

# Development of Bisphenol S-Free Syntans for Leather Manufacture

Riccardo Pasquale<sup>1</sup>

<sup>1</sup>GSC Group S.P.A., Via dell'industria, 5, 36054 Montebello Vic.no, Vicenza Italy, +39 0444 670949,  
[riccardopasquale@gscspa.it](mailto:riccardopasquale@gscspa.it)

## Abstract

The leather industry is increasingly challenged by the hazardous nature of bisphenol S (BPS) and the stringent regulations imposed by the European Chemicals Agency (ECHA) on its use in leather and related chemicals. This study aims to develop a sustainable, economical, and industrially viable process for producing bisphenol-free syntans based on traditional and highly effective di-hydroxy di-phenyl sulphone (DDS) based polymer.

Our research evaluated commercial alternatives from 2023-2024, primarily based on phenolic syntans, which may still contain bisphenol F. However, this phenolic syntans exhibited reduced efficacy in terms of retanning power, requiring higher quantities to achieve the same performance as DDS-based syntans. This raised the question of whether it was feasible and worthwhile to retain the former BPS-based chemistry while eliminating BPS to maintain performance levels.

The GSC Group has pioneered a manufacturing and synthetic route to eliminate all bisphenols from syntan production (bisphenol A, F, S etc.), resulting in bisphenol-free versions of existing products that offer equal or superior performances. This development not only complies with regulatory requirements but also supports the industry's transition towards safer and more sustainable practices.

**Keywords:** Bisphenol S, phenolic syntans, leather manufacture, ECHA regulations, sustainable processes, bisphenol-free syntans.

## 1 Introduction

A central challenge in the modern leather industry has been reconciling industrial growth with environmental sustainability. Among the most promising strategies explored was the adoption of bio-based carbon chemicals, which operate within the "fast" carbon cycle (Schlesinger, 1997) (R. Pasquale, 2024). These compounds leveraged the natural carbon sequestration capacity of plants, which rapidly absorbed atmospheric CO<sub>2</sub> during their growth phase. In parallel, other approaches focused on chemical innovation, aiming to redesign conventional tanning processes to reduce or eliminate the use of hazardous substances.

Historically, the leather industry has relied heavily on synthetic tanning agents (syntans) to enhance key leather properties such as softness, fullness, and color uniformity. However, many of these syntans were based on phenol condensation chemistry, particularly involving bisphenol S (BPS) generation, and/or often resulted in the formation of bisphenol F (BPF) as a by-product. Both compounds have come under increasing regulatory scrutiny due to their potential environmental and health risks. In response, the European Chemicals Agency (ECHA) introduced stricter regulations governing the use of bisphenols, compelling the industry to seek safer and more sustainable alternatives (EU, 2024). To comply with these regulations, many chemical suppliers attempted to reduce bisphenol content by diluting standard syntan formulations with inert materials. While this strategy appeared to lower the concentration of bisphenols, it proved ineffective in practice. Achieving comparable performance in leather processing required significantly higher dosages of these diluted products, which ultimately led to an equal or even greater total bisphenol load in the overall mass balance. Furthermore, the increased volume of chemicals introduced additional logistical and environmental burdens, including higher transportation demands, expanded storage requirements, and a larger carbon footprint. As such, these dilution-based strategies failed to deliver meaningful improvements in either sustainability or regulatory compliance.

Alternative approaches based on phenolic syntan chemistry were also explored, particularly the development of hybrid DDS syntans. However, these products often exhibited limited retanning performance, ultimately falling into the same limitations as their predecessors. This study described the development and implementation of a new generation of syntans, specifically designed to eliminate free bisphenol species. These novel products were engineered to comply with the latest regulatory requirements concerning bisphenol content in both chemicals and finished leather. Importantly, they maintained (or in some cases exceeded) the performance of conventional syntans. As such, they represented a significant advancement in syntan chemistry and leather processing technology, supporting the industry's transition toward safer, more sustainable practices.

