Salt and acid-less tanning system from Buckman

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Due to the limited options available and the higher cost involved in treating wastewater, Total Dissolved Solids (TDS) in effluent is an increasing concern to the tanner. While TDS levels are affected by several different processes and chemicals, one of the biggest contributors is common salt (NaCl). Effluents with high levels of NaCl concentration can increase the salinity of soil and therefore render the effluent unsuitable for use in irrigation. While salt from curing is responsible for the major portion of TDS, salt used in pickling is the next biggest contributor to TDS levels in effluent. It is estimated that around 75% of TDS in the effluent due to added salt (not including the salt from curing) is from pickling. As tanners do not have any control over the incoming salt from curing (unless they process fresh substrates), their best option for reducing TDS in effluent is to reduce pickling salt. Any major reduction in salt application in pickling, or indeed complete elimination of the pickling stage, could significantly reduce TDS levels in the tanning liquor. This paper gives an overview of an application that completely eliminates the pickling stage, reduces the use of basic chromium sulfate and also eliminates the basification stage in chrome-tanning skins and limed split hides. This process has demonstrated significant reductions in TDS in the tanning liquor, in the use of water, in the levels of chrome powder used and in the length of process time, whilst leading to improved wet blue and crust properties.

Figure 1

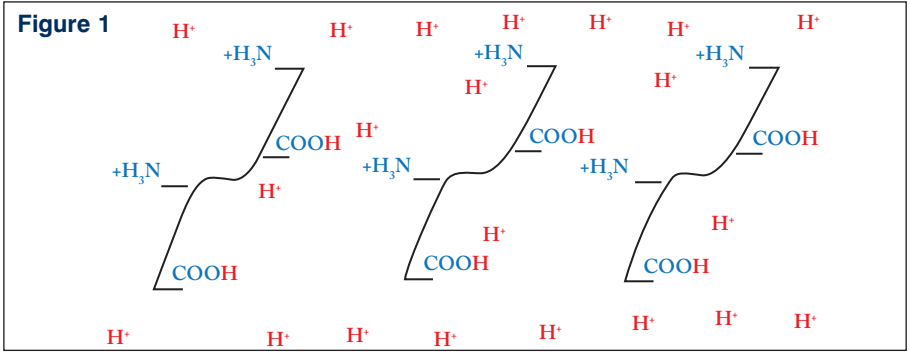


Figure 2

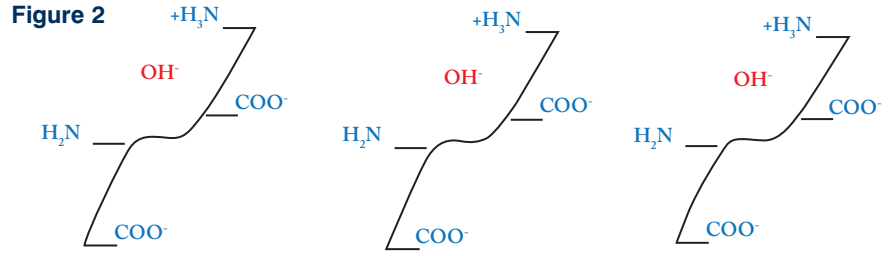


Table 1: Conventional chrome tanning process

Process	%	Products	°C	Run	Stop	#	pH	Be	Remarks
Pickle	100.00	Water	20						
	8.00	NaCl		5'				7	
	0.60	NCOOH		15'x2					
	1.00	H_2SO_4		20'x5					
				120'			3.8		
Chrome tan	7.00	Chrome powder							
	0.15	Busan 30L							
	0.50	HCOONa		120'					Penetration OK
	100.00	Water		15'					
	0.25	MgO		60'					
	0.20	MgO		420'			3.8		

The pickling process

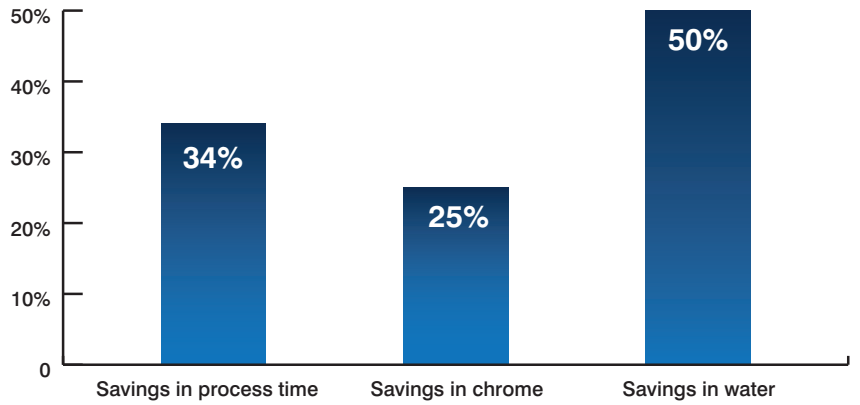
In conventional beamhouse processing, following the deliming and bating stages, the pelt is still in a highly anionic and alkaline state. Since the pH of the pelt is much higher than its pK, the carboxylic endings of collagen are ionised (-COO-). While most of the amino endings of the collagen are also ionised in the cationic form NH_3^+, some amino side chains from lysine and arginine remain in their anionic NH_2 form. Providing the deliming has been done appropriately, the calcium ions will no longer be bound and most of the ionised carboxylic groups will therefore be "free", as shown in *Figure 1*. This makes collagen a perfect reactive site for cationic compounds, such as basic chromium sulfate.

