusion and the world’s “ultimate sustainable material” will also return to its upward growth trajectory in this sector.

In 2016 approximately 1.35 million people died on the roads⁽²⁾. Tomorrow, stress free and most importantly safe “driverless” cars will lead to the removal of the current inefficiencies and obstacles (like traffic lights for example) thus more efficient road utilisation will ensue and more people will increasingly choose this mode of transport. Productivity increases, not only cost savings, will also be a

huge draw, instead of the drudgery and fatigue of driving, people will be able to work, socialise, or even sleep on longer journeys using off peak times, all leading to increased importance and use of leather in vehicles. Above and beyond its economic durability, highly desirable and unique aesthetic/haptic, safety and comfort characteristics, leather is also indispensable in automotive applications due to its structural flexibility, and performance profile. To secure the future of leather in such automotive applications we need to maximise its performance and simultaneously improve sustainability.

Topical physical technical performance challenges and issues

Only a relatively small number of large cattle hides are “flawless”, something the automotive industry always seems to seek particularly for smooth articles with a natural





appearance. In reality, a variety of raw materials, bulls and cows, different weight classes and with varying degrees of “natural imperfections”, have to be used. An overview (Fig. 1) is given of the top automotive leather types produced in the world and the top raw materials consumed in their production.

With leather, especially regarding physical properties, it is a complex interlinked area and processing must be carefully controlled to avoid issues arising with potentially serious consequences. On visiting one of the top five auto-leather upholstery OEM component manufacturers, when asked what the single biggest technical challenge they had with leather, expecting the answer “looseness”, they replied “bagging”. (Bagging is where after stretching it does not return to its original dimensions after the load is removed.) If this appears after actual use in vehicles, it results in a catastrophic return of complete seating units to the manufacturer. It is vital when flat leather is transformed into a new component shape that the correct process and conditions are used. In the principal market, footwear upper, it is well documented how leather is easily and permanently lasted by heat setting e.g., with advanced conditioning HVA (High Velocity Air) machines at up to ~120°C (or Near Infrared) followed by vacuum chambers for moisture removal. A dome plastimeter is used for assessing the plasticity or “set” properties of leather (and to check the performance of heat setting machines). In shipping containers temperatures can easily reach 55°C and relative humidity (RH) exceeding 80%, so a high degree of permanent set is important from the very start, let alone after years of serviceable life in the final article. Set should be ca. 80-85%. However, in automotive parts, leather treatment appears more variable and more “covert”, although tests, e.g., CEN/TS14689 “Determination of bagginess...” suitable for upholstery leather are known. Temperatures used in processing have been reported up to 220°C and even hot air guns have been seen where ~500°C localised temperatures are reached. This can have serious implications for the leather, the finish and physical performance properties and should be avoided. The new shape formed should be maintained throughout its serviceable life and be resistant to new forces, for example, high in-vehicle temperatures and stresses so the leather needs to be correctly manufactured,

not only to avoid bagging.

As expected for an engineering environment, physical properties of leather in OEM specifications outnumber chemical ones by about 5:1 (Fig. 2).

Leather uniqueness comes with certain challenges, namely topographic, stratigraphic variations and fibre run, etc. Machinery and drying techniques have progressed in automotive leather manufacture but the inherent variations in the substrate have not been overcome so the best opportunity we have today to increasingly achieve the required performance, and uniformly, are with the new advances in chemistry. Varying degrees of elasticity (recoverable deformation, an extreme example is rubber) and/or plasticity (permanent deformation) can easily be achieved with leather depending upon its treatment, thus the risk of bagging can be eliminated. Virtually every OEM supplier has requested “high performance crust” (naked/no or low finished more natural appearing leather) and although today this is not possible, the drive to make incremental steps towards such goals means that we need more than ever to look at ways to enhance the performance of the underlying substrate itself. Covid-19 has also presented new opportunities: transport leather with its smooth almost continuous finished surface film presents an easy to disinfect and cleanable “barrier” to ingress in comparison to other highly open, hyper-porous and absorbent textiles.

