CHEMISTRY OF SYNTANS AND THEIR INFLUENCE ON LEATHER QUALITY

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ABSTRACT

The first syntan, Neradol D, was a condensate of phenolsulfonic acid and formaldehyde. While this chemistry allowed more efficient use of vegetable tannins, it was not advantageous to be applied on leather alone and has to be considered an auxiliary. Incorporating urea into the phenolsulfonic acid - formaldehyde condensation established a second generation of syntans with significantly improved lightfastness. Replacement syntans were developed to substitute vegetable tannins, giving rise to leathers of good softness and fullness. The formaldehyde condensation of dihydroxy diphenyl sulfone (sulfone) can be considered a further development of the replacement syntans with lower residual monomers. In order to compare these four generations of syntans, poly-condensates of a comparable molecular size had to be synthesized. These tested in hydrothermic denaturation of skin powder and applied in sole tanning and re-tanning. The resulting leathers were compared in various aspects of performance including shrinkage temperature, softness, fullness, light fastness, and rest monomers.

INTRODUCTION

Since the introduction of the first syntans one hundred years ago their role in the tanning process has changed significantly. While initially they were used as dispersers and accelerators for vegetable tannins, they were applied as sole tanning agents later, and with the wide acceptance of chromium or glutaraldehyde tanning they are currently mainly used in the re-tanning process. Increasing technical requirements of leather quality could be achieved through modification of their chemistry.

The first syntan Neradol D allowed more efficient use of vegetable tannins, and was applied as an auxiliary.

Incorporating urea into the condensation of the first generation syntan established a second generation of syntans with significantly improved leather properties.

Replacement syntans were developed to replace vegetable tannins, giving rise to leathers of good softness and fullness.

The formaldehyde condensation of dihydroxy diphenyl sulfone can be considered a further development of the replacement syntans, enabling the production of soft and full leathers with lower rest monomers values. As will be shown in this article, the dihydroxy diphenyl sulfone based syntans also fulfill the definition of optimized replacement syntans.

Approaches to compare different chemistries of syntans have been made in the past. H. Erdmann compared Neradol D based syntans that varied in sulfonation degree.[1] He correlated the influence of particle size in syntan solutions, indirectly measured via viscosity of the solutions, with their tannin content.

A widely used analytic tool to evaluate the molecular weight of polymers and polycondensates is the gel permeation chromatography. As will be shown in this article, the molecular weight of a polycondensate plays an important role for the tanning power, as well as for the leather properties. Different molecular weights within the same chemistry can lead to different shrinkage temperatures and leather properties.

In order to compare four generations of syntans polycondensates of a comparable molecular size had to be synthesized. These were applied in sole tanning and the resulting leathers were compared concerning shrinkage temperatures and in various aspects of performance including softness, fullness, light fastness, and rest monomers. Another way to quantify the tanning power of a tanning agent is the hydrothermic denaturation of skin powder that can be measured via differential scanning calorimetry (DSC).

EXPERIMENTAL

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

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analytes on the basis of size. For characterization the weight average molecular weight (M_w) was used.[2] Calibration was achieved with polyacrylates of defined molecular sizes.

The sole tanning was carried out with bovine pelt in a procedure published by Lollar and Tu.[3] A two hour fixation in a separate float generally increased the shrinkage temperature by 1 to 2 degrees Celsius as recommended in the stated article.

The Differential Scanning Calorimetry (DSC) is a thermoanalytical method in which the heat uptake of two samples is compared.[4] 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 carried at pH of four. The lightfastness was determined via Xeno test in a Suntester according to DIN EN ISO 105-B06.

RESULTS AND DISCUSSION

First and Second Generation Syntans

First generation syntans were made from phenolsulfonic acid and formaldehyde.[5] As can be seen in Figure 1 in the top line, initially phenol is reacted with sulfuric acid in about a one to one ratio to form an intermediate: phenolsulfonic acid. Two of these intermediates can subsequently react with one equivalent of formaldehyde to form a methylene bridged dimer of phenolsulfonic acids. With increasing amounts of formaldehyde used, longer condensates so called polycondensates can be synthesized, as reflected by the substituent R in the structure in the top right of Figure 1, meaning the structure continues with more phenolsulfonic acids being bridged by methylene groups deriving from formaldehyde. The third step of the synthesis of a 1st generation syntan is the neutralization, in which the pH of the so far acidic reaction is raised by addition of for instance sodium hydroxide to a pH meaningful for the application of the resulting product.

