NOVEL RETANNING AGENTS WITH LESS BISPHENOL CONTENT - A SUSTAINABLE APPROACH TO LEATHER MANUFACTURE

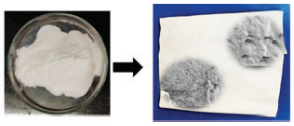
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Abstract

A phenol-based retanning agent with lower bisphenol content has been developed using innovative process technology and monomer chemistry. The results showed that newly developed phenolic syntan with lower levels of bisphenol S and F as a good alternative to commercial phenolic syntans.



Novel retanning agent Post tanned leather

Introduction

- Environmental issues are now a major concern for the leather industry globally. The most recent issues confronting the leather industry are those related to bisphenol regulations.
- Bisphenols are known endocrine disruptors, both for human health and the environment. Most synthetic tanning agents used in leather processing are phenol and sulphone based, and these syntan may contain Bisphenol S and F. Phenol Sulfonic condensates are polymers made from phenol sulfonic monomer with the aldehyde. These polymers are commercially called phenol/sulphone based syntan and are primarily used in the leather industry for pre-tanning, tanning, and retanning.
- To reduce the limits of bisphenol in those polymers, novel phenolic syntan was developed with modification in the process and monomer chemistry and achieved leather properties similar to commercially available syntan.
- In this study, a comparison was made between commercial phenolic syntan and novel phenolic syntan. The leather obtained from both control and experimental leather were analysed by using SEM, physical characteristics etc.,

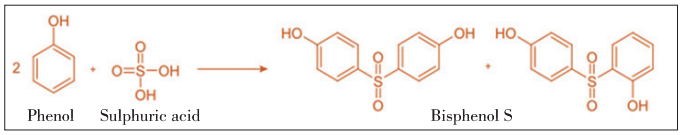
Materials and Methods

✓ Synthesis of Novel retanning agent and their characterisation

✓ Application of syntan on the leather specimen and its characterisation

Novel retanning agent

- Bisphenols are formed as by-products of the phenolic syntan manufacturing process as side reactions.
- Traditionally, phenolic syntans are produced by sulphonating phenol with sulphuric acid or oleum in a mole ratio of 1:1.05 to 1:1.20 for 3-5 hours at 110-115^{0}C. Due to the reaction condition, Bisphenol S will be formed as a by-product.



Phenol Sulphuric acid Bisphenol S

Presently, sulphonation of phenol and sulphuric acid at low temperatures results in a very less amount of Bisphenol S formation. This is confirmed by the analysis of PSA by LCMS-MS.

Trials	Condition	Bisphenol S	Free Phenol
Example-1	95-100^{0}C	> 500 ppm	> 5500 ppm
Example-2	80-85^{0}C	> 300 ppm	> 4500 ppm
Example-3	70-75^{0}C	< 100 ppm	< 100 ppm

To avoid the Bisphenol F formation, a novel phenolic syntan was developed by sulphonating at a lower temperature than usual and replacing the phenol with a phenolic derivative during second condensation stage, resulting in relatively low levels of Bisphenol S and Bisphenol F.

LCMS-MS Results

Phenolic Syntan	Bisphenol S	Bisphenol F	Bisphenol A	Free Formaldehyde	Free Phenol
Novel Phenolic Syntan	< 100 ppm	< 20 ppm	BLQ	< 100 ppm	< 100 ppm

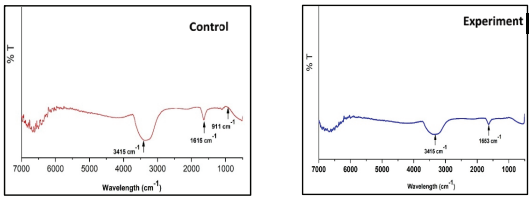
- BLQ - Below the Limit of Quantification

Results and Discussion

General characteristics of the product

Colour	White
pH	3.0 – 4.0
Solubility	Soluble
Moisture Content	6.0 % (Max.)