## 2 Materials and Methods

### 2.1 Chemical analyses

Bisphenol quantification in both chemicals and leather samples was carried out in accordance with ISO 21135:2024 and ISO 11936:2023, respectively. Analyses were performed using a *Perkin Elmer ALTUS A-10* HPLC system equipped with a C18 column (150 × 4.6 mm) and a diode-array detector (DAD). Analytical standards for bisphenol A, S, and F were sourced from *Aldrich*. Thermogravimetric TGA analyses were performed on a *Pyris TGA 8000* from *Perkin Elmer*. FTIR analyses were recorded on a *Frontier* from *Perkin Elmer* using ATR as a probe sample; the attribution of the bands from the FTIR spectra was carried out according to strong (s), medium (m), weak (w) and broad signals. For the analysis of the liquid syntans, the samples were dried at 150°C and placed on the ATR probe; the FTIR spectra were recorded with 4 cm<sup>-1</sup> resolution and a wavenumber range from 4000 to 380 cm<sup>-1</sup>. The background consisted of 4 scans, as well as the analysis. Shrinkage temperatures T<sub>s</sub> (°C) were recorded on a *Giuliani Tecnologie Original Torino 1973* according to UNI EN ISO 3380:2015, following the standard heating temperature of the leather in the water-bath.

## 2.2 Chemical preparation

The chemicals used in this study were sourced by GSC Group in accordance with internal manufacturing protocols and quality control standards. Bisphenol S (BPS), purchased from *Aldrich*, was used as a reference compound throughout the experimental procedures.

## 2.3 Leather preparation

The hides used in this study were sourced from standard suppliers in accordance with GSC Group procurement protocols. They were subsequently prepared following specific procedures developed by the company's technical department. The application of syntans, as well as the comparative evaluation between different formulations, was carried out according to internal methodologies for both the tanning and retanning phases. Leather quality was assessed through a series of standardized tests commonly employed in the automotive sector, although our main focus was the bisphenol content and the effects on leather. Additionally, light and heat fastness were evaluated to determine suitability for upholstery applications. The finishing procedures for automotive, upholstery, and leather goods articles followed proprietary GSC Group protocols. However, it is important to note that the syntan developments described in this work did not directly influence the finishing stages, which remained consistent across all samples.

## 3 Results and discussion

This study presented recent advancements in the synthesis and application of synthetic tanning agents (syntans) for leather processing. The primary objective was to develop a sustainable, cost-effective, and industrially scalable process for producing bisphenol-free syntans, while maintaining (or even enhancing) the performance of conventional DDS-based products. GSC Group focused on preserving the advantageous characteristics of DDS chemistry while redesigning the production process to meet modern environmental and regulatory standards. This included ensuring that the final products complied with stringent safety requirements, as documented in their respective Safety Data Sheets (SDS). A key goal was to maintain the same application levels in leather manufacturing, and in some cases, to reduce them, without compromising performance. A significant portion of the research was dedicated to optimizing the DDS synthesis process, particularly by minimizing the presence of free bisphenol S (BPS) in the final product. Through the refinement of reaction conditions and purification steps, the process effectively reduced residual BPS content, thereby aligning with current environmental and toxicological regulations.

The conventional manufacturing route for DDS-based syntans typically begins with the sulfonation of phenol using sulfuric acid, yielding phenol sulfonic acid as the primary intermediate (Figure 1, black path). A second equivalent of phenol is then introduced, leading to the formation of dihydroxy diphenyl sulfone (BPS), predominantly in the thermodynamically favored 4,4'-isomer form. To facilitate this condensation, the reaction is conducted at elevated temperatures and under reduced pressure, which also helps the distillation of by-products. The resulting BPS is subsequently condensed with formaldehyde (optionally in the presence of urea) to form the acidic DDS blend, which is then sulfonated and dispersed in water. Among all stages, the condensation between the second phenol equivalent and phenol sulfonic acid was identified as the primary source of residual free BPS in the final product. Thermal optimization alone proved insufficient to meet the increasingly stringent thresholds set by the European Chemicals Agency (ECHA). In contrast, first-condensation phenolic syntans follow a different synthetic route (Figure 1, blue path). After sulfonation, phenol is directly condensed with formaldehyde, followed by a second sulfonation step. These syntans do not generate BPS or BPF, although trace levels may still be detected. However, second-condensation phenolic syntans—where a second phenol equivalent is introduced after formaldehyde condensation—are directly responsible for the formation of BPF. Following synthesis, syntans may undergo atomization and be marketed in powder form, in line with standard industrial practices.