For the second generation syntans that were developed in the late 1920's urea was incorporated into the polycondensation with formaldehyde.[6] Two equivalents of formaldehyde can react with one equivalent of urea. This building block can bridge two equivalents of phenolsulfonic acid, as depicted on the bottom row of Figure 1. With higher amounts of urea and formaldehyde longer chains of polycondensates with higher molecular weight can be synthesized.

On the basis of a similar average molecular weight of these two polycondensates (6.000 Dalton for the first generation syntan and 7.000 Dalton for the second generation syntan) the differences on leather quality is striking. As shown in Table I, the polycondensate made with urea (second generation syntan)

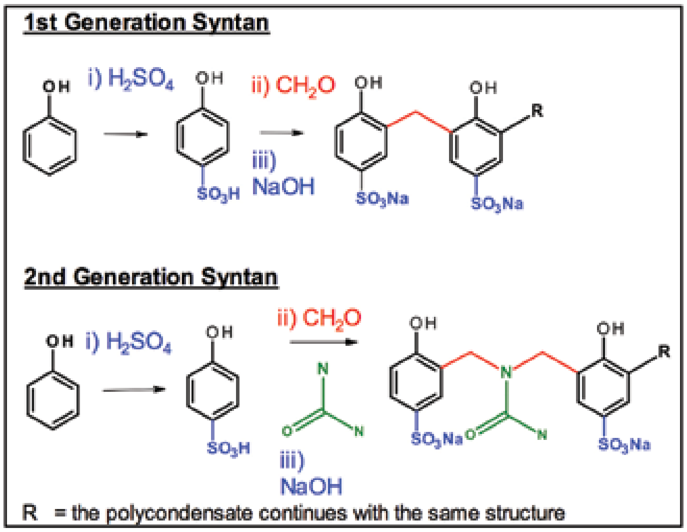

Figure 1. Synthesis and structure of 1st and 2nd generation syntans.

TABLE I
Comparison of 1st and 2nd generation syntans.

Syntan	Mol.weight [g / mol]	Shrinkage temperature (Ts)	DSC Onset T [K] at pH = 4	Leather quality after sole tanning
1st Generation: Phenolsulfonic acid plus formaldehyde	6.000	71°C	+ 17 K	Poor softness and fullness, yellowing, poor lightfastness
2nd Generation: Phenolsulfonic acid plus urea plus formaldehyde	7.000	73°C	+ 21 K	Good softness and fullness, no yellowing, improved lightfastness

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 better than the first generation syntan. This is also the cause for leathers tanned with first generation syntans showing a strong tendency to yellowing, if exposed to daylight.

While the difference in leather quality and lightfastness is large, the differences in shrinking temperature is smaller, with the second generation syntan giving rise to two degrees higher shrinkage temperature. A more pronounced effect was observed in the differential scanning calorimetry (DSC) where application of the second generation syntan to skin powder resulted in a four degree Kelvin higher onset temperature than skin powder treated with a first generation syntan. Superior fibre stabilization of the second generation syntan compared to the first generation syntan go along with improved leather quality.

Second Generation Syntans and Replacement Syntans

Replacement syntans were developed to replace vegetable tannins.[7] They can be made either on the basis of the chemistry of first generation syntans or second generation syntans. Their structural requirements can be easiest demonstrated using the scheme depicted in Figure 2 taken from the "Fundamentals of Leather Manufacturing" by E. Heidemann.[8] In Figure 2 the tanning power increases from the structure on the bottom line to the structure in the top line. In contrast to this observation the solubility diminishes from bottom to top. A first generation syntan is depicted in the bottom line, with good solubility, but low tanning power. Optimized tanning powder in Figure 2 is assigned to the syntan in the top line, but due to missing water solubility this is only theoretically true. Replacement syntan combine structures of the top and bottom structures as depicted in the second and third line of Figure 2, leading to water soluble polycondensates in which not all the phenolic moieties are sulfonated.

