



Syntans: improved performance for automotive leathers

Jochen Ammenn, BASF SE, Germany



The development of syntans for the use in automotive leather has been driven by two major technical requirements:

- Improved light fastness properties and
- Low residual monomer concentration - such as phenol and formaldehyde - within these products

As a result of chemical developments, both of these requirements can finally be met.

The development of syntans

The first generation syntan was developed and marketed one hundred years ago by BASF as a condensate product of phenolsulfonic acid and formaldehyde^[1]. Applications in the tanning process employing this product allowed a more efficient use of vegetable tannins but, when applied as a single tanning agent, it failed to meet the quality and requirements of leather. Because of improvements that were gained in the dispersion and leveling of vegetable tanning agents by this new product, it was considered as an auxiliary^[2].

A second generation of syntans was created by the incorporation of urea into the phenolsulfonic acid – formaldehyde condensation. This opened the door for further development of syntans that could be used to replace vegetable tannins, known as replacement syntans.

A further development of replacement syntans can be considered as formaldehyde condensation products of dihydroxy diphenyl sulfone (DHDPS). Provided this chemistry is carried out under carefully controlled conditions, this can give rise to leathers with lower residual monomers.

Properties of first and second generation syntans

The properties of these three generations of syntans were

compared in a series of investigations, based on the synthesis of poly-condensates of comparable molecular size. Each has been used as a single tanning agent to create leathers which were then compared for various aspects of performance including softness, fullness, light fastness and shrinkage temperature. In addition, the performance of these syntans was compared based on their influence on hydro-thermic denaturation of skin powder measured using Differential Scanning Calorimetry (DSC). The techniques used in these investigations are described in *Panel 1*.

Panel 1: Techniques employed in the investigation.

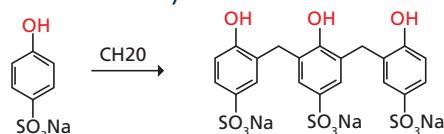
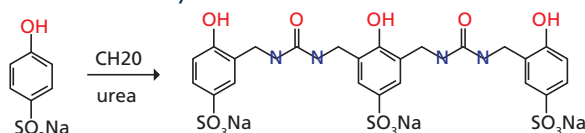
In order to measure the molecular weight of the different syntans, gel permeation chromatography was applied. This is a size exclusion chromatography (SEC) that separates analytes on the basis of size. For characterisation, the average molecular weight (Mw) was used^[3].

The single tannages were carried out with pelts in a procedure published by Lollar and Tul^[4]. A two hour fixation in a separate float generally increased the shrinkage temperature by 1° to 2°C as recommended in the publication^[4].

The Differential Scanning Calorimetry (DSC) is a thermo-analytical method in which the heat uptake of two samples is compared^[5]. Two samples of skin powder were shaken for 6 hours in water, one with a syntan, the other without syntan. After filtration, the samples were analysed in a DSC device for heat uptake. In the diagrams, the difference in heat uptake between the syntan treated samples to the untreated skin powder sample is shown as onset temperatures in degrees Kelvin. This measurement was done at 5 different pH-values ranging from pH = 3 to pH = 7.

The synthesis and structure of the first generation syntans (made from phenolsulfonic acid and formaldehyde^[3]), and second generation syntans (where urea was incorporated into the polycondensation with formaldehyde^[2]) is indicated in *Panel 2*.

While keeping the average molecular weight of these two polycondensates similar, the results on the leather quality were strikingly different in two distinct aspects:

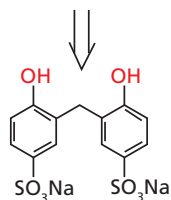
**Panel 2: Synthesis and structure of 1st and 2nd generation syntans.****1st Generation Syntan****2nd Generation Syntan**

- The second generation syntan (where urea was incorporated into the polycondensate product) when applied as the single tanning agent gave softer, fuller, and whiter leathers than pelts tanned with a first generation product.
- The second generation syntan yielded significantly better light fastness results when compared to the first generation syntan.