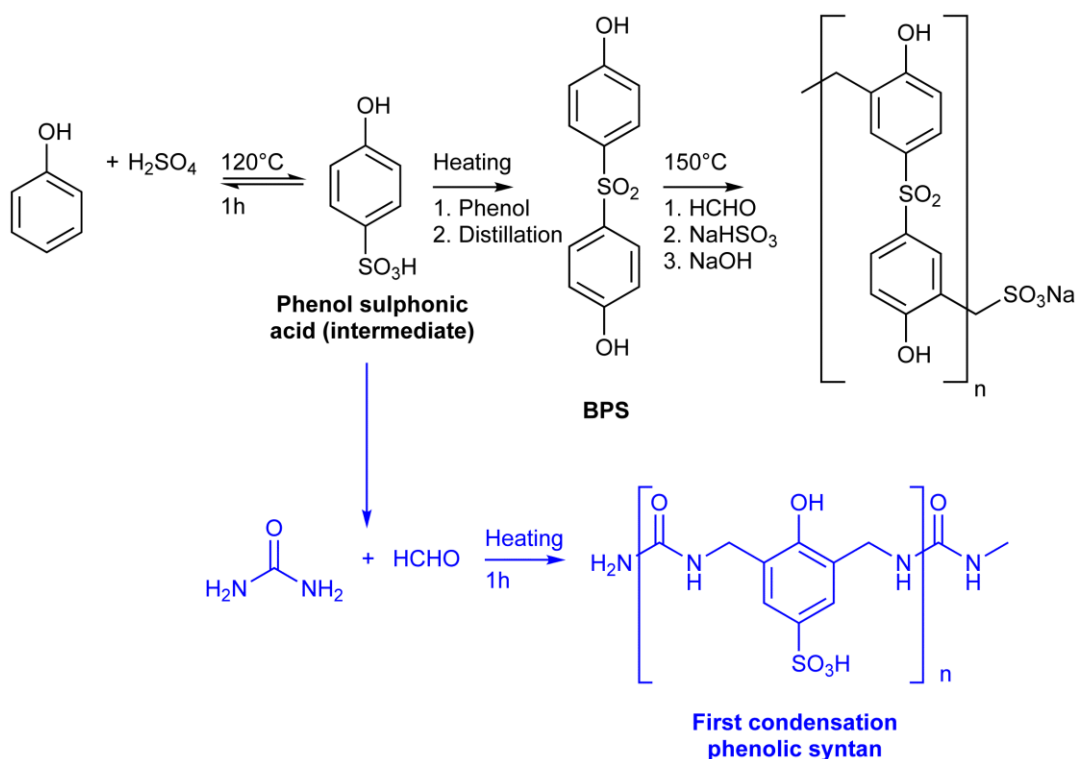


Figure 1: reaction scheme for syntan manufacture.

To overcome these challenges, GSC Group developed an innovative synthetic and manufacturing route that completely eliminated bisphenols—including BPA, BPF, and BPS—from the production process. This advancement enabled the creation of bisphenol-free syntans that matched or exceeded the performance of their conventional counterparts. The new process employed standard monomers and reagents, but introduced modified polymerization strategies to produce highly pure DDS-based syntans without relying on hazardous free-bisphenol intermediates. A multi-step approach was adopted to address the most critical stages in both DDS and phenolic syntan synthesis. This included enhanced temperature control during phenol condensation in the DDS process, improved dispersion techniques for both DDS and phenolic syntans, and a specialized post-reaction treatment designed to reduce residual bisphenol content (regardless of its origin) to negligible levels. These innovations ensured full compliance with current legal and ECHA regulatory requirements. The resulting syntans demonstrated excellent retanning performance, consistent color development, and superior leather softness. In addition to their technical performance, they offered significantly improved environmental and toxicological profiles, representing a major step forward in the development of sustainable leather processing technologies.

### 3.1 The role of BPS in retanning: evaluating its contribution to leather performance

The retanning effect in leather processing is primarily governed by the interaction of (poly)phenolic compounds with the quaternary structure of collagen. These interactions occur through two principal mechanisms: hydrogen bonding and aromatic ring stacking. In the first mechanism, phenolic hydroxyl groups form medium to strong hydrogen bonds with collagen chains, inducing irreversible structural modifications that enhance hydrothermal stability and extend the material's shelf life. The second mechanism involves  $\pi$ - $\pi$  stacking interactions between aromatic rings in the phenolic compounds and the side chains of collagen proteins. These ordered, non-covalent interactions further stabilize the protein matrix. Together, these molecular interactions define the retanning efficacy of a given syntan.