Traditional versus state-of-the-art beamhouse processes

Raw hide possesses the highest physical strength and any processing step, chemical or physical, that causes a change in the structure of skin has an effect on it. Physical properties, including elasticity, are profoundly affected by beamhouse processing. Physical properties deteriorate post slaughter due to natural autolysis and proteolytic activity that cannot be stopped and, therefore, traditional lengthy soaking processes reduce leather quality. Physical properties are further reduced by dated liming processes that rely on high alkalinity and strong swelling to achieve fibre splitting/“opening up”. Alkaline hydrolysis, pH gradients, excessive osmotic and lyotropic swelling with its peptisation effect where even strong covalent bonds are possibly broken (it is remarkably easy to under- or over-lime) and all these phenomena reduce physical performance and cause looseness too. Attempts to control this swelling with additives e.g., amine (or buildup of these in recycling), or organic sulfur based swelling regulators, can result in additional problems e.g., odour, worsening effluent and sustainability issues.

Although generations of tanners used lime, it was not until the 1980s that the process function and its effects on key constituents HA (Hyaluronic Acid) and DSP (Dermatan Sulfate Proteoglycan) was really understood. Tanners have long desired a solution to this conundrum in how to:

- reduce processing time
- improve leather quality/performance and
- overcome effluent/sustainability issues like sludge (1kg lime generates ~2.5Kg sludge) sulfide, salt and COD simultaneously.

The revolutionary patented X-Zyme* system was first introduced in 2013⁽³⁾. Now Peltec X-Zyme SLR (with the ideal activity pH of 9.0-9.8) a non-collagen active glucanase enzyme, starts lime-free fibre splitting/“opening up” of the fibre bundling of the DSP in a similar way that lime is doing but in soaking, already reducing process time and

Fig.2: Examples of auto-specification types.

Physical

Looseness	Finish adhesion
Tear strength	Rub fastness wet / dry
Veininess	Seam fatigue
Thickness	Martindale Test
Thickness of finish	Taber test
Density	Shrink behaviour
Tensile strength	Dirty / oil repellency
Elongation at break	Soiling and cleaning behaviour
Load-displacement curve	Stick slip behaviour
Stitch tear	Metamerism
Stress strain curve	Resistance to sun & hand creams
Elongation and return	Burning behaviour
Static / permanent elongation	Emissions
Bending force	Fogging
Water resistance	Formaldehyde
Sweat resistance	Potential for mold growth...
Permanent folding behaviour	
Hydrolysis resistance	Chemical
Heat resistance	Smell/Odour
Light resistance	Grease content
Water vapour transmission	pH value & difference
Ageing resistance	Chrome content...
Colour stability	



eliminating the reduction in physical performance caused by the old lime processes. Furthermore, it increases sustainability (50% less water, ammonia and COD reduced by 20-35% and ~40% respectively). By replacing lime with this non-proteolytic (non-collagen) active enzyme, instead of a protease, there is zero risk of looseness or “nubuckation” and you get the maximum retention of physical properties. The tanners not yet benefiting from these advantages tend to be those that were pushed by others to use proteases for liming and got burnt with loose and grain damaged leather. Remnant hair, especially short hair was a persistent quality challenge and even relatively small defects like this can contribute to costly poor cutting coefficients. A patented enzyme Peltec X-Zyme U⁽⁴⁾ uniquely ensures the rapid degradation of the pre-keratin in the basal membrane so that both long and short “winter” hair are effectively removed [with reduced sulfide usage ~45% (hair burn) and ~25% (hair save)]. OEM's want uniformity for high cutting yields but traditional beamhouse processes with alkaline swelling emphasise growth marks, neck wrinkles and belly draw. By avoiding this with the successful patented enzymatic system, the leather is more uniform and valuable.

Post liming: deliming, bating and pickling key points

With traditional liming, deliming is absolutely critical as a high angle of fibre weave (poor physical strength) can also be processed induced if swollen in liming and not properly delimed⁽⁵⁾ leading to poor physical strength. For optimum leather performance, deliming must be uniform, complete and carried out with ammonium-free products for smell, effluent and sustainability issues.

