



Leather tanned with ProWhite Tanning. Credit: United Chemicals

Low chrome options for high exhaustion tanning

United Chemicals has developed the ProWhite Tanning System to add value to the leather industry by offering more environmental applications.. ProWhite are tanning processes without a pickling stage, carried out at neutral pH and are environmentally benign, significantly reducing the consumption of acids, bases, sodium chloride and water. The tanning system decreases the cost of waste streams for tanners due to the effective tanning action. Remaining amounts in the tanning bath pose no threat to the environment, and the clean and bright wastewater is easier to treat.

Although environmental impact has become an important issue for the leather industry today, it still requires some technological developments in terms of ecological compatibility. It is known that productions in low sustainability and low consumption models generate the basis of the problems of deterioration of the natural balance based on the increase in waste load in today's developing world; and these problems are seen as the most important agenda items of recent years.

Leather production covers tanning processes and the homogeneous distribution of various chemical substances on the leather's cross-section and surface to make the structural texture open, firm, flexible and durable. For the more traditionally used chemicals, typically less exhaustive in their nature, certain quality problems such as colour, appearance and form can arise in the manufactured leather—this in addition to the more concentrated wastewater baths. Tannery

wastewater is a powerful pollutant that can cause severe environmental problems because of its high organic and inorganic loads, suspended solids, and high contents in chromium, chloride, ammonia, sulfide, oil and grease, among others. It is of great importance for the leather industry, in order to transfer production to future generations, to develop environmentally compatible technologies.

Today, social sensitivity regarding ecological production and the reason for developing environmentally friendly products and technologies for the sustainability of leather industry creates the main principle and concept. In addition to meeting the REACH regulation criteria of leather products produced with the targeted method, it is aimed to meet the physical and chemical test criteria of manufactured leather products in terms of performance characteristics compared to the conventional production systems. Moreover, considering the recent studies of Leather Working Group



Table 1: ProWhite recipe with combination of chromium.

PROCESSING METHOD	%	PRODUCTS	TEMP.	RUNNING TIME	pH/Be	REMARKS
DELIMING	50	WATER	38			
	1	UNICAL KG (organic acids for deliming)		30'		
	0.5	AMMONIUM SULPHATE		30'		
	0.5	UNICAL KG		30'		CHECK DRAIN
BATING	100	WATER	38			
	1	UNILASE PEP 1000 (pancreatic enzyme product)				
	0.3	UNICAL KG		45'		DRAIN WASH
TANNING	80	WATER	30		4-5 Be	
	1	FORMIC ACID		2X10' + 90	4.2	
	4	ProWhite PL (polymer tanning agent)				
	1	POLYSOFT S205 (polymer-based softener)		120'		
	6	ProWhite W (tanning agent)				O/N
MORNING	1	FORMIC ACID		10'		
	0.2	UNIXOL FN (fungicide)		60'		
		SAMMYING-SETTING OUT, SHAVE: 1,2-1,3 MM				
WASH	300	WATER				
	0.3	FORMIC ACID				
	0.2	UNISOL DN (washing agent)		60'		DRAIN/WASH/DRAIN
CR-COMBINATION	100	WATER	38			
	3	CHROMIUM		60'		
	1	SODIUM FORMATE		30'		
	1	SODIUM FORMATE		60'		O/N
NEUTRALISATION	150	WATER	38			
	1.5	SODIUM FORMATE				
	0.5	SODIUM BICARBONATE		60'	5.4	D/W/D
RETANNING	80	WATER	30			
	3	UNISIN EZN (acrylic polymer)		20'		
	5	MIMOSA				
	5	POLYTAN DC (dicyandiamide-polyacrylic based resin)				
	5	ProWhite W				
	2	UNISET BROWN GL (dyestuff)		90'		
FATLIQUORING	100	WATER	50			
	4	POLYSOFT FWN (polymerized ester)				
	4	POLYSOFT SS (polymeric softener)				
	2	POLYSOFT S205				
	2	POLYSOFT WPX (waterproof fatliquor)		60'		
	1	FORMIC ACID		2X10' + 30'		
	2	UNIXOL FX (fixating agent)		30'		

(LWG), which consists of member countries worldwide, it is seen that an awareness is being created for the production of clean leather. In companies producing leather; studies are encouraged to use less water and chemicals, less energy, minimum waste volume and pollution load, and reuse of wastes generated. In this context, development of tanning methods for the leather industry with high exhaustion, more reactive in a short time, with reduced waste volume and pollution load is the most important goal for United Chemicals.

The company has worked towards this goal with ProWhite Tan which enables sustainable leather production and producing all types of chrome-free high-quality leather. This tanning system not only provides better tanning process in terms of process time, energy and cost savings, but also offers high exhaustion rate and cleaner environment in an eco-friendly way.