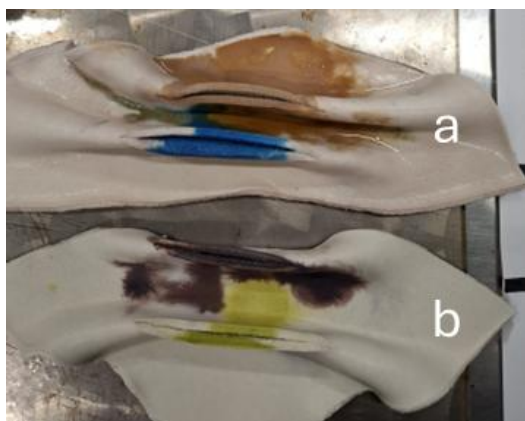
A central question addressed in this study was whether free bisphenol S (BPS) contributes more significantly to retanning performance than polymeric syntans. This raises a broader concern for the leather industry: should attention be focused on the presence of free monomers (such as BPS, which can be present at levels up to 15000 ppm) or are polymeric structures alone sufficient to ensure optimal performance?

Among bisphenol compounds, BPS is the largest, most rigid, and structurally constrained. In contrast, bisphenol F (BPF) is smaller and more flexible. Molecular rigidity plays a critical role in interaction strength: less flexible molecules are more effective in forming hydrogen bonds and  $\pi$ - $\pi$  stacking interactions, as they resist conformational adaptation to the collagen structure (C. F. Lim, 2007). From a theoretical standpoint, BPS should therefore be more effective in retanning than BPF. However, experimental evidence demonstrated that the retanning performance of free BPS is limited. Although it is capable of interacting with collagen, its effectiveness as a monomer was found to be inferior to that of polymeric DDS-based syntans.

### 3.1.1 Tannage comparison between BPS and DDS syntan

A series of controlled experiments were conducted to assess the tanning/retanning performance of free bisphenol S (BPS) in comparison to standard DDS-based syntans. In the first trial, the focus was addressed to tanning properties; a 5% aqueous solution of BPS, neutralized with caustic soda, was applied to hides prepared according to GSC Group's standard protocol. The resulting leather exhibited poor visual quality and a shrinkage temperature of approximately 64 °C. Additionally, the material performed inadequately during mechanical operations such as pressing and samming, and a substantial portion of the BPS was found to leach into the water floats, indicating limited fixation to the collagen matrix. In a second trial, the BPS concentration was increased to 10%. The treated leather showed improved visual characteristics, appearing notably white, and the shrinkage temperature rose to approximately 68 °C. However, the leather required plenty of formic acid for fixation and became excessively stiff, which negatively impacted its mechanical workability, particularly during pressing and samming operations. These findings confirmed that while free BPS is capable of interacting with collagen, its retanning efficacy as a monomer is limited.

In contrast, standard DDS-based syntans demonstrated superior performance under identical conditions. At 5% concentration, the DDS syntan achieved a shrinkage temperature of approximately 65 °C, while at 10%, it reached around 70 °C. This enhanced performance was attributed to the polymeric nature of the DDS syntan, which incorporates multiple phenolic units within a rigid, interconnected framework. Such a structure enables a higher density of interactions with the collagen matrix, offering greater structural stability and more effective retanning than isolated bisphenol molecules. These results clearly indicated that the superior performance of DDS syntans arises not from the presence of free BPS, but from the polymeric architecture itself, which provides both functional efficiency and regulatory advantages.



**Figure 2: cross-section colour with different indicators; a) refers to 10% BPS solution, b) refers to standard syntan 10% solution.**

Figure 1 illustrates the visual appearance of leathers treated with 10% solutions of free BPS and standard DDS syntan, accompanied by cross-sectional pH assessments using ferric chloride ( $\text{FeCl}_3$ ) and Bromocresol Green (BCG) indicators—applied to the upper and lower halves of each sample, respectively. Sample a, treated with the 10% free BPS solution, exhibited no significant pH reduction following overnight drum rotation under standard acidification conditions. In contrast, sample b, treated with the standard DDS syntan, reached a pH of approximately 4.2, indicating effective acid penetration and fixation. Furthermore, the  $\text{FeCl}_3$  indicator revealed a markedly more intense complexation response in the syntan-treated sample, suggesting a higher density of reactive sites or stronger interaction with the collagen matrix. Notably, no significant differences were observed between the standard DDS syntan and its low-bisphenol variant under these test conditions, confirming that the reduction of free bisphenols did not compromise the syntan's functional performance.