The latest industrially produced microbial enzymes are highly specific and give the benefits of animal extracted pancreatic enzyme type results like full flanks, tight grain and optimised physical performance but without the unwanted side effects of “wild-mix” animal extracted enzymes. These should be non-elastolytic so give no negative effect on veins and as well as ammonium-free for better sustainability.

Traditional pickling is time consuming and can reduce leather performance due to acid hydrolysis, but simply substituting it with masking systems can lead to reduced chrome fixation, negatively affecting physical properties.

Hydrolysis inhibition with Blancorol HP speeds up acid penetration, reducing process time and maintains leather performance. Reduced acid swelling leads to a ~44% reduction in salt use and increasing sustainability⁽⁶⁾.

Tanning increasingly in focus

With traditional beamhouse problems largely tackled, tanning comes increasingly and unfairly in focus. Although it is true traditional chrome tanning can waste approximately 40% of the offer, today a high exhaustion system with Blancorol HR can achieve a top LWG score with a sustainable uptake of over 97% and tighter leather as a result. Chromium is infinitely recyclable.

Certain physical properties of pickle-free polycarbamoylsulfonate or (PCMS) X-Tan tanned leather can be around double that of conventional wet white. Attempts to maintain this through retanning could be a major step forward for automotive leather. Sustainability profile of this AOX-free, non-sensitising product is also improved as any excess tannin hydrolyses to non-toxic, easily biodegradable substances, the TDS is reduced by about 75% and chlorides

by about 99%⁽⁷⁾. This eliminates potential issues concerning the application of aldehydes in tanning leather. Tanners have reported that the longer aldehyde “tanned” intermediates are stored the looser it becomes, probably due to the reversible Schiff-base reaction/hydrolysis unlike PCMS which fixes covalently and is more resistant to hydrolysis but gives biodegradable leather. PCMS tanning, followed by a high exhaust organo-chrome self-basifying retanning agent Blancorol RC gives a leather very similar to full chrome but tighter and with a dramatic reduction of chrome in the effluent by a factor of ~10, plus metal-free shavings leading to a massive improvement in sustainability.

The importance of preservation

Irrespective of the tanning used, if the leather is wet, physical performance can rapidly deteriorate due to microbial action, which may initially seem invisible. However, it can replicate exponentially during storage and/or shipping. The quality of leather intermediates are given the maximum protection with the world's first patented eutectic and Lanxess' most comprehensive fungicidal system Preventol U-Tec G with the broadest spectrum effect. This low toxicity, solvent and emulsifier-free product reduces emissions and is biodegradable in the effluent improving sustainability⁽⁸⁾.

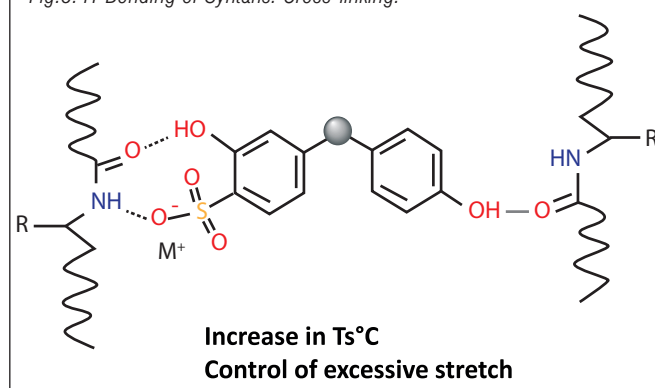
Retanning: Neutralisation, syntans and vegetable-free trend

Neutralisation is often not given enough attention but is fundamental to retanning. Using a unique high fastness ideal buffering profile product, Tanigan PAK avoids sudden pH shifts and ultimately results in more uniform physical properties and performance. It also modifies the I.E.P., (Isoelectric Point) allowing retanning at lower pH, giving tighter leathers and reduces both chrome leaching and alkaline salt usage.