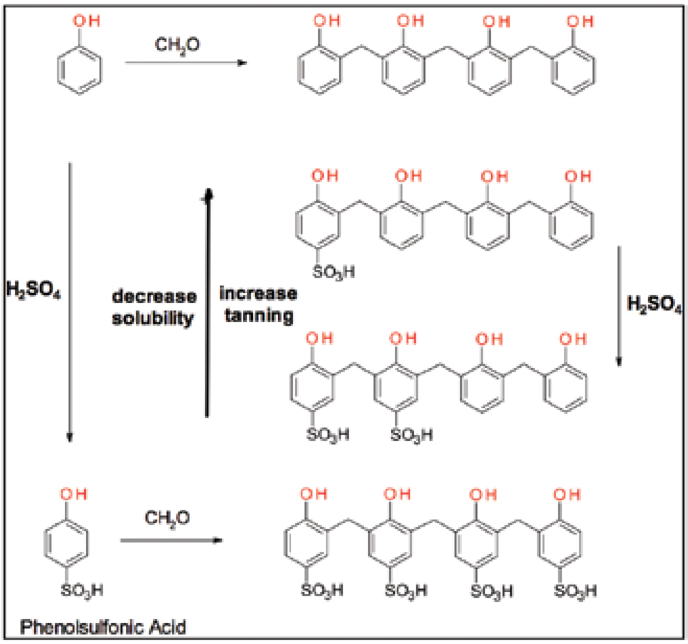

Figure 2. From the "Fundamentals of Leather Manufacturing" by E. Heidemann (p. 398): Relation between degree of sulfonation and the ability to tan of syntans

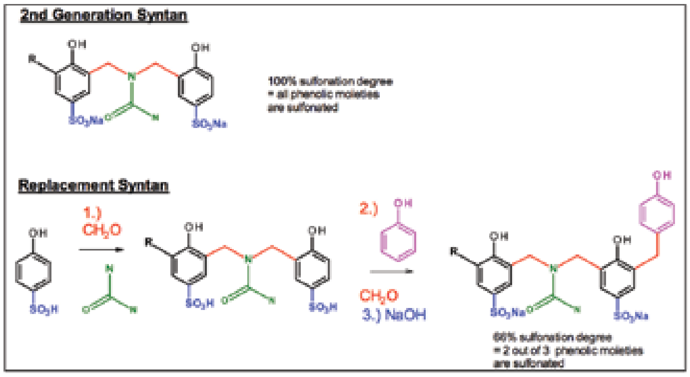

Figure 3. Structure of 2nd generation syntan; synthesis and structure of a replacement syntan.

TABLE II
Comparison of 2nd generation and replacement syntans.

Syntan	Mol.weight [g / mol]	Shrinkage temperature (Ts)	DSC Onset T [K] at pH = 4	Leather quality after sole tanning
2nd Generation: Phenolsulfonic acid plus urea plus formaldehyde	9.000	74°C	+ 20 K	Good softness and fullness
Replacement Syntan: Phenolsulfonic acid plus urea plus formaldehyde; followed by phenol and formaldehyde	9.000	72°C	+ 23 K	Improved softness and fullness

As depicted in Figure 3, both phenolic moieties of the second generation syntan are sulfonated giving rise to complete sulfonation. The sulfonation degree is consequently 100 percent. On the other hand in the structure of the replacement syntan in Figure 3 only two out of three phenolic moieties are sulfonated, while one remains un-sulfonated. This corresponds to a sulfonation degree of 66 percent. This kind of replacements syntan was synthesized by adding phenol and formaldehyde to a second generation syntan, prior to neutralization, as shown in Figure 3.