### 3.2 Characterization of bisphenol-free syntans

The characterization of syntans focused on evaluating their structural integrity, solid content, and bisphenol concentration. The analysis concentrated on liquid syntans, comparing a benchmark DDS-based formulation—containing approximately 10,000 ppm of free BPS and 40% dry residue—with a low-bisphenol alternative developed by GSC Group.

#### 3.2.1 TGA analysis

Thermogravimetric analysis (TGA) was performed to compare the thermal behavior of the benchmark DDS syntan and its low-bisphenol counterpart. Liquid samples were placed in ceramic crucibles and subjected to a controlled heating program from 30 °C to 900 °C at a rate of 25 °C/min under an air flow of 25 mL/min. An isothermal step under aerobic conditions followed to determine the residual ash content. The presence of approximately 1% free BPS in the benchmark sample did not result in any discernible differences in thermal decomposition behavior. Both syntans exhibited similar mass loss profiles, with a total weight reduction of approximately 60% at 120 °C (Figure 3). The residual ash content for both samples was around 6% by weight. Although free BPS is known to decompose near 320 °C, no distinct thermal transition or peak attributable to BPS was observed in the thermograms or their derivative curves. These results indicated that the thermal stability of the syntans was governed primarily by the polymeric matrix, and not significantly influenced by the presence or absence of free BPS.

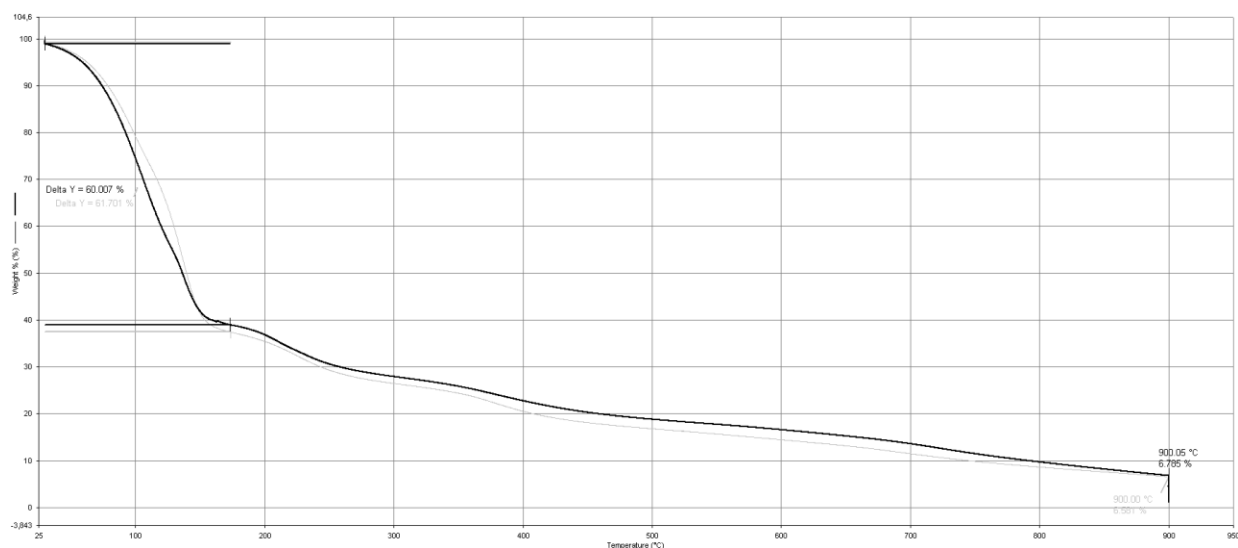
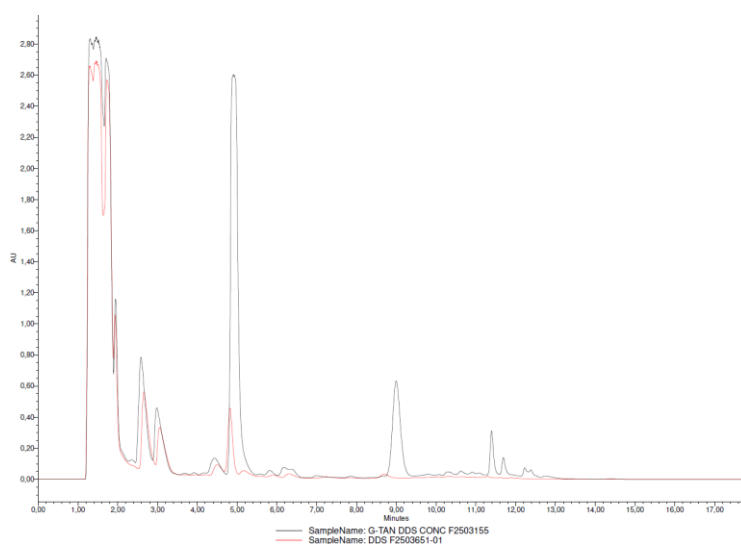


Figure 3: TGA profile for a) standard DDS syntan (black curve) and b) low BPS version of the syntan by GSC group (Grey curve).

