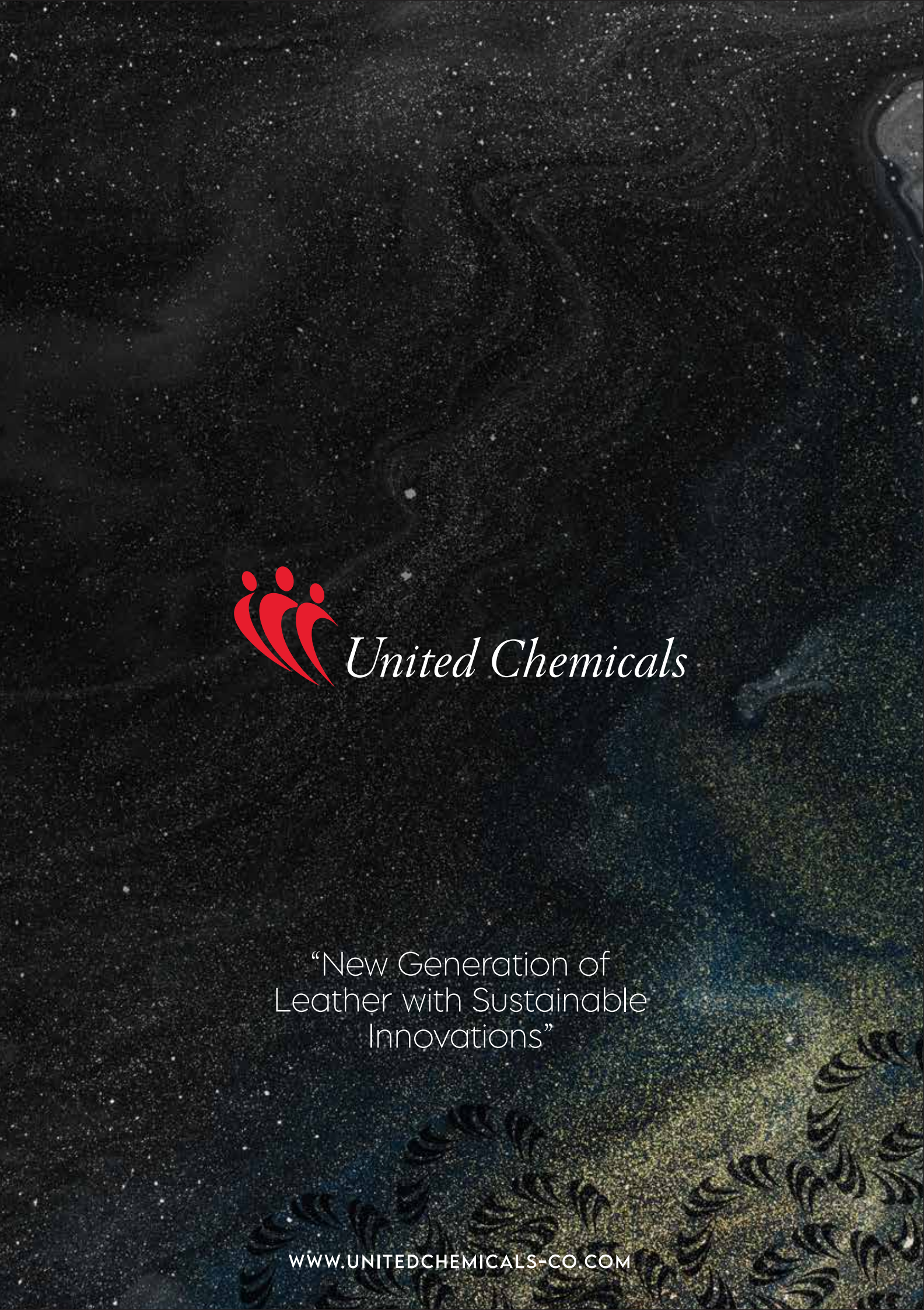

United Chemicals
"New Generation of
Leather with Sustainable
Innovations"
WWW.UNITEDCHEMICALS-CO.COM

Leather is a unique, flexible and durable material obtained from livestock by-products through various processes in which different chemicals are employed. The uniqueness and beauty of leather as a natural product are unmatched with similar man-made synthetic products. It takes time with application of technical expertise and passion to come up with finished leather ready for production of various leather articles. Leather making involves four steps namely; pre-tanning, tanning, post-tanning and finishing. Tanning process is the most important step as it brings actual conversion of raw hides and skins into leather by means of stabilizing collagen against heat and enzymatic attack. Although many tanning methods are known since ancient time, the most deployed method is chrome tanning.

