



Hybrid chrome tannage coupled with recycling for minimisation of residual chrome from tanning

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In the leather industry, the awareness of environmental problems has increased considerably and, during recent years, protecting the environment has become a global issue. In fact, regulatory pressures oblige tanners to make continuous improvements in the processing operations, and consumers are looking more closely at whether hazardous substances are present in leather and leather articles.

According to the World Commission on Environment and Development, sustainable development is defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs".

Today, 80-90% of leathers in the world are tanned with chrome. The increasing requirements of producing safe leathers in a sustainable way have led Silvateam to develop a new technology that permits:

- Increase the fixation of chrome oxide to the leather fibres;
- Minimise the use of chrome salts in the tanning processes;
- Reduce the chrome content in wastewaters.

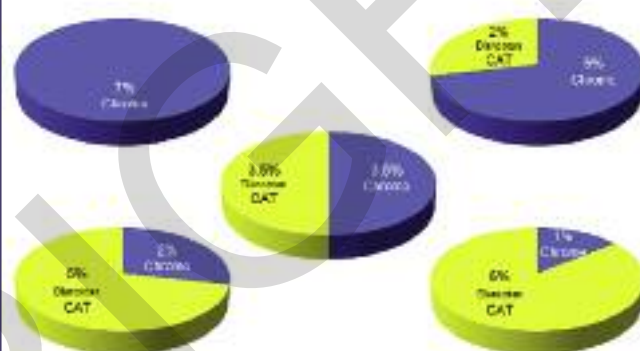
This technology consists of an innovative hybrid tannage using a combination of chrome salts, and Blancotan CAT, a new syntan with a cationic charge based on a dihydroxydiphenyl-sulfone condensation product.

Synergistic effects with chrome

This product can be used alone directly on pickled hides as a pretanning agent to provide a user friendly free-of-chrome process for a wide range of leathers. Alternatively, it can be used in combination with conventional chromium salts in any proportion to obtain low chrome tannages with high exhaustion floats.

Several hybrid tanning combinations have been assessed

Panel 1: Chrome and Blancotan CAT tannages.



Panel 2: Chrome and combination tannage and exhaustion floats.

Chrome (%)	Blancotan CAT %*	Cr ₂ O ₃ residual (%)	pH	Exhaustion (%)
1.0	6.0	0.02	4.93	90.4
2.0	5.0	0.03	4.70	92.8
3.5	3.5	0.03	4.70	95.9
5.0	2.0	0.04	5.06	96.2
7.0	-	0.31	3.82	78.7

using this product in comparison with chrome only tannage. The total amount of tanning agents used for each trial was always the same, being equal to 7% on pelt weight as indicated in *Panel 1*.

Where these combinations are used, a strong complex is created with chrome resulting in an effective tannage which allows a high pH during basification (pH > 5.0) without

Panel 3: Examples of chrome uptake in chrome and combination tannages.





Panel 4: Examples of chrome uptake in chrome and combination tannages.



chrome precipitation. This enables an almost total chrome exhaustion of the residual floats.

Hybrid tannage vs chrome tannage exhaustion floats

The chrome exhaustion of different floats has been analysed at the end of these tannages in terms of pH, Cr_2O_3 residual (%) and exhaustion (%) according to UNI EN ISO 17075. These findings are summarised in *Panel 2*.

In all combinations a higher exhaustion is achieved when compared to using chrome alone. The best performance - up to 96% - is obtained in the combination containing Blancotan CAT at a dosage of 2%.

Panel 3 shows wet blue leathers and floats at the end of tannage in the early investigation using hybrid tannage at different dosages and with chrome only. The high exhaustion of the chrome combination tannages is easily observed in the floats, and shows a very clear solution when compared to the

chrome tannage alone: these comparisons can also be observed in comparison with distilled water in *Panel 4*.

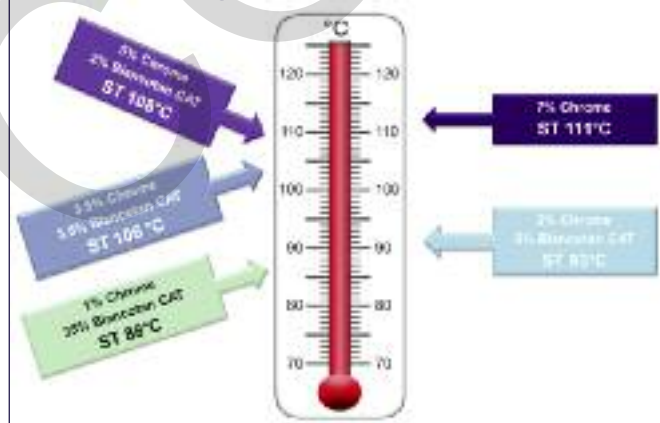
The more tanning material fixed, the higher the hydrothermal stability and increased shrinkage temperature resistance of the leather. This is illustrated in the shrinkage temperatures of different wet blue leathers from investigations in *Panel 5*.