### 3.2.2 Free-bisphenol assessments

A central objective of this study was the quantification of free bisphenols in syntan formulations. Using the ISO 21135:2024 analytical protocol, the newly developed syntan produced via the GSC Group process demonstrated a substantial reduction in free bisphenol content. Specifically, the improved DDS-based syntan contained approximately 200 ppm of free BPS, with no detectable traces of bisphenol F (BPF) or bisphenol A (BPA). High-performance liquid chromatography (HPLC) was employed to characterize the chemical profile of the syntans. The resulting chromatograms revealed distinct peaks corresponding to various components, identified based on their retention times (Figure 4). The most soluble fractions of the syntans were detected between 1.00 and 2.35 minutes. Residual phenol and formaldehyde appeared at approximately 3.10 minutes, while BPS was identified at around 5.00 minutes. BPF, when present, eluted later, at approximately 9.00 minutes. The chromatogram of the low-bisphenol syntan clearly demonstrated a reduction in BPS concentration from approximately 10,000 ppm in the benchmark sample to below 200 ppm, as illustrated in Figure 4. This confirmed the effectiveness of the modified synthesis and purification strategy in minimizing free bisphenol content, thereby ensuring compliance with current regulatory standards.

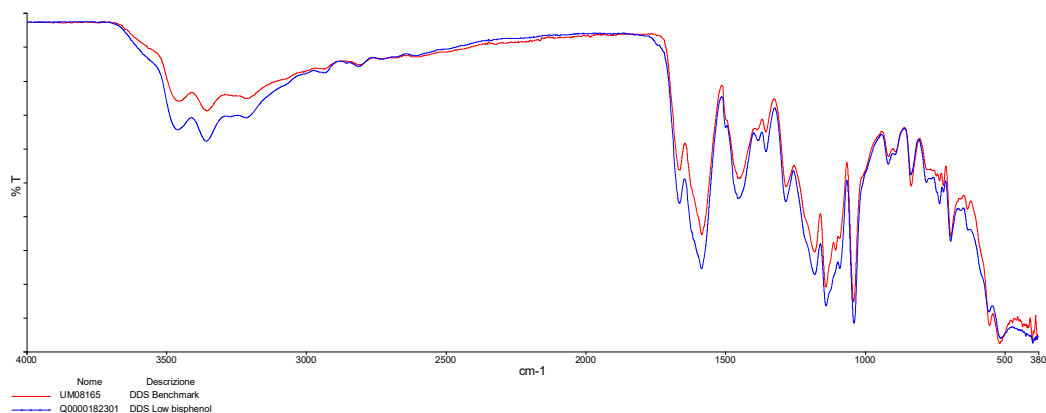


**Figure 4: HPLC chromatograms for the benchmark syntan (black curve) and the low bisphenol syntan by GSC Group (red curve).**

