# Structure-Activity-Relationships of Synthetic Organic Tanning Agents

***Dr. Jochen Ammenn[1]*[*], Franz Glocknitzer[1], Dr. Franca Tiarks[2], Dr. Gerhard Wolf[1]***

[1] BASF SE, EVX/L - G100, 67056 Ludwigshafen, Germany

[2] BASF Auxiliary Chemicals Co Ltd; G-EVX/LGD; 300 Jiangxinsha Road, Pudong; 200137 Shanghai, China

**Abstract:** In this paper the structure of various syntans are studied and compared to natural tanning agents. Following structure-property relationships were found in reference to tanning efficiency:

- Although many natural tannins contain methoxy groups, we could not positively proof a tanning effect of methoxy groups as such.
- The spacer group between the phenol moieties does play a role in tanning. Comparing different spacers the benzyliden spacer proofed to be most beneficial for shrinkage temperature. However based on physico-chemical properties (solubility, accessibility) the methylene and sulfon spacer appear more favorable.
- Natural tannins frequently contain higher oxidized moieties based on catechol or pyrogallol. Trials showed that their influence on the shrinkage temperature was less pronounced than the effect on lightfastness of the obtained leathers, with the phenol based product giving best lightfastness.
- The molecular weight of condensates influences the tanning capacity. We used products of three different molecular weights all containing the sodium salt of phenolsulfonic acid and achieved shrinkage temperatures that differed significantly and increased with molecular weight of the condensate.

**Key words:** Syntan; Structure-Activity Relationship;Formaldehyde Condensate; Sulfon

## Introduction

Ninety eight years ago the first phenol formaldehyde condensates were merchandised under the trade name Bakelit® [1]. Two years later *Stiasny* succeeded in making Bakelit® like condensation products which were water soluble, resulting in the first synthetic tanning agents (syntans), marketed by BASF as Neradol D® [2]. Since than new generations of syntans have been developed.

In this paper we investigated the influence of different structure parameters of syntans on their performance in the tanning process.

We compared the structure of syntans among each other and set them against to natural tanning agents. In focus of this investigation stood four questions:

1) Many natural tannins contain methoxy groups. Does the methoxy group as such have a tanning effect?

2) The spacer group between the phenol moieties does play a role in tanning. Comparing different spacers, which one is the optimal?

3) Natural tannins frequently contain higher oxidized moieties based on catechol or pyrogallol. Do these perform better than phenol based moieties?

4) How does the molecular weight of condensates influences the tanning capacity?

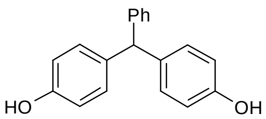
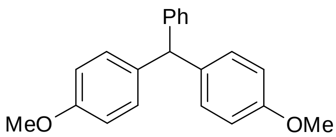
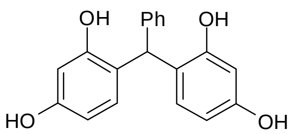
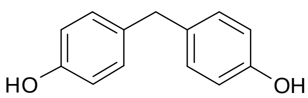
[*] Phone: +49 621 60-99786, Fax: +49 621 60-99381, E-Mail: jochen.ammenn@basf.com

In the following paragraphs the answers on these questions are shortly summarized.

**Influence of the Methoxy group**

Many natural tannins contain methoxy groups while syntans do not. While it would be difficult and elaborate to synthesize syntans containing methoxy groups, different building blocks of syntans could be found in the literature [3].

Comparing 4,4‘-Dihydroxy-triphenyl methane with its oxygen methylated analogue 4,4‘-Dimethoxy-triphenyl methane shows clearly that the shrinkage temperature of pelt tanned with these compounds in presence of an organic solvent decreases from 85 °C to 60 °C actually below the shrinkage temperature of untanned pelt.

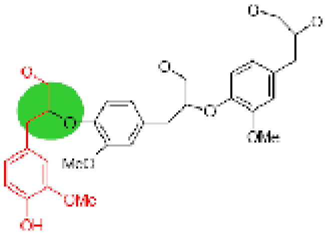
| Substance | Structure | Shrinkage Temp. | Uptake | Leather Quality |
|---|---|---|---|---|
| 4,4‘-Dihydroxy-triphenyl methane |  | 85 °C | 52 % | very good |
| 4,4‘-Dimethoxy-triphenyl methane |  | 60 °C | 12 % | untanned |
| 2,2‘,4,4‘-Tetrahydroxy-triphenyl methane |  | 92 °C | 50 % | very good |
| 4,4‘,-Dihydroxy-diiphenyl methane |  | 74 °C | 27 % | poor |

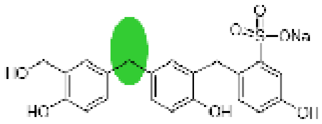
The high shrinkage temperature of untanned pelt resulted from a dehydrating and degreasing procedure with ethanol and acetone applied in the series of experiments [3]. The low shrinkage temperature of 4,4‘-Dimethoxy-triphenyl methane could also result from a very low uptake of the substance out of the float, nevertheless no evidence of a positive tanning effect of methoxy functionalities as such could be found.