This shows that the shrinkage temperatures from these hybrid systems are slightly lower than the traditional chrome tanning, but this rises proportionally when increasing the dosage of chrome. However, if the shrinkage temperatures are lower this does not affect the outcome from the wet blue sampling or shaving operations.

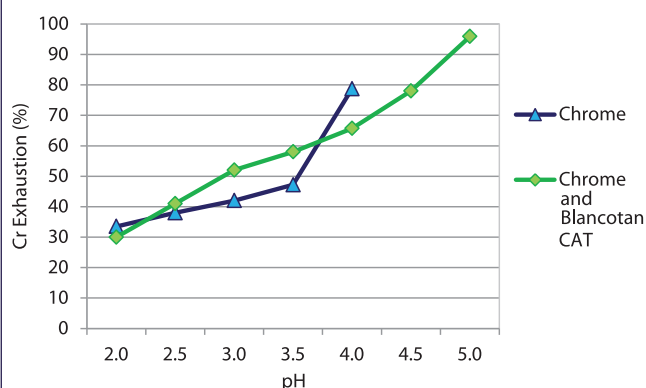
Higher chrome exhaustion

A comparison of chromium exhaustion percentages in floats using these hybrid tannages and chrome only at different pH

Panel 5: Shrinkage temperatures of hybrid and wet blue tannages.



Panel 6: Hybrid tannages comparison vs chrome exhaustion at different pH values.



**Panel 7: Example of tight shoe upper leather.****Panel 8: Nappa shoe upper leather.**

values is given in *Panel 6*. Here, the chrome only system can only achieve 79% chrome exhaustion in comparison with the hybrid system that attains a 96% value.

In further investigations, a series of leather articles were developed to evaluate both the handling characteristics and the repeatability of the results for the different types of tanning. Some comparative examples are shown in *Panel 7* and *Panel 8*, where firm, tight shoe upper leather and a nappa shoe upper have been created.

Recycling within the hybrid tanning system

Because of the excellent chrome exhaustion at the completion of tannage of the hybrid system, the final tanning float has been recycled for the pickling of subsequent loads of leathers. This creates wastewaters free of chrome residuals and with a very low amount of chlorides and sulfates.

After a first standard pickle and hybrid tannage, the float after basification has a Baume value of between 5.5° and 7°. This value is suitable to be used for pickling the next load of hides, and no further addition of salt is needed to avoid acid swelling. All that is required is the correct addition of acid to provide the pH as required for the pickling process. This procedure is indicated in *Panel 9*.

Since this is a system with recycling of residual floats, the accumulation of any residual products was measured. The main parameters from chrome tannage, and the hybrid tannage coupled with recycling - chlorides, sulfates, nitrogen and total solids - are given in *Panel 10*.

Advantages from hybrid chrome tanning, coupled with recycling for subsequent pickling/tanning

This new hybrid tannage system enables almost total fixation of chrome in leather. Coupled with the recycling of the used tanning float for the subsequent pickling process, it also avoids any addition of salt to the pickle float. It also means that the small quantity of residual chrome from the hybrid chrome tanning bath is also retained and available for fixation within the tanning-pickle cycle, thus causing a further lowering in the quantity of chrome discharged.

These developments by Silvateam offer a major step towards the avoidance/elimination of chromium within tannery sludge, reduced costs for disposal, and the possibilities of alternative uses for sludge.

The key benefits are summarised:

- High percentage of Cr_2O_3 fixed to the leather fibres - up to 98/99% - in hybrid chrome tanning using Blancotan CAT when coupled with recycling.
- 75% reduction in sodium chloride and 20% reduction in sodium sulfate in wastewaters from tanning.
- Reduced purchases/use of sodium chloride
- Chrome free sludge.
- Versatile hybrid wet blue leathers.
- Uniform and excellent fullness of leathers.
- Extremely light wet blue leather colours.
- Leathers with good dyeing characteristics, such as intense and brilliant colours. ☺

Panel 9: Hybrid tannage with recycling of exhausted float for the subsequent pickling process.**Panel 10: Pollution load using hybrid tannage when recycled for pickle process vs chrome tannage.**

Pollution load	Hybrid tannage with recycling	Chrome tannage
Total solids (%)	3.0 - 4.0	7.5 - 8.5
Sulfates (mg/l)	4,500 - 5,500	15,000 - 17,000
Chlorides (mg/l)	50 - 100	20,000 - 22,000
Nitrogen (%)	0.04	0.11
Ashes (%)	3.0	6.0 - 7.0
Chrome exhaustion (%)	98.0 - 99.7	78 - 85

* Microbiological analysis on residual floats (bacteria and moulds) are in progress.