FTIR – Fourier transform infrared spectroscopy



- The FTIR spectrum of control exhibited a peak of oxirane group at 910.2 cm^{-1} and another peak of hydroxyl group was observed at 3415.0 cm^{-1}. Apart from the oxirane absorptions this product shows the bands corresponding to the stretching C=C of aromatic rings at 1615 cm^{-1}.
- Whereas in the FTIR spectrum of experimental sample disappearance of peak of oxirane group was observed. The intensity of stretching aromatic rings at 1653 cm^{-1} are reduced compared to the control. So, this indicates that the prepared phenolic syntan has reduced bisphenol content.

Scanning Electron Microscopic (SEM) Analysis

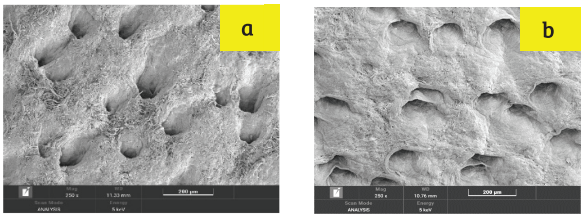


Figure 1. SEM grain surface images of leather specimen with (a) Commercial Phenolic syntan and Novel Phenolic syntan (b) with magnification of 250x

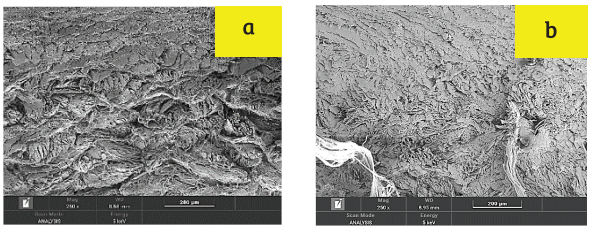


Figure 2. SEM Cross sectional images of leather specimen with (a) Commercial Phenolic syntan and Novel Phenolic syntan (b) with magnification of 250x

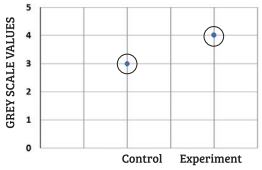
a - Control - Commercial Phenolic syntan
b - Experiment - Novel Phenolic syntan

- SEM results clearly show that the experimental leather's (b) grain surface was better than control leather (a), with the experimental leather exhibiting better grain characteristics, smoothness, and compact fibre bundles.
- Based on the SEM images, it can also be concluded that the filling up of fibre bundles in the experimental leather (b) was better.

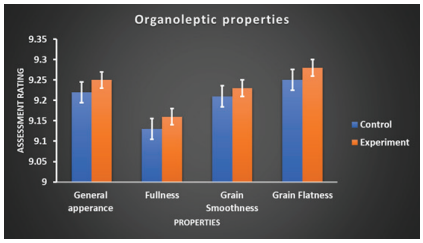
Physical and organoleptic properties of leather

Experiments	Tensile strength (Kg/cm^2)	%Elongation at break	Tear strength (Kg/cm)
Control	229± 0.1	49 ± 0.3	45 ± 0.5
Experiment	236 ± 0.3	53 ± 0.5	46 ± 0.5

According to the results, the physical characteristics of the experimental leather were better compared to the control leather.



- The experimental leathers have a light fastness of 4 on the Greyscale, whereas the control leather has a light fastness of 3. This clearly shows that light fastness of Novel Phenolic syntan was better than Commercial Phenolic syntan



The grain pattern and fullness of the experimental leather were superior to that of control leather. This may probably be due to the improved penetration of the product on leather.

Conclusion

- The result shows that bisphenol content is very less compared to Commercial Phenolic syntan.
- Physical properties of leather with Novel Phenolic syntan are better than Commercial Phenolic syntan.
- Fibre structure shows smoothness, better grain characteristics and compact fibre bundles.
- Novel Phenolic syntan suitable for universal application as the replacement syntan.
- It can be used as a co pretanning syntan for wet white leather.
- The treated leather will impart a tight and mellow handle with good fullness.

References

1. Jochen Ammenn, C. Huebsch, Schilling, B. Dannheim: Chemistry of syntans and their influence on leather Quality, JALCA, Vol. 110, 349-354, 2015.
2. M. Tomita, M. Tokitaka: Dihydroxy–diphenylsulphone and Salicylic Acid Derivatives in the After treatment of Dyed Nylon, Coloration technology, Vol. 96 (6), 286-310, 1980.