In order to compare second generation syntans and replacement syntans, polycondensates of a comparable size (9.000 Dalton) we synthesized. After sole tanning with both polycondensates the leather tanned with the replacement syntan turned out to be softer and fuller. This is the main reason of the huge economical role replacement syntans still play today. As a matter of fact, the shrinkage temperature of pelt treated with a second generation syntan is actually two degrees higher than pelt tanned with a replacement syntan of comparable molecular size. Within the differential scanning calorimetry (DSC) analysis the replacement syntan results in three degree Kelvin higher onset temperature than the second generation syntan, as can be seen in Table II. The unsolved problem with both polycondensations is the problem of unreacted restmonomers like phenol and formaldehyde. The formaldehyde can be measured after derivatization with dinitro phenyl hydrazine in solution deriving from leather extraction according to ISO 17226. For the second generation syntan used here after application as a retanning agent on wet blue a value of 60 ppm was found. The free formaldehyde of the corresponding wet blue was 8 ppm. The phenol can be quantified via HPLC after calibration with phenol solutions. For the replacements syntan 6000 ppm phenol was found in the product.

Comparing three replacement syntans with different average molecular weight significant differences were found. As shown in Table III a molecular weight of 2.100 Dalton gives rise to 10 degrees less shrinkage temperature and less soft leathers than a molecular weight of 9.000 Dalton within the same chemistry and same sulfonation degree, confirming that the molecular weight or the length of the chain of the polycondensates have an important impact on fiber stabilization and leather properties. Increasing the molecular weight further to 15.000 Dalton does not result in further increased shrinkage temperature, but decreases the softness of the resulting leather made via sole tanning. The data acquired from DSC measurements confirms the trend in the results of the shrinkage temperatures rather precisely. The softness can be quantified according to DIN EN ISO 17235. In this measurement a steel cylinder of defined mass is pressed with a defined speed into a framed piece of leather and the resulting area increase of the leather is measured. Larger numbers describe bigger area increase indicating more softness of the leathers. As shown in Table III an optimal softness is reached with a molecular weight of 9.000 Dalton, while longer or shorter chains of the same replacement syntan chemistry with the same sulfonation degree result in less softness.

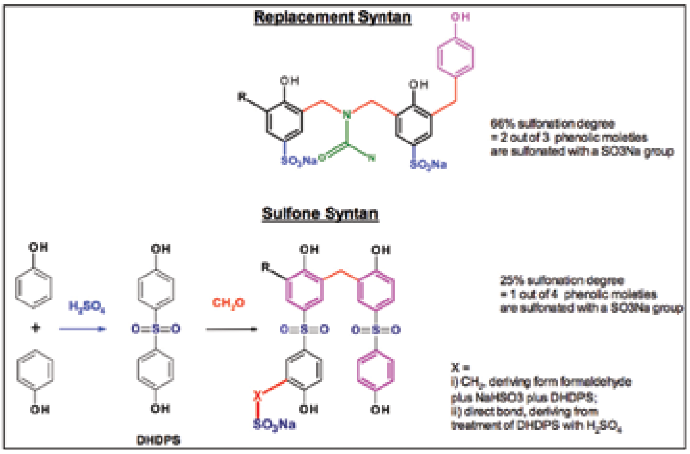

Figure 4. Structure of a replacement syntan; synthesis and structure of a sulfone syntan.

TABLE III
Comparison of three replacement syntans with different average molecular weight.

Syntan	Mol.weight [g / mol]	Shrinkage temperature (Ts)	DSC Onset T [K] at pH = 4	Softness (ISO 17235) after sole tanning
Replacement Syntan 1 (small mol. weight)	2.100	62°C	+ 13 K	0,6
Replacement Syntan 2 (large mol. weight)	9.000	72°C	+ 20 K	2,8
Replacement Syntan 3 (extra large mol. weight)	15.000	72°C	+ 19 K	1,1

TABLE IV
Comparison of replacement and sulfone syntans.

Syntan	Mol.weight [g / mol]	Shrinkage temperature (Ts)	DSC Onset T [K] at pH = 4	Leather quality after sole tanning
Replacment Syntan: Phenolsulfonic acid plus urea plus formaldehyde; followed by phenol and formaldehyde	2.100	62°C	+ 13 K	Insufficient softness and fullness
Sulfone Syntan: DHDPS plus formaldehyde	3.000	70°C	+ 23 K	Improved softness and fullness

Besides the chemistry covered here, there are other ways of combining sulfonated and un-sulfonated aromatic moieties to achieve replacement syntan properties, for instance by starting from naphthol or cresol instead of phenol, or by incorporating a methylene group deriving from formaldehyde between the aromatic moiety and the SO3Na-group.[9] An excellent review about the various possibilities for the synthesis of replacement syntans is given by G. Reich.[10]