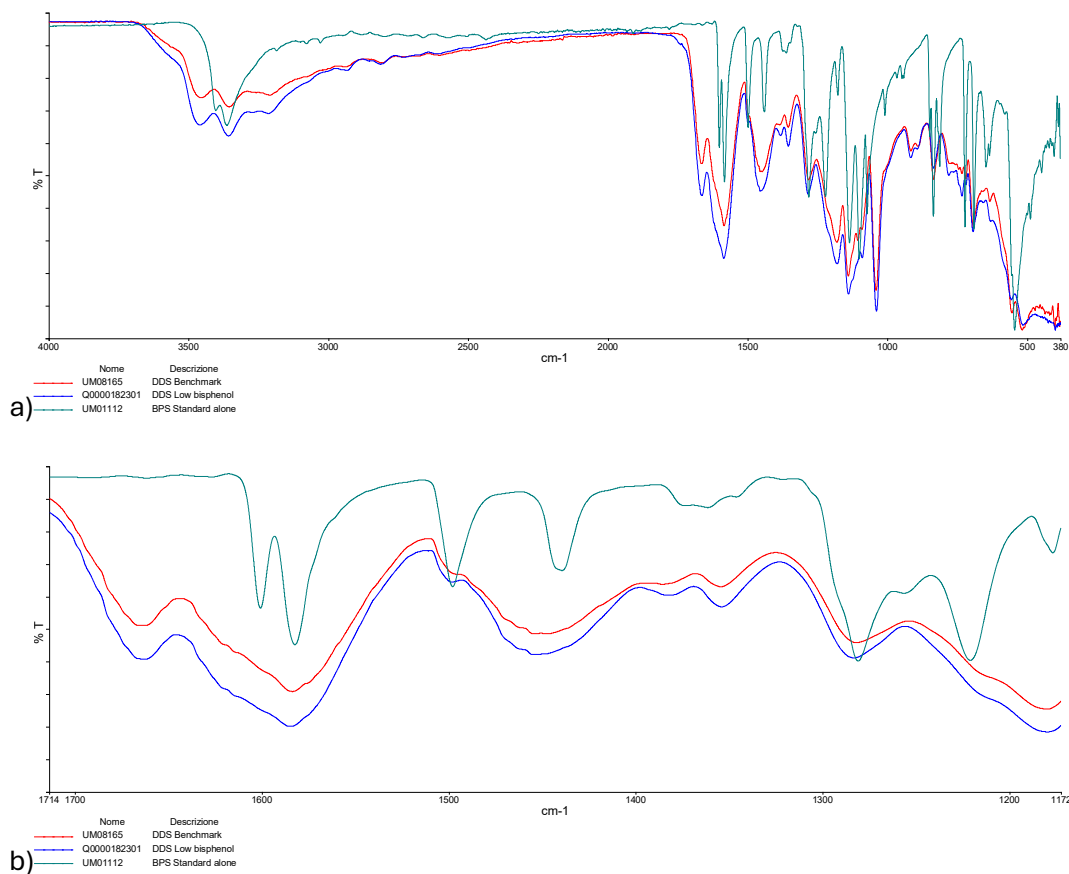
### 3.2.3 FTIR comparison

FTIR spectroscopy was employed to investigate potential structural differences between the benchmark DDS syntan and its bisphenol-free counterpart. The interpretation of the spectra was based on the methodologies described by Nandiyanto *et al.* and D'Eusanio *et al.* (A. B. D. Nandiyanto, 2019) (V. D'Eusanio, 2025). The comparative analysis, illustrated in Figure 5, revealed no significant differences in the functional group composition between the two samples. In the figure, the red trace corresponds to the benchmark syntan, while the blue trace represents the bisphenol-free version. The spectral analysis identified three key regions. In the range from 3730 to 2500  $\text{cm}^{-1}$ , both samples exhibited strong absorption bands attributed to O–H stretching and aromatic and aliphatic C–H stretching vibrations. Between 1830 and 1513  $\text{cm}^{-1}$ , characteristic bands associated with substituted benzene rings were observed. In the region from 1500 to 1320  $\text{cm}^{-1}$ , both syntans displayed similar absorption patterns, consistent with 1,4-disubstituted aromatic rings. Although this region could also reflect the presence of free BPS, its contribution could not be clearly isolated, except for a medium-intensity signal at 1498  $\text{cm}^{-1}$ , which may be partially attributed to BPS (see Figure 6 a and b). Further analysis of the 1320 to 1064  $\text{cm}^{-1}$  region revealed bands corresponding to benzenic C–H vibrations. Additionally, strong absorptions between 1064 and 960  $\text{cm}^{-1}$  confirmed the presence of sulfonic groups, indicating successful sulfonation in both samples. The fingerprint region below

1000  $\text{cm}^{-1}$  followed the same pattern for both syntans, reinforcing the conclusion that the removal of free bisphenols did not alter the fundamental chemical structure of the product.