Automotive applications usually demand high fastness and low residual monomer contents, which is why Lanxess has focused on the development and manufacture of high performance polymers that includes Tanigan “syntans” which are also legally defined as polymers. Syntans are still completely indispensable today because they eliminate excessive stretch and elasticity through cross-linking (important to eliminate bagging) (Fig.3).

We are being increasingly asked by our customers for “vegetable-free” solutions, and these can only be largely replaced by syntans. Five of the most commonly reported reasons underlying this trend include:

Fig.3. H-Bonding of Syntans: Cross-linking.





- (i) higher affinity veg- tannins reportedly result in greater area loss
- (ii) naturally highly variable seasonal (heterogeneous) veg- tannins believed to in turn increase the variation in leather character, properties and performances
- (iii) veg-tannins have clearly demonstrable lower fastness to light and heat, including Tara which is surprisingly poor and
- (iv) veg-tannins naturally contain unwanted “other” products classed as “non-tannins” (up to 50%), and comparatively worse COD and water consumption.

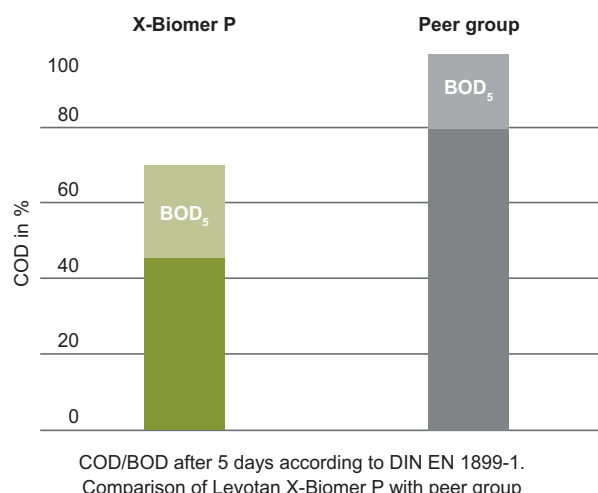
These non-tannins are typically polyphenols of low molecular weight (Mw) ca., < 500, problematic sugars and a variety of acids and salts which can negatively influence the character of leather and can play havoc with other retanning and dyeing materials depending upon content. Some customers have asked to avoid insoluble particles (Mw ca., >6,000 in veg-tannins) which have reportedly contributed to problems, such as finish adhesion failures. Veg-tannin solutions are colloidal in nature, containing particles from low molecular weight compounds that are too small for effective cross-linking, to high molecular weight compounds which are either insoluble or too large for cross-linking with polypeptide chains. Only the particles in the range of ca., 500 - 3,000 Mw are likely to associate with protein molecules. Our customers, supplying industries in a precise engineering environment, are increasingly demanding products that lead to higher leather uniformity and reliable, repeatable and robust processing. Just as natural “wild mix” enzyme extracts have largely been replaced with industrially produced highly specific enzymes, so too are natural sourced “wild mix” tannins under similar suspicion.

In direct contrast, our precisely tailor-manufactured syntans are made to defined particle size distributions and in addition have active product contents of virtually 100%. Any coincidental claimed properties like “CrVI scavenger” of certain variable veg-tannins have been reliably replaced by industrially produced products where, in this case, the activity is now both totally reliable and easily measurable e.g., Tanigan SR-C01 and/or Relugan RV. Tara (*Caesalinea Spinosa*) based on galloylated quinic acid, a hydrolysable (or pyrogallol) tannin, has been applied in automotive leather with a mesh of ca. 150-200. The product must be de-ironed and not exposed to iron in leather manufacture otherwise it will strongly discolour turning the leather dark purple-grey. In contrast, selected Tanigan syntans do not react with iron. As correctly predicted in 1999 by Dr. Magerkurth, “offer of conventional products, especially vegetable extracts will be minimised, to keep the advantages of polymers”⁽⁹⁾. One of the, if not the, “last frontier” for replacement syntans in automotive leather is arguably print definition and/or retention. Whilst this may not be achieved by one single syntan currently, one of the closest has proven to be Tanigan FT which, if used in conjunction with the appropriate supporting resin, adequate embossing properties are possible.

