

## 100 Years of Syntans: How Chemistry Enabled Increasing Performance on Leather

Jochen Ammenn

BASF SE, Ludwigshafen, Germany, Phone: +49-621-6099786, Fax: +49-621-6099381, e-mail: [jochen.ammenn@basf.com](mailto:jochen.ammenn@basf.com)

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### 1. Introduction

The first syntan, marketed one hundred years ago by BASF, was a condensate of phenolsulfonic acid and formaldehyde[1]. It's application in the tanning process allowed more efficient use of vegetable tannins. Applied as a sole tanning agent it resulted in insufficient leather quality and thus had to be considered an auxiliary[2].

Incorporating urea into the phenolsulfonic acid - formaldehyde condensation about 15 years later established a second generation of syntans and opened the door for the development of replacement syntans that could be used to replace vegetable tannins.

The formaldehyde condensation of dihydroxy diphenyl sulfone (DHDPS) can be considered a further development of the replacement syntans and - provided this chemistry is carried out under drastic conditions - can give rise to leathers with lower rest monomers.

In order to compare these three generations of syntans, poly-condensates of a comparable molecular size were synthesized. After sole tanning these syntans were compared in various aspects of performance on leather including softness, fullness, light fastness, shrinkage temperature. Beyond that the syntans were compared concerning their influence on hydrothermic denaturation of skin powder measured via Differential Scanning Calorimetry (DSC).

### 2. Materials and methods

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

The sole tanning was carried out with pelt in a procedure published by Lollar and Tu [4]. The two hour fixation in a separate float generally increased the shrinkage temperature by 1 to 2

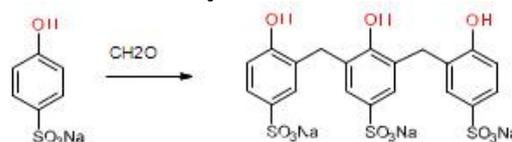
degrees Celsius as recommended in the stated article[4].

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

### 3. Results and discussion

First generation syntans were made from phenolsulfonic acid and formaldehyde[3]. For the second generation syntans that were developed in the 1930's urea was incorporated into the polycondensation with formaldehyde[2].

#### 1st Generation Syntan



#### 2nd Generation Syntan

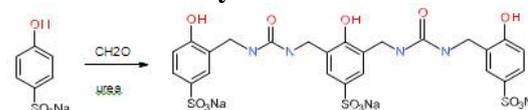


Figure 1. Synthesis and structure of 1st and 2nd Generation Syntans

On the basis of the same average molecular weight of these two polycondensates the differences on leather quality is striking. The polycondensate made with urea (second generation syntan) applied in sole tanning gives softer, fuller, and whiter leathers than pelt tanned with a first generation syntan. Another remarkable difference is the lightfastness in which second generation

syntan is significantly better than the first generation syntan.

A major difference in reactivity between these two polycondensates can be assigned to the bridging methylene groups deriving from reacted formaldehyde. As shown in figure 2, in the first generation syntan this methylene group is activated by aromatic groups on both sides. In the second generation syntan the

### 1st Generation Syntan

methylene group  
activated from both sides

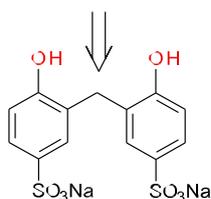


Figure 2. Reactivity of 1st and 2nd Generation Syntans

While the difference in leather quality and lightfastness is large, the differences in shrinking temperature is small, with the second generation syntan giving rise to 2 degrees higher shrinkage temperature.

A similar trend was observed for the Differential Scanning Calorimetry (DSC) where application of the second generation syntan to skin powder results in a 4 degree Kelvin higher onset temperature than the first generation syntan.

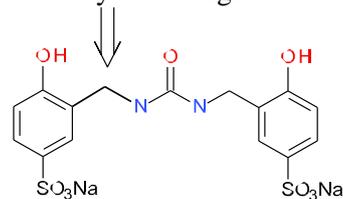
The second generation syntans were the prerequisite for the development of replacement syntans, which were optimized for tanning power in order to replace vegetable tannins. The difference between a replacement syntan and a second generation syntan is the sulfonation degree, with the replacement syntan having a lower sulfonation degree meaning that not all the aromatic moieties are sulfonated[6]. An excellent review about the various possibilities of achieving this was given by G. Reich[7].

Within this work here is a focus on replacement syntans made from phenolsulfonic acid, phenol, urea, and formaldehyde. The replacement syntan is compared to a second generation syntan made from phenolsulfonic acid, urea and formaldehyde. The here stated replacement syntan has a sulfonation degree of ~70%, while the remaining aromatic moieties of this replacement syntan are not sulfonated as depicted in figure 3.