Replacement Syntans and Sulfone Based Syntans

The molecule dihydroxy diphenyl sulfone (DHDPS) is made by condensing two equivalents of phenol with on equivalent of sulfuric acid, as shown in Figure 4. In this building block the SO2 group just bridges two phenolic moieties without enhancing solubility. Condensing this building block with formaldehyde gives rise to sulfone 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 in order to take advantage of the increased solubility of deprotonated DHDPS. For an important paper about the low reactivity and low solubility of DHDPS with formaldehyde see G. Reich.[11] After the formaldehyde condensation of DHDPS the problem of low solubility remains. This challenge can be overcome by sulfonation; either by direct treatment of the starting material DHDPS with sulfuric acid or by indirect sulfonation with one equivalent of formaldehyde reacting with NaHSO3 or with Na2SO3 prior to the addition of DHDPS. This way water soluble DHDPS derivatives can be formed that can be incorporated into the DHDPS formaldehyde condensations, thus delivering water soluble polycondensates. For this study we focused on polycondensates in which one out of two DHDPS building blocks is sulfonated. This corresponds to the sulfonation degree of 25% of the phenolic moieties as depicted in Figure 4.

The polycondensate of DHDPS with formaldehyde (sulfone syntan) was compared with a replacement syntan of a comparable average molecular weight. After sole tanning with both polycondensates major differences were found. As shown in Table IV, the shrinkage temperature of the sulfone syntan was 8 degrees higher and the leather quality remarkably improved. In the DSC analysis the effect is even more pronounced with the sulfone syntan giving rise to 10 Kelvin higher onset temperature. The replacement syntans can reach the leather properties of a sulfone syntan, provided they reach a higher molecular weight. But with increasing molecular weight the ability to penetrate evenly through the leather decreases. The sulfone syntans reach beneficial leather properties already on the basis of a small molecular weight combined with good penetration characteristics. For this reason sulfone syntans can be considered a further development of the replacement syntans.

It should be taken into account that the sulfonation degree of the two chemistries compared here are not the same. With the sulfone syntan having a sulfonation degree of only 25%, while the replacement syntan is characterized by a sulfonation degree of 66% increased shrinkage temperatures or onset temperatures of the sulfone syntans can be explained through the theory of E. Heidemannn. Coming back to Figure 2 any syntan with a sulfonation degree of 25% meaning one out of 4 phenolic moieties is sulfonated is predicted to have a higher tanning power than the corresponding syntan with a higher sulfonation degree. The advantage of a sulfone syntan is that this low sulfonation degree can be reached in a rather comfortable way, while replacement syntans with a sulfonation degree of 25% are prone to solidify already in the reaction vessel prior to neutralization and therefore prior to any chance to interact with collagen.

Major differences can be found concerning the rest monomers. In this aspect the sulfone syntans have significant lower values compared to replacement provided this chemistry is carried out under drastic conditions. These drastic chemical conditions like elevated temperatures and pressure enforce the incorporation of rest monomers like phenol and formaldehyde into the polycondensate. We found the same amount of free formaldehyde according to ISO 17226 in wet blue re-tanned with 8% sulfone syntan as for the untreated wet blue alone (both 8 ppm). The phenol was determined via HPLC and calibrated phenol solutions. The value for the sulfone syntan was 100 ppm phenol in the product.

CONCLUSIONS

The second generation syntan applied in sole tanning gives softer, fuller, whiter, and more lightfast leathers than pelt tanned with a first generation syntan, but induces 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. Both polycondensates give rise to similar shrinkage temperatures, provided they have similar molecular weights. Both chemistries 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 residual monomers, while keeping high levels of softness and fullness as well as high shrinkage temperatures. Sulfone based syntans fulfill the prediction of Heidemann that low sulfonation degrees give rise to higher tanning power. This low level of sulfonation that can be reached with sulfone based chemistry would cause classical replacement syntans to solidify already under reaction conditions. Therefore sulfone based syntans can be considered a further development of replacement syntans.

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