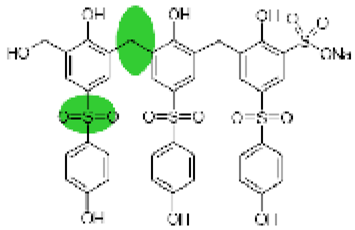
**The optimal spacer**

The most obvious similarity of natural tanning agents and syntans is the phenol moiety they contain. Though a huge difference between natural tanning agents and syntans is the way these phenol moieties are connected.

So we raised the question: Which is the optimal spacer between phenol moieties?







**Lignin** | **Phenol based Syntan** | **Sulfon based Syntan**

$CH_2$-$CH_2$-O-spacer between phenols | $CH_2$-spacer between phenols | $CH_2$- and $SO_2$-spacer between phenols

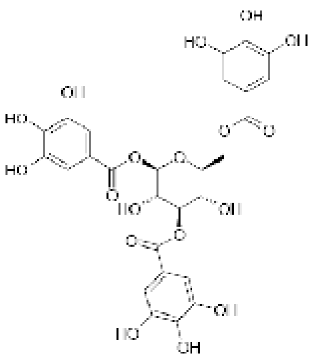
In the literature we found a comparison between a methylene, carbonyl, and benzyliden spacer between phenols. Within this group the benzyliden spacer was most beneficial regarding shrinkage temperature [3].

Additionally we compared the carbonyl spacer with the sulfon spacer, as present in sulfon retanning agents. Since we saw no benefit in a dehydrating and degreasing procedure with ethanol and acetone and also no advantage in using mixtures of organic solvents with water, we applied conventional aqueous tanning methods. Only small differences between the carbonyl spacer and the sulfon spacer were seen in performance.

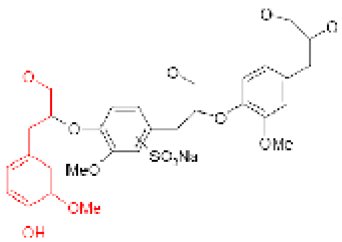
Comparing all mentioned spacers the benzyliden spacer was most valuable in terms of a high shrinkage temperature. But based on physico-chemical properties, such as solubility or accessibility of chemical synthesis the methylene and sulfon spacer appear more favorable.

**Catechol versus Pyrogallol versus Phenol**

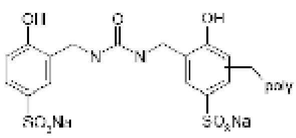
Natural tannins frequently contain higher oxidized moieties based on catechol or pyrogallol as building blocks.



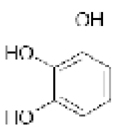
**Corilagin / Gallotannin / Quebracho**



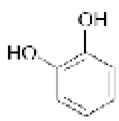
**Ligninsulfonate**



**Syntan**

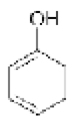


**Pyrogallol**



**Catechol**

**Phenol**



But, do pyrogallol or catechol tan more effectively than phenol?

We tried to pursue this question not as before on the basis of isolated, defined small molecules, which could serve potentially as building blocks for condensations, but based on polycondensates.

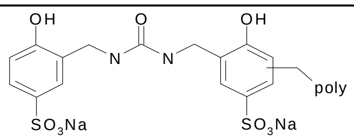
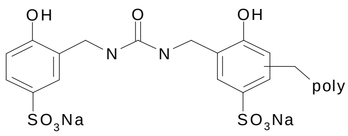
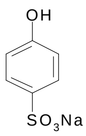
Therefore we condensated phenol, catechol and pyrogallol with urea and formaldehyde to obtain water soluble products. However the influence these different retanning agents showed on the shrinkage temperature was less pronounced than their effect on lightfastness of the obtained leathers. Clearly the phenol based product gave rise to best lightfastness.

**Impact of Molecular weight**

Although the phenol, catechol, and pyrogallol based products were synthesized under the same chemical reaction conditions, they resulted in different average molecular weights.

This raised the question: has the size of condensates any influence on the tanning capacity?

We used products of three different molecular weights all containing the sodium salt of phenolsulfonic acid and achieved shrinkage temperatures that differ significantly and increased with size.

| Class | Polycondensate | Molecular Weight | Shrinkage Temp. |
|---|---|---|---|
| highly condensed |  | 6600 g/mol | 70 °C |
| medium condensed |  | 1943 g/mol | 64 °C |
| un-condensed |  | 108 g/mol | 47 °C |

Therefore we can state that the molecular weight has a tremendous effect on the tanning effect.

We could show that different structure-property or structure activity relationships do exist in the class of synthetic organic tanning agents, which can further be exploited to develop optimized syntans.

## References


[1] e.g. US patent 0 942 699, L. H. Baekeland, *Ind. Eng. Chem.* 1909, *1* (3), 149–161

[2] H. R. Procter, S. Hirst, W. Möller, Ed. Stiasny, *Fresenius' Journal of Analytical Chemistry* 1920, *59* (2-3), 97-99; R. Lauffmann, *Colloid & Polymer Science* 1916, *19* (1), 36-46

[3] S.-T- Tu, R. M. Lollar, *JALCA* 1950 (*45*), 324-3248