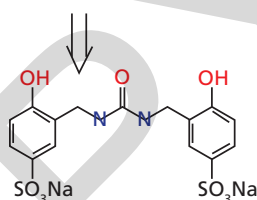
The main difference in reactivity between these two polycondensates could be traced to the bridging methylene groups that were derived from reacted formaldehyde. This is illustrated in *Panel 3*:

Panel 3: Reactivity of 1st and 2nd generation syntans.**1st Generation Syntan**

methylene group
activated from both sides

**2nd Generation Syntan**

methylene group
activated by the aromatic moiety;
de-activated by the nitrogen



In the first generation syntan, this methylene group was activated by aromatic groups on both sides of the molecule. In the second generation syntan, the methylene group was activated by only one aromatic group, while the nitrogen (deriving from urea) de-activated the methylene group on the other side. This appears to explain the better light fastness that resulted from a lower rate of light induced oxidation.

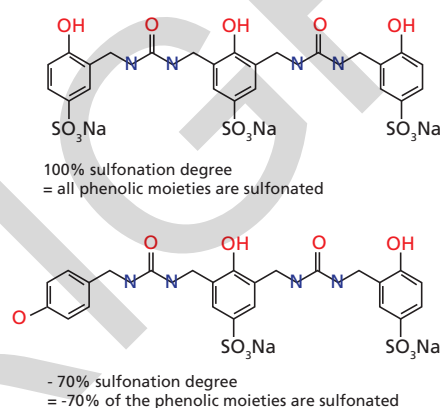
The differences in leather handle/softness characteristics and light fastness significant, the difference in shrinking temperature between the two leathers was small. The second generation syntan only rose two degrees Kelvin in shrinkage temperature. A similar trend was observed by using the DSC, where the application of second generation syntan to skin powder resulted in a four degrees Kelvin higher onset temperature than first generation syntan.

Properties of second generation and replacement syntans

These second generation syntans were the prerequisite for the development of replacement syntans, which were optimised for

tanning power in order to replace vegetable tannins. The difference between a second generation syntan and replacement syntan is the degree of sulfonation, where the replacement syntan has a lower sulfonation degree. This means that not all the aromatic moieties are sulfonated^[6,7].

Within this study there was a focus on replacement syntans made from phenolsulfonic acid, phenol, urea, and formaldehyde in comparison with the second generation syntan made from phenolsulfonic acid, urea and formaldehyde. In this situation the replacement syntan had a sulfonation degree of approximately 70%, while the remaining aromatic moieties were not sulfonated. This is shown in *Panel 4*:

Panel 4: Structure of 2nd generation syntan and replacement syntan.

Here, the replacement syntan was compared to a second generation syntan of the same average molecular weight, in which all aromatic moieties were sulfonated (ie. sulfonation degree = 100%). After a single product tanning with both polycondensates, the leather tanned with the replacement syntan turned out to be a little softer and fuller, but with less light fastness.

However, the shrinkage temperature of the second generation syntan was two degrees higher than that of replacement syntan. Within the DSC analysis, the replacement syntan resulted in four degrees Kelvin higher onset temperature than the second generation syntan.

These differences in both analyses were small. However, the unsolved problem with both polycondensations products was the issue of unreacted residual monomers such as phenol and formaldehyde.

The properties of sulfone syntans

The formaldehyde condensation of DHDPS can be considered a further development of replacement syntans. Due to the low solubility of DHDPS in water – below pH 8, being the pKa of this molecule – the reaction is carried out preferably above this pH, that is under basic conditions.

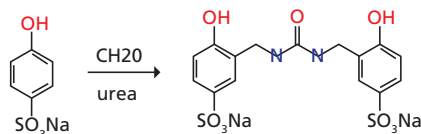
As a further step in the investigations, a polycondensate of DHDPS with formaldehyde (sulfone syntan) was compared with a second generation syntan of the same average molecular weight. The synthesis and structure of both of these products are illustrated in *Panel 5*.