OVERVIEW ON CHROME TANNING

Chrome tanning involves the application of basic chromium sulphate containing 33% basicity and 23% chromium (III) oxide (Cr_2O_3) that forms complex with collagen molecules via covalent bonds to stabilize collagen against heat and enzymatic attack, rendering it flexible and non-degradable. Chrome tanning remains the most favorite technology in the leather industry worldwide due to its ability to produce leather with attributes desirable for high-quality leather. Nevertheless, the technology has been censured globally for its serious environmental pollution and adverse effects on human health and other organisms. Developing alternative tanning materials and technologies capable of producing leather of high quality has remained a challenging scientific and industrial inquiry. Of all chromium salt entering the tanning liquor during tanning, only 55-70% is fixed in the eather and the rest gets its way to the effluent. Chromium concentrations in spent liquor has been reported to be in the range of 2000 ppm to 5000 ppm, while environmental regulation agencies worldwide allow as less as 2 ppm total chromium for the discharge of effluent into inland water bodies. Practically, reduction of chromium to permissible level is possible, but it is highly capital intensive, increasing tannery operational costs. This challenge calls for 2 appropriate technologies to minimize or eliminate chromium in effluent for leather industries to be sustainable.

Moreover, chrome tanning produces huge amount of solid wastes in form of chrome shavings, trimmings and buffing powder that are generated during corresponding processes. Chromium shavings alone contribute around 75% of solid wastes generated from leather manufacturing. Since they are non-degradable due to strong crosslinking bonds formed between chromium and collagen of hides during tanning, chrome shavings in landfills introduce challenges similar to those posed by plastic wastes. In particular, the negativity of the amount in effluents onto the sludge quality and the possibility of the formation of hexavalent chromium compounds in products and sludge wastes over time are the proof that the sustainability properties of chromium tanning method could no longer be foreseen. With the increased interest in avoidance of certain chemicals and industrial products that are particularly harmful to our environment, the chromium tanning technology is not able to meet the requests including green approach and also it's not surprising that many brands are becoming ingenious in pointing out attributes that play to this script. So, we hereafter will be hearing the claims for "chrome-free" leathers.

ALTERNATIVE METHODS

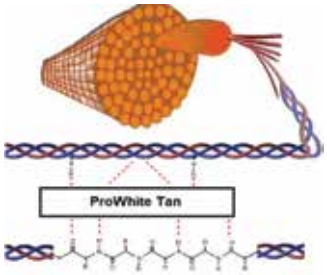
A number of alternative metal tanning agents like zirconium, aluminum, titanium and zinc have been investigated by many researchers during the last decades. However, it is well known fact that metal tanned leathers have lower fastness properties compared to wet-blue leathers such as lower thermal stability, tensile strength and fullness. Depending on these properties, the usage performance of chrome-free wet-white leathers is lower. Moreover, considering both the chrome and other inorganic pollutants contaminate air and water and vegetable and organic tanned leathers are also known to be poorly biodegradable, which results in high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), the combination tanning systems were considered as suitable tanning method to overcome these problems arising from single tanning systems. Consumers' anxieties about the possible damages of metals to human health and REACH restrictions on heavy metals, phenols and aldehydes, also conduced the metal-free production systems to be highlighted.

The challenge had been set to find a tanning process that would be faster and more efficient than the current chrome or wet-white processes, would not have the limitations of veg-tanning, would use less chemicals and would not be based on metals, aldehydes or phenols. For these reasons, it is 3 inevitable to search for alternative tanning, retanning and production technologies and focusing on the metal-free product systems to provide the sustainable development and sustainability of the industry.

NOVEL METAL-FREE LEATHER PRODUCTION SYSTEM

In order to struggle with the mentioned aspects, United Chemicals R&D laboratories has developed a new range called as ProWhite Tanning for chrome-free and metal-free leathers towards a sustainable leather making process. Compared to regular tanning operations, ProWhite yields a simple process method, reduces the time and energy required for tanning and most importantly, allows the reuse of the tanning bath.

