

New dyeing, fatliquoring and retanning compact material for ecological leather processing

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Retanning of leathers represents one of the most versatile and innovative process in leather manufacturing. Last time, a large range of multifunctional products have been designed in order to obtain leathers with different characteristics like: waterproofing, washability, fullness.

Our researches have developed a new multifunctional product for dyeing, fatliquoring and retanning of leathers in a new compact process.

We have studied the chemical stability of dyeing, retanning and fatliquoring product, the reproducibility of its performances on leathers and the structured capacity of collagen fibers, by using SEM analysis.

The technological versatility of new retanning product has been assessed by performing different kind of leathers, from very soft to firm leathers. The influence on leather dyeing of compact material and vegetable extracts has been assessed by using CIELAB program and spectrophotometer measurements of chromatic characteristics, the softness of leathers has been assessed by using leather softness tester.

The main physical-mechanical characteristics of compact manufactured leathers were assessed in comparison with leathers processed with compact agents, available on market and standard values.

The new product assures a compact retanning process with important time and water saving. The synergetic effects of new product components have allowed saving chemical materials also and an important reduced impact on wastewaters pollution. The assessment of ecological impact of compact retanning process has recorded the decreasing of COD and BOD5 of wastewaters. We have performed a new method for environmental impact estimation, the measurement of anti-oxidizing capacity of retanning wastewaters, by measurement of chemiluminiscent properties. The new method, applied for complex matrix of retanning wastewaters gave us quick information on the environmental impact of different retanning processes.

Introduction

Reducing hide processing operations is imperatively required because of the growing demands of lowering the environment impact of leather manufacture activities, water consumption, auxiliary chemicals, and the last but not the least, of increasing output.

Synthesis chemistry have made significant progress in preparing some multipurpose polymers [1] as retanning-fatliquoring, retanning-waterproofing agents [2] which enable some complex characteristics to be reached in a compact processing system.

For these purposes, another achievement was the compact retannage step by means of newly prepared blends of neutralization, fatliquoring and retanning agents [3, 4]. These

products are favourable as they are entailing significant savings in time and water consumption as well as increase in safety and process quality.

This paper presents a new retanning material, which is a blend of fatliquoring, dyeing and retanning agents.

The behaviour in time of the new retanning material, its multiple actions, characteristics of the resulted leather as well as its environment and economic effects were investigated and the results support the new approach in retanning leather.

Materials and Methods

To perform a compact leather retanning process, a retanning agent formulation like a paste for fatliquoring, dyeing and filling purposes has been thought.

The best variant - EUROCOMPACT- storage stable was selected as the result of the trials conducted with 5 technological variants on the pilot and industrial plants for 12 months; it have imparted leather physical-chemical and aesthetical characteristics, comparable to the control and standard variants. Control variants are compact retanning materials with multipurpose neutralization, filling and fatliquoring action.

The action of the above compact retanning material and of the vegetable tannins, depending on their offers, on the leather softness, physical-mechanical characteristics and black colour depth was investigated.

Leather softness tests were performed with Softness Tester ST-300, colour depth was assessed on a spectrophotometer and by spectrum data processing by means of CIELAB software.

The ecological impact of new product and technology has been assessed by measurement of COD, BOD and chemiluminiscent characteristics of wastewaters.

Multiple action of the new material has been proved by preparing some leather sorts with varying softness and setting up the material ratios for them.