After a single product tanning with both polycondensates, no major difference was found in the tactile properties or light fastness of either of the resulting leathers. In addition, no significant difference was found in either shrinkage temperature

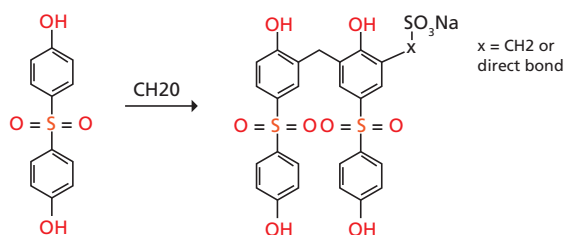


Panel 5: Synthesis and structure of 2nd generation syntan and sulfone syntan.

2nd Generation Syntan



Sulfone Syntan



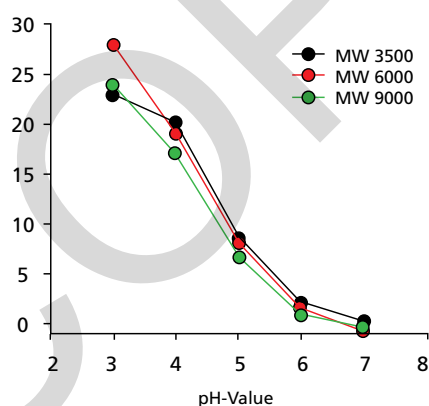
or onset temperature of DCS.

However, major differences were found concerning the residual monomers. In this aspect, provided that the chemistry is carried out under carefully controlled conditions, the sulfone syntans show significant lower values that achieve baseline results.

Comparison between three different types of second generation syntans

No major differences could be found between second generation, replacement or sulfone syntans at different molecular weights when it comes to shrinkage in temperatures (71°–74°C). The same is true for the DSC, where at pH4.0, no major difference could be found. These findings are illustrated in *Panel 6*:

Panel 6: DSC analysis of three 2nd generation syntans with different average molecular weight.



Findings from the study

- Second generation syntans applied as single tanning systems gave softer, fuller, whiter, and better lightfast leathers compared to pelts tanned with first generation syntans, but induced only marginally higher shrinkage temperatures.
- The difference between a second generation syntan and a replacement syntan was that leathers tanned with replacement syntans were fuller and softer but less lightfast. Both

polycondensates gave rise to similar shrinkage temperatures, but left the problem of unreacted monomers like phenol and formaldehyde.

- Sulfone tanning agents can be considered as solving the problem of residual monomers, while keeping high levels of softness and fullness as well as high shrinkage temperatures.

This class of products enables the manufacture of automotive leather with high aesthetic value, high light fastness properties and low residual monomers. ☺



References

- [1] E. Stiasny, Patentschrift 58405, 1913.
- [2] Bibliothek des Leders (1990), Umschau Verlag, Frankfurt, Band 3, p. 50-66.
- [3] Lathe, G.H.; Ruthven, C.R.J. The Separation of Substance and Estimation of their Relative Molecular Sizes by the use of Columns of Starch in Water. *Biochem J.* 1956, 62, 665–674.
- [4] S.-T. Tu, R. M. Lollar, *JALCA* 1950 (45), 324-328.
- [5] Wunderlich, B. (1990). *Thermal Analysis*. New York: Academic Press. pp. 137–140.
- [6] E. Heidemann, *Fundamentals of Leather Manufacturing*, 1993, Roether, Darmstadt, p. 397-411.
- [7] G. Reich, *Das Leder* 1956, 7(12), 289 – 297: Herstellung synthetischer Gerbstoffe durch Mischkondensation sulfonierter und unsulfonierter Komponenten.

Further information

Recommended reading concerning possibilities within the sulfonation of syntans: G. Reich, *Das Leder* 1956, 7(12), 289 – 297: Herstellung synthetischer Gerbstoffe durch Mischkondensation sulfonierter und unsulfonierter Komponenten.

The low reactivity of DHDPS with formaldehyde: G. Reich, G. Hebestreit, *J. f. Prakt. Chemie* 1963, 19, 303–308.

Acknowledgements

This work was a shared investigation between BASF leather development and the FILK institute in Freiberg Germany. DSC analysis performed by Michaela Schroepfer. Input on the chemistry/history of syntans by Prof. Reich.