Conventional chrome-tanning employs a pickling process in which organic and inorganic acids are used to bring down the pH from an alkaline to acidic state. When pelts are pickled to a pH slightly below 3.0, the remaining un-ionised NH_2 groups from lysine and arginine are ionised to NH_3^+ and the carboxylic groups of collagen convert to their molecular and "blocked" form -COOH. When the carboxylic groups are blocked, and the amino groups are positively ionised, no bonding site for basic chromium exists and the pelts

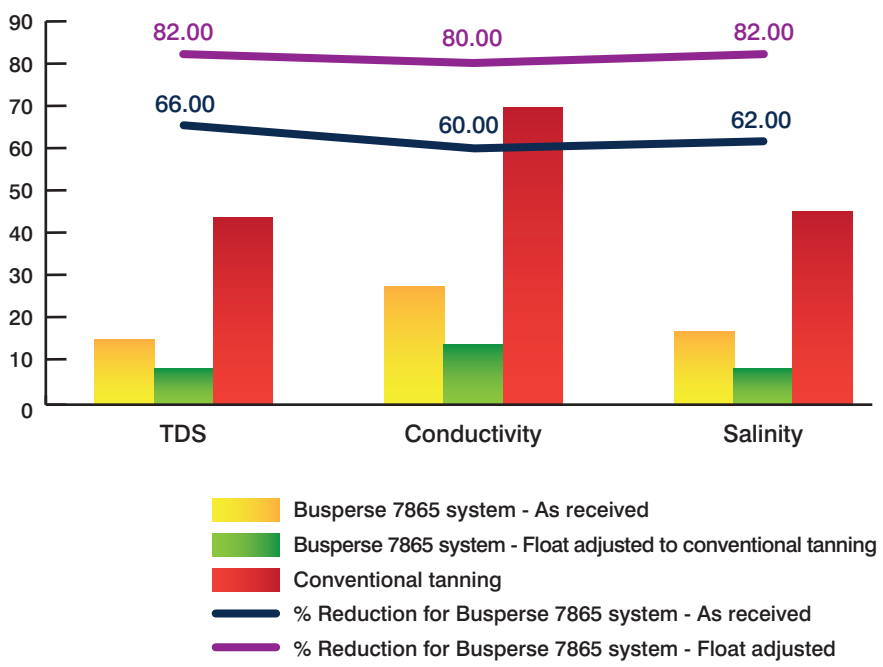
Table 2: Busperse 7865 process

Process	%	Products	°C	Run	Stop	#	pH	Be	Remarks
Chrome tan	60.00	Water	20						
	2.50	Busperse 7865		30′			5.5		Cut section will be more than 7.0
	5.00	Chrome power							
	0.15	Busan 30L							
	0.50	NCOONa							
	0.50	Chrome stable fatliquor		120′					Penetration OK
	40.00	Water		420′				3.7	Drain, wash, pile

Graph 1: Percentage savings in chrome tanning



Graph 2: Reduction in TDS, salinity and conductivity in tanning liquor



become less reactive (see *Figure 2*) and therefore the penetration of basic chromium sulfate is improved.

Since pickling is generally done down to a pH of around 2.8 – 3.0, common salt (NaCl) is used to control acid-swelling of the pelts. As NaCl is chemically neutral and has very high solubility in water, it is difficult to remove using common effluent treatment methods.

Trials with the complexing system Busperse 7865

Busperse 7865 is a novel complexing agent which simplifies chrome-tanning by eliminating the pickling and basification processes. This product has been designed to form weak complexes with basic chrome powder, thus reducing the affinity of basic chrome to pelt. Even though the pH of both the pelt at the surface and the cross-section are higher than with conventional chrome-tanning, the weakly complexed chrome has reduced reactivity and can penetrate into the pelt. Since the affinity exerted by the carboxylic groups to chrome is stronger, this weak complex will break down to allow the released basic chrome to covalently react with the carboxylic group to complete the tanning. *Tables 1* and *2* outline the processes for conventional chrome-tanning and for chrome-tanning using Busperse 7865 respectively.