The unique feature of chromium as a simple tanning agent is that it confers high hydrothermal stability to the leather; whilst this is not essential for all leather goods, it is critical for



Table 2: Properties of ProWhite leathers.

Leather	Shrinkage Temperature (Ts, °C)	Tensile Strength (N/mm ²)	Tear Strength (N/mm)	Light Fastness (Grey scale)
Pickled cattle	65	13.51	45.32	-
ProWhite tanned	74	19.85	66.34	4
ProWhite-Cr tanned	85	20.25	71.18	4
Wet-blue	102	21.27	72.03	4

Table 3: Characteristics of ProWhite system.

Properties	ProWhite	Chromium	ProWhite-Cr
Production time (hour)	10	>20	12
Heavy metal content	No	Yes	Slightly
Chromium in spent liquor	-	1100 mg/L	56 mg/L
Float uptake (%) (Chromium)	-	73.4	91.1
Float uptake (%) (ProWhite)	92	-	-
Properties of 8% remain wastewater Properties of 26.6% remain wastewater			
COD	127 mg/L	1413 mg/L	
pH	7.38	4.01	
Chloride	-	22000 mg/L	

most applications, particularly for shoe upper leather which is likely to encounter stringent conditions during the manufacture of shoes. ProWhite Tanning System is suitable for all items and can be used in combination with all tanning and retanning agents.

With the developed tanning system (Table 1), it will be possible to combine chromium tanning to enhance the hydrothermal stability of the leathers.

The properties of leathers produced by ProWhite system and wastewater characteristics are shown in Tables 2 & 3.

Shrinking is a phenomenon associated with dimensional changes of a hide/skin when subjected to heating. Conventionally measured with shrinkage temperature, the temperature reached with ProWhite is satisfactory (74°C) when compared to the other wet-white systems. Moreover, it can be enhanced, if necessary, by the introduction of small amounts of crosslinkers such as chromium. ProWhite Tan offers perfect dyeability and high dye affinity, allowing for very bright colours as well as improving the physical and mechanical properties of material in all leather applications such as shoes, garments, upholstery and automotive and meeting all the requirements for these applications.

Exhaustion rates of chemicals used

in tanning processes, one of the most important factors of leather production, remain between 60-70%; it can result in low performance of leather products and problems such as chemical waste, polluted water and increased energy consumption. The remaining process water, with unbounded chemicals is highly complex and contains high concentrations of organics and other toxic chemicals, such as chlorides and chromium, which inhibit the activity of microorganisms during biological oxidations and are not removed completely from the wastewater. This situation causes the high input and treatment costs for the companies and the disadvantage in the competition. Furthermore, the residues in wastewater/released float as metal, free phenol and formaldehyde, etc., do not make ecological compatibility possible, which significantly damages the reputation of the leather industry.

Globally, 90% of the leathers in the leather sector are tanned using basic chromium sulphates (BCS) at approximately 50-70% chromium uptake. This poor uptake results in material wastage on one hand and ecological imbalances on the other. The international specification for the discharge of chromium in wastewater is in the range of 0.1-2 ppm. Even a

high-exhaust chrome tanning system does not provide such low concentration. Concerns have been expressed about the toxicity of chromium(III). Discussion exists regarding the possible conversion of chromium(III) to chromium(VI) in certain soil conditions. Moreover, the disposal of chromium containing solid wastes and sludge poses major challenges. Overall, the popular chrome tanning method has come under the close scrutiny of the environmental authorities in both the industrialised and developing countries due to increased awareness about environment and health. Hence, there is constant search for eco-benign tanning materials and methods.

Because of the environmental character of ProWhite Tan and the high exhaustion in tanning, the wastewater is very clean, particularly with respect to COD and its chloride value when compared with a wet-blue process.

Pickling plays a key role in chrome tanning since acidification of the pelt allows a prompt absorption of the water-soluble basic chromium sulphate into the collagen scaffold. Adversely, at this pH, acid swelling of the pelt occurs causing a non-reversible denaturation of the collagen structure. This phenomenon may be inhibited by different kinds of salt; typical values of NaCl concentration in the pickling float are around 8-12% w/w. As a result, about 20,000 mg/l chloride can be found in the spent tanning liquor. Approximately three hundred thousand tons of salt are used around the globe in the pickling process every year, quite an alarming situation from an environmental point of view as the post-treatment of chloride is both difficult and expensive.

Increasing environmental awareness around the world has shown the necessity to work in a more environmentally and ecologically sustainable fashion for the leather production industry. Studies on the chemicals used in leather production and the waste loads brought about by preferred production methods have gained momentum in order to be more purified nowadays. Moreover, it is important to use water resources efficiently in consideration of the commercial competitive conditions in the industrial sector. Less water use and more float exhaustion systems are required. 🌍