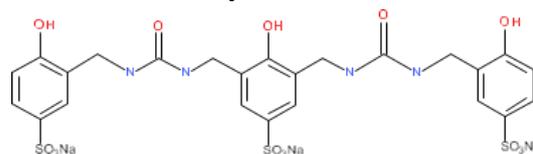
methylene group is activated by only one aromatic group, while the nitrogen on the other side, deriving from urea, de-activates this methylene group which can be the explanation for better lightfastness due to a lower rate of light induced oxidation.

### 2nd Generation Syntan

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

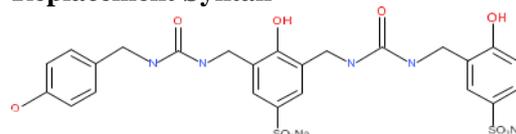


### 2nd Generation Syntan



100 sulfonation degree = all phenolic moieties are sulfonated

### Replacement Syntan



~ 70% sulfonation degree  
= ~70% of the phenolic moieties are sulfonated

Figure 3. Structure of 2nd Generation Syntan and Replacement Syntan

This polycondensate is compared to a second generation syntan of the same average molecular weight, in which all aromatic moieties are sulfonated (sulfonation degree = 100%). After sole tanning with both polycondensates the leather tanned with the replacement syntan turns out to be a bit softer and fuller, but less lightfast. The shrinkage temperature of the second generation syntan is two degrees higher than replacement syntan. Within the Differential Scanning Calorimetry

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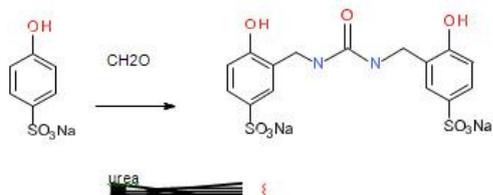
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(DSC) analysis the replacement syntan results in four degree Kelvin higher onset temperature than the second generation syntan. The differences in both analyses are small. The unsolved problem with both polycondensations is the problem of unreacted restmonomers like phenol and formaldehyde.

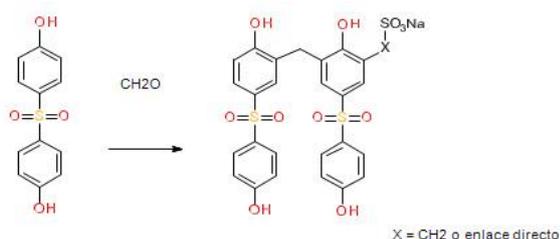
The formaldehyde condensation of dihydroxy diphenyl sulfone (DHDPS) can be considered a further development of the replacement syntans. Due to the low solubility of DHDPS in water below a pH of 8, which is the pKa of this molecule, the reaction is preferably carried out above this pH, meaning under basic conditions. For an important paper about the low reactivity of DHDPS with formaldehyde see G. Reich[8].

The polycondensate of DHDPS with formaldehyde (sulfone syntan) was compared with a second generation syntan of the same average molecular weight. After sole tanning with both polycondensates no major differences were found.

## 2nd Generation Syntan



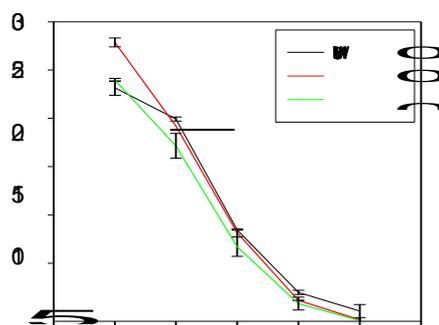
## Sulfone Syntan



Neither in shrinkage temperature nor in the onset temperature of DCS significant differences were found. Major differences can be found concerning the rest monomers. In this aspect the sulfone syntans have significant lower values achieving down to baseline values, provided this chemistry is carried out under drastic conditions.

Comparing the three different second generation syntans with different average molecular weight no major differences could

be found between them concerning shrinkage temperatures (71 – 74°C). Same is true for the Differential Scanning Calorimetry (DSC) where at pH = 4 no major differences could be found, as can be seen in figure 5.



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Figure 5. DSC analysis of three second generation syntans with different average molecular weight

## 4. Conclusions

The second generation syntan applied in sole tanning gives softer, fuller, whiter, and lightfaster leathers than pelt tanned with a first generation syntan, but induce only marginally higher shrinkage temperatures.

The difference between a second generation syntan and a replacement syntan is that leathers tanned with replacement syntans are a bit fuller and softer but less lightfast. Both polycondensates give rise to similar shrinkage temperatures, but leave the problem of unreacted monomers like phenol and formaldehyde.

The sulfone tanning agents can be considered the answer to solving the problem of the remaining rest monomers, while keeping high levels of softness and fullness as well as high shrinkage temperatures.

## 5. References

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## 1. Acknowledgements

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