The simplicity of the process using Busperse 7865 is quite clear when comparing the systems shown in *Table 1* and *Table 2* where the processing time can be reduced by one-third, process water can be reduced by half, and the addition of basic chromium sulfate can be reduced by one-quarter as shown in *Graph 1*.

In addition to the savings in time, chemicals and water, results show that a key benefit of this complexing system is an approximately 65% reduction in Total Dissolved Solids (TDS) from the chrome tanning float. However, when the float levels are normalised to the conventional system, which uses more water (100% float versus 60% for the complexing system), this equates to around 80% reduction in TDS levels. Similar reductions in salinity and conductivity are also observed as shown in *Graph 2*.

Laboratory trials have indicated that, when compared to conventional tanning system, absorption and fixation of

chrome was significantly better with the new complexing system. These benefits not only allow tanners to reduce the dosage of basic chromium sulfate, but also lead to a reduction in chrome content in the effluent. Numerous laboratory trials showed around an 18% reduction in chrome on an 'as-received' basis was noticed in the effluent. This percentage takes on more significance as the total effluent load from Busperse 7865 was only around 25% of the regular effluent load. As such, when the chrome content is calculated by equating float-loads, theoretical values showed a huge 82% reduction. This is another important benefit to the tanners as, in addition to common salt, chrome in the effluent is a major concern. *Graph 3* highlights the reduction of Cr_2O_3 in effluent.

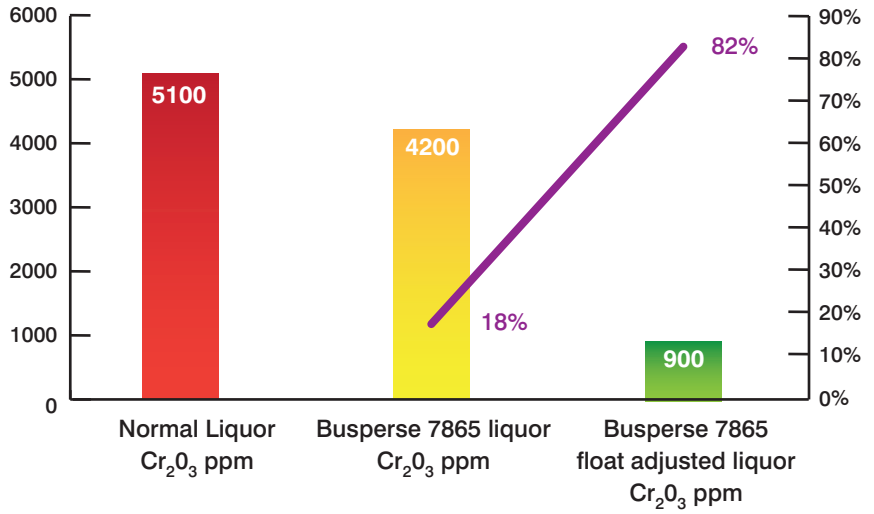
It was observed from the numerous trials that even after reducing the dosage of basic chrome powder by 25%, the Cr_2O_3 content in hides processed to wet blue with the complexing system was significantly higher than in conventionally tanned wet blue hides. Results from these trials indicate an increase of around 12% in Cr_2O_3 content in wet blue as indicated in *Graph 4*.

In addition to higher Cr_2O_3 levels in wet blue, crust leathers developed from the complexing system in the laboratory trials showed comparatively better bursting strength, tensile strength and elongation-at-break properties. Percentage increases of these properties have been noticed to be around 6% to 8% as shown in *Graph 5*.

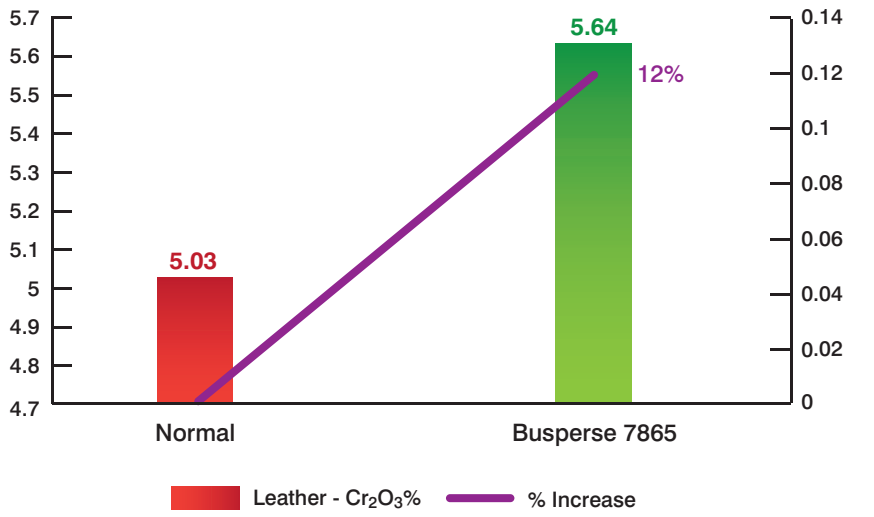
Wet blue tanned by the complexing system can be further processed like the wet blue from conventional tanning to various articles and various colours with slight adjustments in wet-end processing, as shown in *Figure 3*. In addition to the improvement in the strength properties mentioned, finished leathers from the complexing system wet blue generally exhibit better fullness, roundness and body.