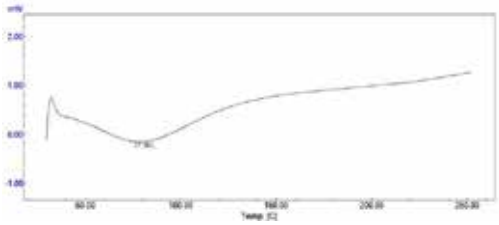
This new polymeric tanning system is a versatile system used either as a tanning agent for metal-free leathers or as retanning agent in re-tanning process where alone is capable to produce white or pastel shades products. It has unique properties such as higher solubility and higher amount of reactive terminal groups that can interact with reactive groups in collagen of the hide/skin and chrome complex for desired tanning outcome. It also promotes high pigmentation effect, giving a tight, well-structured crust with a fine tight and smooth grain in a simple and environmentally friendly way. In semi-chrome articles promotes a pale colour and cleaner shades maintaining fullness and roundness. It has good resistance to electrolytes and could be combined with metal tanning/retanning materials (chrome, aluminum or zirconium) or other tanning/retanning materials (vegetable, aldehyde or syntan). This new polymeric tanning system is already in production and being tested at several customers. Outputs of the produced leathers with the new generation products of United Chemicals are summarized as follows:



PHYSICAL AND THERMAL PROPERTIES

The shrinkage temperature test is one of the most important properties providing information about the degree of tanning because the better the crosslink reactions, the better the tanning will be and thus the shrinking temperature of the leathers will increase. Therefore, the shrinkage temperature shows the hydrothermal stability of leather products. Examining the performance properties of the produced leathers, it can be seen that leather samples treated with ProWhite Tanning agent provides 73°C and 75°C shrinkage temperature.

Denaturation temperature by DSC method is an alternative way for determining hydrothermal stability. DSC analyses also showed that application of ProWhite system enhanced the denaturation temperature of the leather.

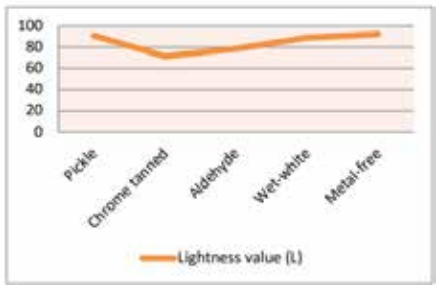


Tensile strength is very important quality feature of materials and plays an important role in quality and performance of the products. Tear load of leathers is also significant in terms of producing the desired final leather goods. Information about the condition and usability of finished leather can be obtained through the investigation of its tensile and tear strength properties. According to literatures, reference values for the tensile strength of leather tanned, based on acceptable quality levels of the leather industry from the United Nations Industrial Development Organization (UNIDO) are at least 9.80 N/mm2. UNIDO established a minimum value of 35 N/mm for tear load. When the strength results are examined; the tensile strength values of the leathers were obtained between 17.76-19.85 N/mm2 and tear strength values of the treated leathers were determined between 49.17-66.34 N/mm.

UNIDO reported the light fastness value of the natural and upper leathers should be not below 3. United Chemicals solution gained the satisfactory fastness values to the leathers in the light of UNIDO indicators. It can be found that all of these physical properties can meet the UNIDO standard requirements for many leather goods, indicating that the new wet-white tannage can be applied in leather manufacture.

	Shrinkage Temperature (Ts, °C)	Denaturation Temperature (Td, °C)	Tensile Strength (N/mm2)	Tear Strength (N/mm)	Light Fastness (Grey scale)
Pickle sheepskin	62	-	12.65	40.26	-
ProWhite tanned (Sheepskin)	73	75	17.76	49.17	4
Pickle cattle	65	-	13,51	45.32	-
ProWhite tanned (Cattle)	75	79	19.85	66.34	4