Resins a mixed history in automotive

Every tanner knows to maximise cutting yield the application of high Mw resins, to selectively fill the flank/belly areas, is necessary and was common practice in auto-leather manufacture for decades. However, genuine resins all involved formaldehyde in their manufacture so could not be

Fig. 4. Lower COD of X-Biomer vs. Peer Product



certified as 100% free of it. The initial chemical industry response was to reduce to a minimum the formaldehyde added, maximise polymerisation and/or add scavengers, but the key property, the selective filling, was either significantly reduced or even completely lost. This conundrum was solved by the development of the first genuine resin that was entirely free from formaldehyde in its manufacture Retigan ZF/Plus⁽¹⁰⁾ and later also by patented functionalised biopolymers with greater sustainability X-Biomer R/RX Liq.,^(11,12) both of which now fully substitute amino resins in auto-leather production.

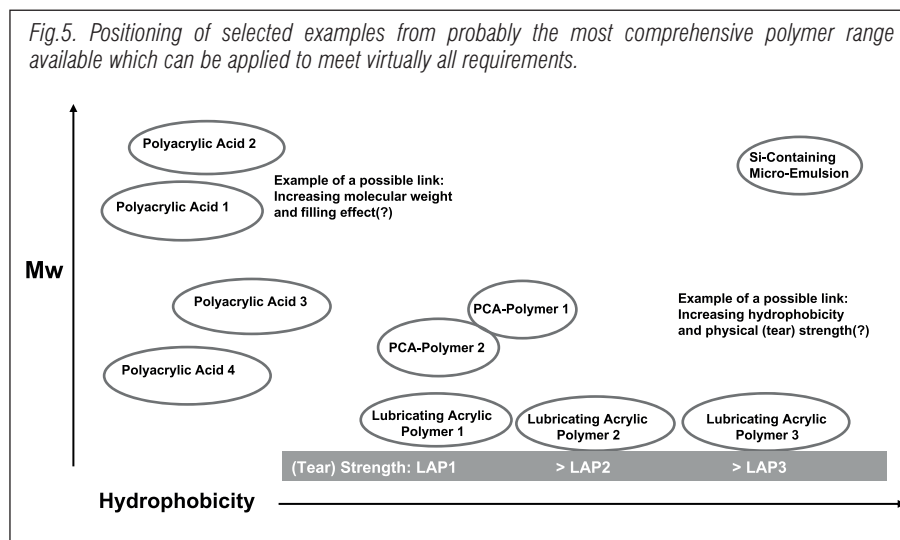
Acrylic and non-acrylic polymers

There is no doubt that acrylics contribute to high performance auto-leather, but we are being increasingly asked about sustainability. First, being highly effective, they only constitute a low single digit percentage of the total retanning. Second, with the recent introduction of the amphoteric Levotan AM the efficiency of the whole retanning has been increased and COD reduced by 40-50%⁽¹³⁾. Thirdly, our patented X-Biomer bio-polymer technology adds renewables to the equation along with decisive advantages such as a less rubbery, more natural leather character and increased sustainability including better biodegradability and reduction in COD (Fig. 4).

The chrome tanning “elasticity” is maintained by the application of acrylics and although some “recoil” is recommended, they are not used alone as this phenomenon needs to be controlled and are limited to filling as they do not cross-link/increase shrinkage temperature. With customers increasingly seeking softer and lighter weight (thinner) leather, these factors can increase the risk of excessive stretch and bagging. We offer a comprehensive range of retanning polymers, both non-acrylic and acrylics, and with the range of leather properties they are able to manipulate, they are well positioned on a variety of parameters against which they can be measured, just two examples of which are given in (Fig 5).