**Figure 5: FTIR comparison of the benchmark syntan (red curve) and the low bisphenol syntan by GSC Group (blue curve).**



**Figure 6: a) FTIR spectra comparison between benchmark, low bisphenol syntans and BPS monomer; b) magnification of the area between 1500 and 1320  $\text{cm}^{-1}$**

### 3.3 BPS-free syntan leather application

A comparative performance evaluation was conducted between conventional DDS syntans and their bisphenol-free counterpart, with a particular focus on liquid formulations containing 40% dry matter. The



application trials included both tanning and retanning processes. Overall, no significant differences were observed between the benchmark syntan and the newly developed product by GSC Group. In the tanning phase, both syntans yielded identical shrinkage temperatures, ranging from 69 to 71 °C. These results were obtained using a 10% syntan solution, as described in section 3.1.1. According to ISO 11936:2023, the BPS content in the leather treated with the benchmark syntan was approximately 1200 ppm, whereas the leather treated with the bisphenol-free syntan contained only 150 ppm. In the retanning phase, particular attention was given to wet-white applications. The trials received positive feedback from GSC Group's technical team, confirming the suitability of the bisphenol-free syntan for this purpose. Furthermore, the chemical oxygen demand (COD) values for both syntans were comparable, averaging around 15,000 meq O<sub>2</sub>/L, regardless of the presence of 10,000 ppm of BPS in the benchmark formulation.

When the bisphenol-free DDS syntan was compared to phenolic hybrid alternatives, a markedly different effect on leather quality was observed. The bisphenol-free syntan delivered the same level of fullness, roundness, and tactile feel as the standard DDS syntan containing BPS. In contrast, the phenolic hybrid systems underperformed in these areas and required higher chemical dosages to achieve acceptable results. Additionally, leathers treated with phenolic hybrids exhibited inferior retanning behavior, with reduced uptake of fatliquors and resins, and a generally less desirable hand feel (see 1). Bisphenol content in the treated leathers was quantified in accordance with ISO 11936:2023. As expected, the results were directly proportional to the amount of syntan applied and its intrinsic BPS concentration. Interestingly, the bisphenol-free syntan led to improved leather color, a result that was somewhat unexpected given that phenolic compounds such as BPS are typically associated with bleaching effects. Finally, assessments of light and heat fastness for leathers retanned with the low bisphenol syntan showed performance levels consistent with those of the benchmark product.

## 4 Conclusion

This study demonstrated the successful development of a new generation of bisphenol-free DDS syntans that meet the leather industry's performance standards while addressing growing regulatory and environmental concerns. The strategy proved effective and highly transferable, offering a scalable solution for reducing bisphenol content across various applications. Through synthetic innovation and analytical validation, the GSC Group eliminated detectable levels of BPF and BPA and reduced BPS to below 200 ppm, without compromising technical performance.

Comparative trials confirmed that the bisphenol-free syntans performed on par with conventional DDS syntans in terms of shrinkage temperature, softness, color development, and fastness. The superior performance was attributed to the polymeric structure of the syntans rather than the presence of free BPS, which showed limited efficacy. Additionally, the new syntans maintained comparable environmental impact, as indicated by similar COD values.

While the complete elimination of BPS remains technically complex, the removal of BPF is readily achievable. This flexibility, combined with regulatory compliance and sustainability benefits, makes the technology a robust and forward-looking alternative. A clearer regulatory framework, particularly regarding BPS, would further support its adoption. Overall, this innovation represents a significant advancement in sustainable leather chemistry, enabling the production of high-quality leather with reduced toxicological risk and environmental footprint.

## 5 Acknowledgements

The authors would like to express their gratitude to *GSC Group S.p.A.* for supporting this research. Special thanks are extended to the Analytical Department for their dedicated efforts in the characterization of the

syntans. The author declares no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## 6 References

- A. B. D. Nandiyanto, R. O. (2019). How to Read and Interpret FTIR Spectroscopy of Organic Material. *Indonesian Journal of Science & Technology*, 97-118.
- C. F. Lim, J. M. (2007). Structural Analysis of Bisphenol-A and its Methylene, Sulfur, and Oxygen Bridged Bisphenol Analogs. *J Chem Crystallogr*, 587-595.
- EU. (2024, Dicembre 19). *Document 32024R3190*. Retrieved from <https://eur-lex.europa.eu/>: <https://eur-lex.europa.eu/eli/reg/2024/3190/oj/eng>
- R. Pasquale, T. P. (2024). The Future of Leather Production Based on Chemicals Evaluation. *Journal American Chemical Leather Association in Conjunction with Modern Tools for Higher Performing Processes and Lower Environmental Impact*, 396-404.
- Schlesinger, W. H. (1997). *Biogeochemistry: An Analysis of Global Change, Third Edition Chapter 11*.
- V. D'Eusario, A. G. (2025). Thermal degradation pathways in multi-component epoxy composites. *Journal of Analytical and Applied Pyrolysis*, 107107.