Colors according to CIELAB-76 system				
	L	a	b	ΔE
Pickle sheepskin	90,9	0,34	5,45	-
ProWhite tanned sheepskin	92,4	0,18	6,16	1,67
Chrome tanned sheepskin	71,4	-8,35	-0,04	22,01
Wet-white tanned (aldehyde) sheepskin	78,6	5,27	39,74	36,76
Wet-white tanned (metal) sheepskin	89,1	-0,72	13,66	8,45



According to the color system of CIELAB-76, the increase in L* value represents the increase of lightness and the decrease in L* value means a decrease of lightness. The increase in the value of +a* indicates an increase in the color red, -a* shows an increase in the color green, +b* demonstrates an increase in the color yellow, and -b* shows an increase in the color blue. L values of the wet-white tanned leathers indicated the satisfactory lightness and whiteness degree. Moreover, metal-free system of United Chemicals provided the better values proved by the Table 2 and Figure 2. With this aspects, metal-free tanned leathers by this system can be easily dyed with the different colors. This means also more dyestuff saving for easy color matching.

RESTRICTED SUBSTANCES

Leather industry has been restricted by some international organizations and exposed to some sanctions as in the other industries. All tanners are facing the same problems of minimizing the environmental and health impact of their processes when selling into the global market. Regulatory pressures oblige tanners to make continuous improvements in the processing operations. The regulatory authorities and consumers are looking more closely at whether hazardous substances, such as certain preservatives, some azo-dyes, and chromium (VI) are present in leather and leather products.

	Formaldehyde amount (ppm)	Chromium (IV) (ppm)
Pickle sheepskin	-	-
ProWhite tanned (Sheepskin)	N.D	<3PPM
Pickle cattle	-	-
ProWhite tanned (Cattle)	N.D	<3PPM

Table lists the content of limited hazardous substances in the metal-free tanned leathers. Both Cr(VI) and formaldehyde are not detected, showing that the leather products can meet the demands of the EU eco-label (2009/563/EC).

COMPARED TO THE CONVENTIONAL SYSTEM

Properties	(United Chemicals)	Chromium
Termal Stability	>70 °C	>90 °C
Softness	Good	Very Good
Grain	Very tight grain	Tight grain
Wrinkles	Less Wrinkles	Wrinkles
Production Time (Hour)	8	>20
Exhaustion rate (%)	>90	75
Heavy metal content	No	Yes
Water-resistant	Good	Good
Colour	White	Blue-Green

United Chemicals solution provides an environmentally friendly and safe leather production process and will have major benefits for tanners, especially those producing leather upholstery for the automotive sector next to the others such as garment and footwear. ProWhite Tanning and Polytan are the new design in metal-free tanning; using novel polymers that is metal-free, formaldehyde-free and phenol-free. This new system provides reduction of production time at least 10 hours and makes the tanning process simpler than before we used to. With this system, it is possible to tan a skin within 2 hours. One of the main advantages of the system is to eliminate the extra salt into the tanning process, commonly introduced at the conventional tanning where the bath is emptied. Instead, when tanning the leather with ProWhite Tanning, bath water can be reused after each tanning process. By doing so, release of chlorides and sulphates to the effluent is significantly reduced, which accounts for the environmental and economic benefits of applying this new system.

KEY NOTES

Due to the lack of predictability of the future in chromium tanning, wet-white technology seems to be ecologically better without any withdrawal from the distinct properties of mineral tannage. A wide variety of different types of leather can successfully be produced using wet white system, including automotive leathers, upholstery leathers, garment leathers and shoe upper leathers. At the same time, different market requirements might possibly be overcome by wet-white technology to have comparable properties to chrome tanned leather such as feel, fullness, softness, and hydrothermal stability. This new innovative tanning system can give to leathers with Ts above 70°C. ProWhite Tanning agent can penetrate evenly into leather matrix and bind tightly with collagen fibers. Moreover, the resultant leathers can meet the official standard requirements of physical properties for leather goods, with no limited hazardous substances, Cr(VI) and free formaldehyde detected. The technological application of United Chemicals system enables a simplification of the current known processes with an environmentally friendly tanning system. New designed system reduces water usage, chemical demand, and the treatment of wastewaters and chemical residue by making it possible to reuse the tanning bath. This will be welcomed by the industry, as it means less corrosion within the tannery, and especially welcomed by those who are already processing green hides to avoid one of the main sources of salt within the tannery.