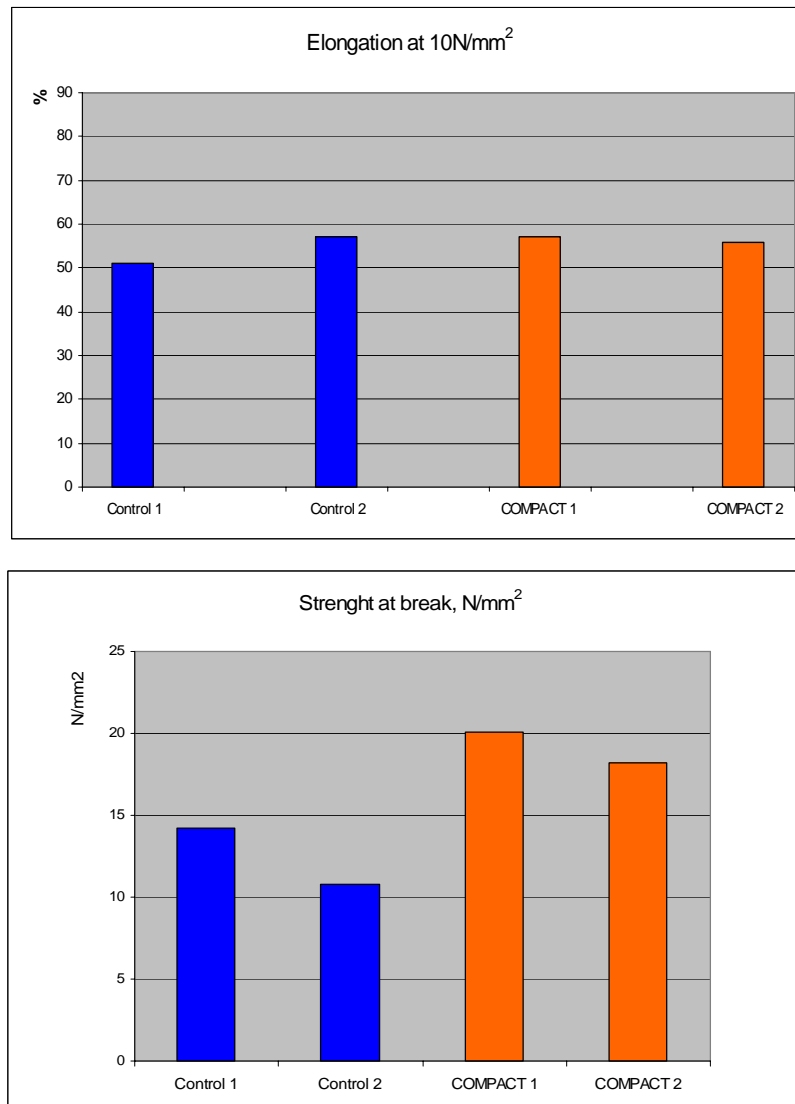
The framework process for the compact retanning is described below:

Post-tanning compact process (Samples I-VII)	Control 1	Control 2
Neutralizing 1,4% sodium formate 20 min run 0,9% sodium bicarbonate 30 min run pH-5,2-5,4 Drain Wash Compact fat/dye/retan	Wash Drain 12% compact neutralizing/retan/fat 30 min run 1% anionic azo dye 30 min run	Neutralizing 1,4% sodium formate 20 min run 0,9% sodium bicarbonate 30 min run pH-5,4-5,5 Drain Wash 12% compact neutralizing/retan/fat 30 min run 1% anionic azo dye 30 min run
8-15% EUROCOMPACT 60 min run 5-12% vegetable tanning material 40 min run 1% formic acid 15 min run pH-3,7 Drain Wash	8% fatliquors 30 min run 1% formic acid 30 min run pH-3,5 Drain	8% fatliquors 30 min run 1% formic acid 30 min run pH-3,5 Drain

Results

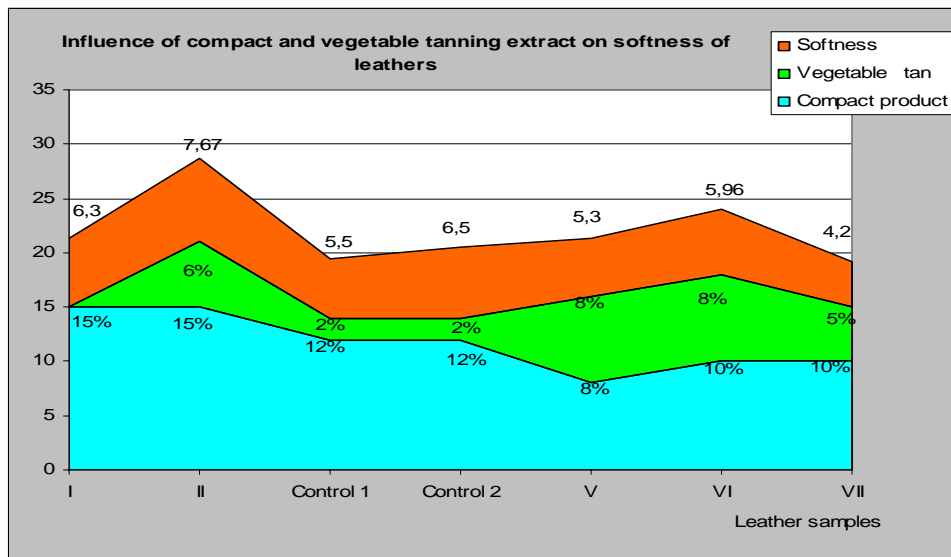
PHYSICAL-MECHANICAL BEHAVIOR

From the physical-mechanical point of view the major strength characteristics are comparable to and within the range of the standard ones, as compared to the control samples prepared with commercially available compact materials, as revealed by the histograms for elongation and tensile strength values, and further exemplified on some parallel samples:

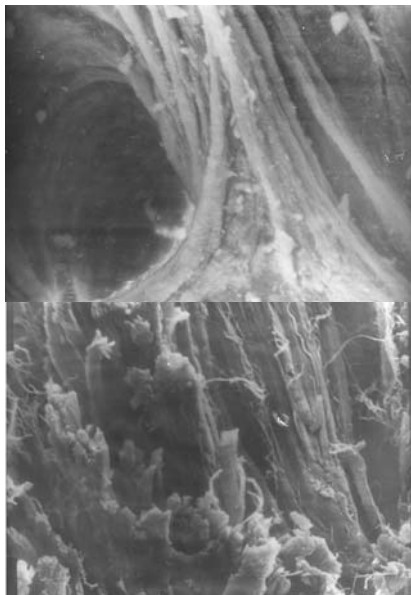


INFLUENCE OF COMPACT MATERIAL AND VEGETABLE EXTRACT ON LEATHER SOFTNESS

Trials have revealed that a compact material offer of 8-15% provides a large range of softness characteristics in leather, related to the vegetable tannin type and offer, from box leather to upholstery and garment leather. Sample VII is represented by shoe upper leather made on the industrial plant.



The aptitude of new compact retanning, fatliquoring and dyeing material for leather structuring can be seen in the following SEM images:



SEM for wet-blue support, 1230x
SEM for control sample, 1600x

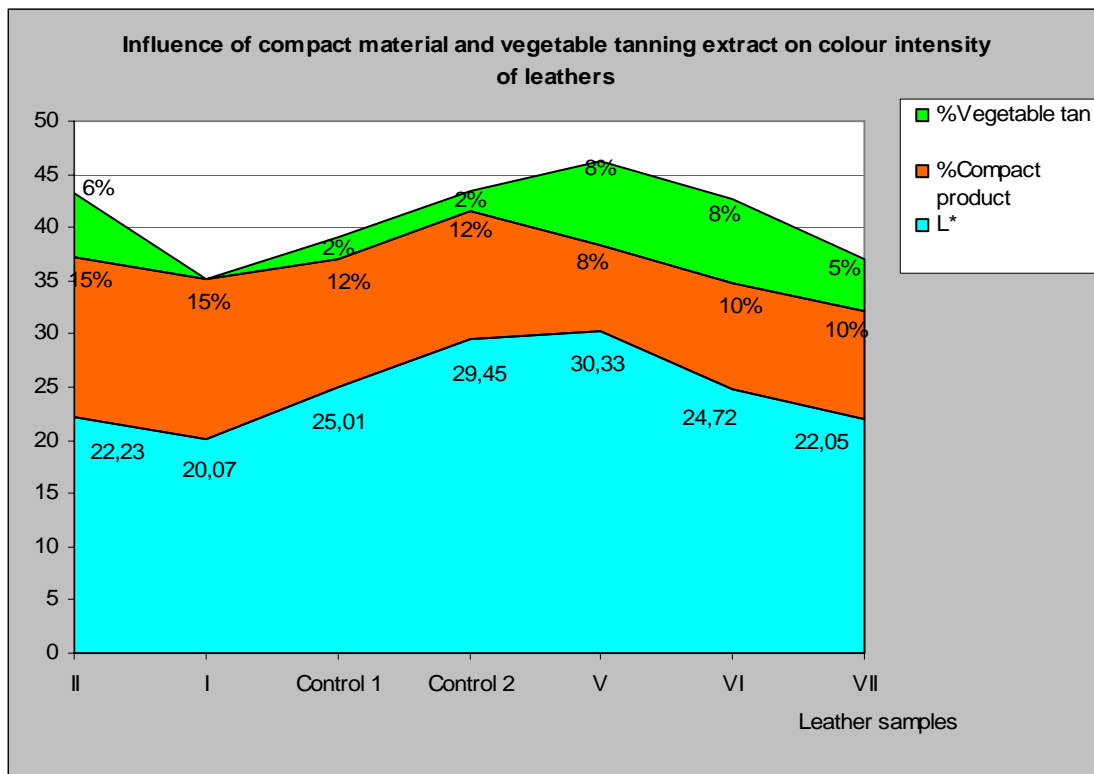


SEM for compact retanned sample (nappa), 1600x

SEM for compact retanned sample (box), 1090x

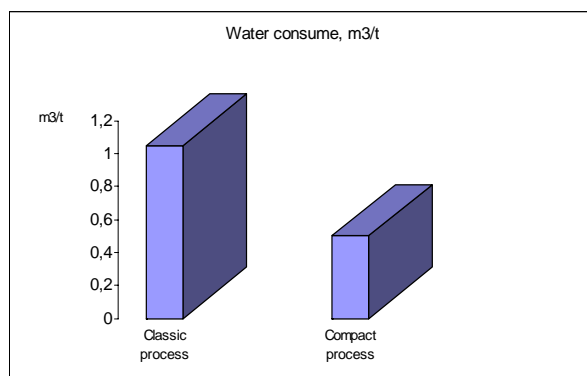
INFLUENCE OF COMPACT MATERIAL AND VEGETABLE EXTRACT ON INTENSITY OF COLOUR

The sample II has shown a maximum black intensity, followed by the sample VII (industrial), with the least vegetable tannin offer.

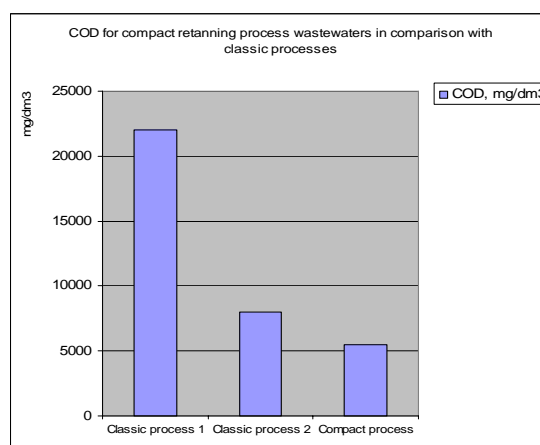
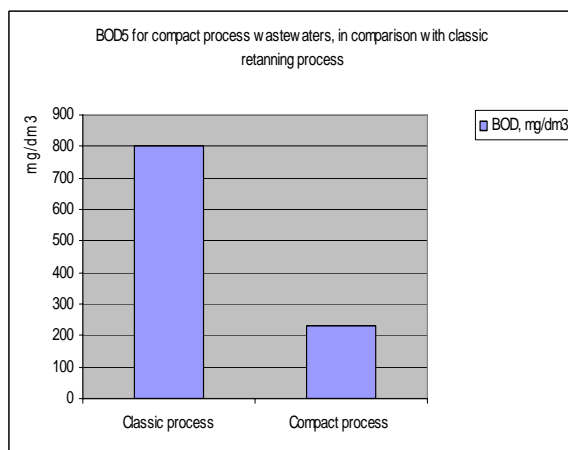


ECOLOGICAL SOUND OF COMPACT RETANNING PROCESS

Water consumption with the compact process is reduced by 60%, being one of the compact process advantages:



COD and BOD₅ values are highly reduced by applying the compact retanning. High penetration ability as a result of the fatliquoring, dyeing and retanning agent synergy in the blend accounts for the high exhaust of the new compact material:



Wastewater from compact process

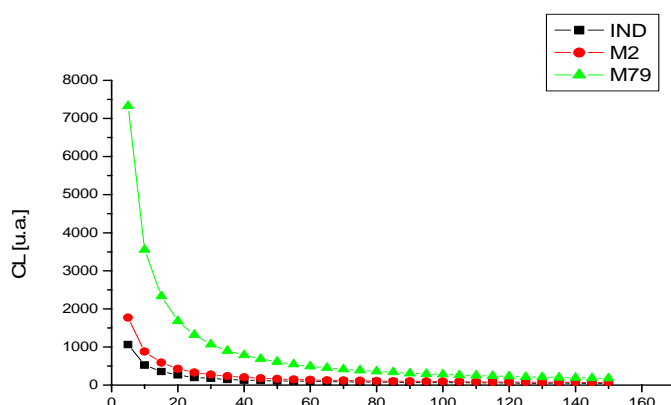
The classical chemical analysis used in the determination of the major pollutants is laborious and requires a long period of time. To get quickly environmental data providing an overall picture of the industry effects on the environment, the method of chemiluminescence was applied in measuring the effluent anti-oxidizing activity. This method was not applied for such effluents so far.