Automotive leather softening technologies

Use of certain conventional fatliquors can quickly lead to “over fatting” giving for instance, patchy dyeing, darker



flanks, and increased specific weight. Lubricating polymers are low to medium Mw, mainly linear, and hydrophobic which gives them softening ability. They are amphiphilic i.e., contain both polar and non-polar groups, like a surfactant. Their performance is strongly affected by composition, Mw and pH and are mainly acrylic or bio-mimicking modified PCA-polymers (Polyamide Carboxylic Acid) based. These are self-emulsifying and are completely free of sulfonic acid groups. Emulsifiers in traditional products can contribute to fogging/TVOC. Distinct advantages also include low specific weight, high exhaustion/low migration, fixing with strong coordination and ionic bonding (unlike fatliquors by Van der Waals - the weakest that can lead to migration and looseness). It can often be heard "everything that fixes reduces tear strength" but importantly these lubricating polymers can actually increase tear strength, whereas over time physical strength of leather traditionally fatliquored can deteriorate and even result in problematic odours. These polymers are highly efficient because they can reach fibril level but at pHs that might not favour tightness, so they are used in combination with complementary retanning agents which enable a lower application pH. From a sustainability point of view, they have excellent exhaustion approaching 100%. Fats and oils burn, so by substituting these with softening polymers, like Levotan L/LB in transport applications, flame resistance is dramatically increased obviating the need for bromine-based products, safety first⁽¹⁴⁾. A new patented silicone-containing micro-emulsion Levotan WS

incorporates coordination functionality, cannot migrate and easily reaches unaided the fibrillary level⁽¹⁵⁾. Softening polymers help to reduce the COD load and thus contribute to sustainability. Like harvested "wild mix" natural enzymes that have been replaced with industrial standardised ones, so too natural "wild mix" variable seasonal fatliquors are also increasingly under suspicion as contributing to variability in auto-leather. As correctly predicted in 1999 by Dr. Magerkurth, "...the application of softening polymers will also increase. This will be mainly at the expense of fatliquors ...because of insufficient fastness properties, oxidation effects and questionable availability in future"⁽⁹⁾. With our extensive acrylic and non-acrylic softening polymer products, we offer probably the most comprehensive and versatile range on the market.

The critical mechanical steps

Tightness (looseness avoidance) is usually the single most important criteria for automotive leather and mechanics play a critical role. Moderate and controlled drying conditions are essential to ensure sufficient softness is maintained at this step, to prepare the leather for staking/milling and thus avoiding the "chicken wire effect". Wet toggling is harsh and, therefore, not recommended for smooth articles. The most common type of drying is vacuum followed by hanging, usually on overhead conveyors to finish the process. Milling in the crust step is necessary for making smooth, soft leather and a pre-staking before this is essential to prepare the leather. Subsequent staking is recommended to help promote a smooth grain again,

although some use re-toggling at this stage to attempt to recover area. Increasingly common is the so-called "TAIC"-system working without vacuum drying, avoiding the grain coming into contact with a hot metal plate, so it is argued to be a more moderate treatment for the grain, which is beneficial, especially for chrome-free leather. The TAIC drying is preceded by the Bauche machine that has a strong setting out action combined with a wet stretching (staking) effect, both of which reduce the elongation. The idea of this system is to dry under conditions in which the leather cannot shrink too much. Excessive shrinkage reduces yield and impacts sustainability and can build up the risk of elongation, even some degree of bagging. ☹

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Acknowledgements: Franz Heinzelmann & Felix Wengenroth

- (1) ILM Jan/Feb 2018
- (2) WHO deaths worldwide global status report on road safety 2018
- (3) Soerensen N., and Tysoe C., et al World Leather Aug/Sept 2013
- (4) Tysoe C., ILM May/June 2014
- (5) Michael A., Leather International, Nov. 2004
- (6) Rabe V., et al World Leather April/May 2019
- (7) Tysoe C., and Reinert J., et al Leather International 2011
- (8) Tysoe C. and Rehbein H., World Leather April/May 2011
- (9) Magerkurth B., World Leather Nov., 1999
- (10) Tysoe C., World Leather April 2007
- (11) Tegtmeyer D., World Leather August/September 2014
- (12) Tysoe C., Leather International September 2014
- (13) Tysoe C., World Leather Oct/Nov 2019
- (14) Reinert J., and Tysoe C., Leather International Oct. 2008
- (15) Tysoe C., World Leather April/May 2018