In addition to all the above benefits, the new complexing system also minimises the risk associated with issues due to improper basification such as formation of chrome patches, an increase in pH with ageing, chrome precipitation and so on, as this system does not employ a basification step in processing. Risks associated with handling highly concentrated inorganic acids such as sulfuric acid are

Graph 3: Chrome reduction in chrome tanning effluent float



Graph 4: Cr_20_3 % in wetblues



Graph 5: Improvements in strength

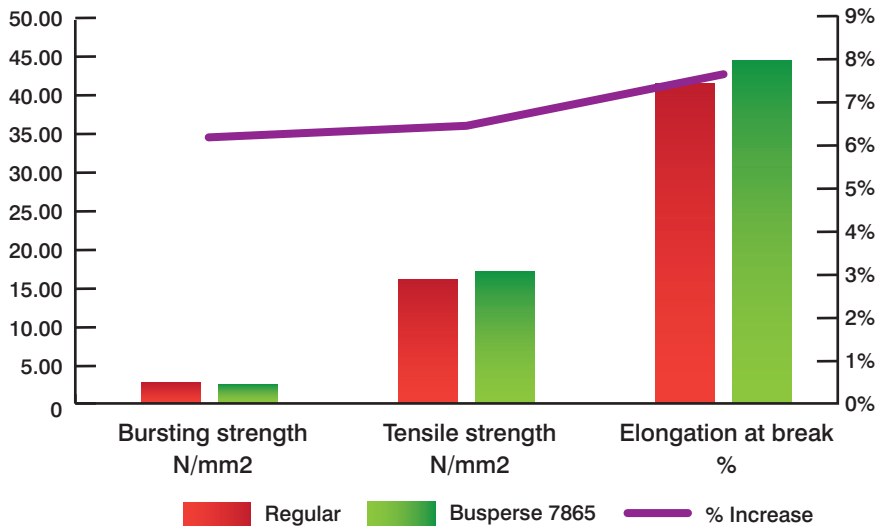
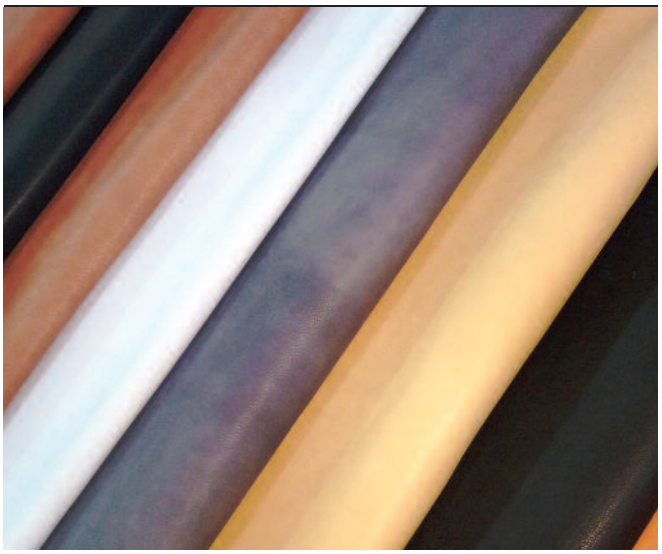


Figure 3



eliminated completely as the new complexing system does not employ any inorganic acids in processing.

Commercial applications of this system have been successfully implemented in several tanneries in number of countries on substrates such as goat, sheep, cow calf, buff calf and lime-split cow hides. *Figure 4* shows a bulk lot of sheep wet blue produced from sheepskins.

Figure 4: Sheep wet blues from Busperse 7865 system

Conclusion

It has been proven by numerous trials that wet blue produced by the new complexing Busperse 7865 system can be successfully used to produce various types of articles, including conventional shoe upper leathers, shoe softy leathers, shoe nappa leathers, garment leathers, leathers for various types of leathergoods and upholstery leathers. This system presents a viable and simple solution to the tanner's search for ways to minimise salinity in effluent, water load, chrome load and time. In addition to those benefits this system also produces leathers with better fullness, roundness, body, tightness and strength properties.