Tests were performed with a Turner Design TD20/20 (USA) chemiluminometer, using the pair luminol – H₂O₂ as generation system, at pH = 8,6 (with the buffer TRIS – HCl).

The liquor resulted from each batch was double filtered to retain all suspended solids with the aim to become clear [5] and subsequently was subjected to the chemiluminescence test.

From the $CL=f(t)$ curves for the evolution of the intensity of the signal in time we have calculated anti-oxidizing activity (AA) and the initial speed of the process (v).

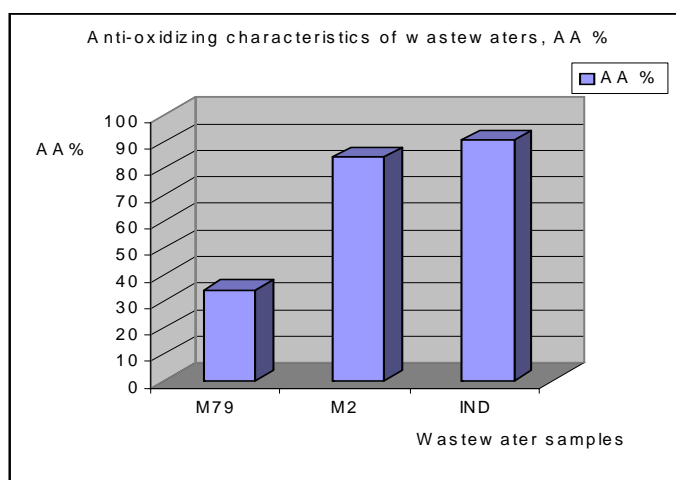
The evolution of chemiluminescence (CL) in time for compact process (M79) in comparison with classical processes (IND, M2)



Time, s

Chemiluminescence characteristics of wastewaters

Wastewater samples	AA %	$v (s^{-1})$
M2- classical process	84,0	354,40
M79- EUROCOMPA CT process	34,0	1466,00
IND- classical process	90,4	212,60

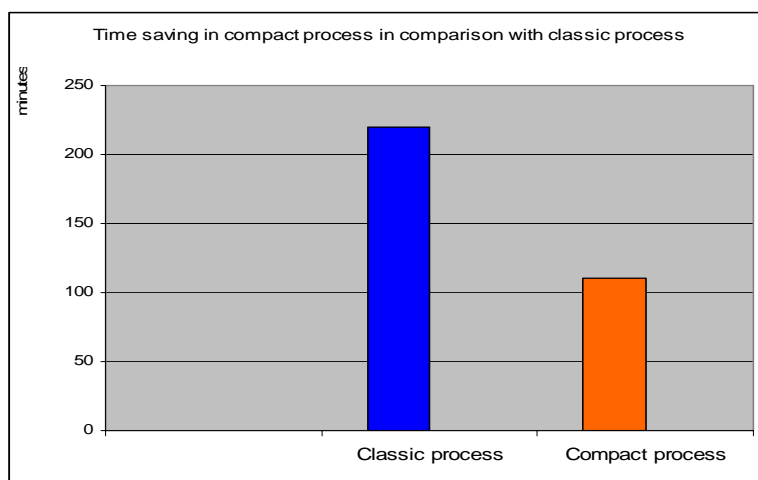


The reduced anti-oxidizing activity of wastewaters from compact retanning process by using EUROCOMPACT product confirms the ecological improved effects in comparison with classical processes.

The durability of the new retanning process was realized by selection of special materials, selected in order to rich the optimized balance leather quality/ecological impact.

IMPROVED PRODUCTIVITY

A significant effect which has been revealed in all experienced compact processes is a highly reduced processing time of retanned leather, as shown in the following histogram:



Conclusion

- Compact retannage of leathers is a suitable solution for an ecological process.
- EUROCOMPACT is a new compact material for fatliquoring, dyeing and retanning of leathers which are storage stable, versatile and comparable in performances with classical materials.
- The environment and output effects introduce the new product as an innovative retanning material.

References

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