BISPHENOLS, A THREAT FOR THE LEATHER INDUSTRY? STRATEGY FOR A SUCCESSFUL REDUCTION OF BISPHENOLS IN LEATHER

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ABSTRACT

Syntans are a key class of products in the leather manufacturing process. They are either made from phenol or from bisphenol S. Bisphenol F can be formed as a side product in the condensation of phenol with formaldehyde and is also found in many syntans.

Bisphenol A is listed in the candidate list of substances of very high concern due to its toxic for reproduction and endocrine disruption properties. It is also recommended for inclusion in the authorization list. Bisphenol A is not a common used monomer for leather. Also Bisphenols S and Bisphenol F came into focus and the regulatory agencies called for evidence for a proposed restriction of all bisphenols.

In this presentation examples will be given how Bisphenols S and Bisphenol F could be reduced significantly through process optimization, maintaining the performance properties of the optimized products on leather. Additionally this presentation will focus on the development of the extraction analytics of bisphenols from leather. Examples will be shown how optimized syntans contribute to optimized leathers concerning bisphenols.

1. Introduction

Bisphenol A (BPA) is common building block in the chemical industry. It has different uses. Major use is in special plastics in which it reacts with other components like epichlorohydrin or polycarbonates. Important concern here is the rest monomeric bisphenol A in the final article, since bisphenol A is listed in the ECHA list of substances of very high concern since 2017 due to its toxicity for reproduction and is investigated for endocrine disruption properties. The world health organization (WHO) has already declared BPA an endocrine disruptor prior to 2017. Studies about the toxicity of bisphenol A have been published abundantly (Eladak2015).

A minor but problematic use of Bisphenol A is in thermo paper used frequently for cash receipts. For this application bisphenol A is not reacted with other components exposing customers to a substance of very high concern in a direct way.

Recently, efforts were started to prevent substitution of bisphenol A with similar structures. In 2021 two calls for evidence where run by national affiliates working on behalf of ECHA for so called bisphenols of similar concern (BosCs) including bisphenol S (BPS) and bisphenol F (BPF).

In the later call, limits of smaller than 10 ppm were suggested for the sum of all bisphenols in the product and the final article. Several studies about the reproductive toxicity of BPS have been published, more recent ones also include BPF (Callie2021).

In leather chemicals BosCs are not used as BPA substitute, since BPA playsno role in theseproducts.

For the syntans as a major class of leather chemicals, BPS is either a starting material or a not intended side product. BPF is a not intended side product.

In this article examples will be given howbisphenol S and bisphenol F could bereduced significantly through process optimization, maintaining the performance properties of the optimized syntans on leather. Additionally, this article will focus on the development of the extraction analytics of bisphenols from leather. Examples will be shown how optimized syntans contribute to leathers with significantly reduced levels of bisphenols.

2. Materials and Methods

2.1 Synthesis of Syntans

For the synthesis optimization of syntans, lab samples were made in an autoclave with magnetic stirring for the sulfone syntans or in glass apparatus with addition funnels and mechanical stirring for the phenolic syntans. Parameters like the equivalents of starting materials, viscosity, pH, and temperature were optimized. The molecular weight was important to ensure the equivalent performance of the optimized syntans compared to the existing production standard. Similar molecular weight is a prerequisite for similar performance (Ammenn2015). Gel permeation chromatograph was applied for this. It is a kind of size exclusion chromatography (SEC), that separates analytes on the basis of size. For characterization of the size the average molecular weight was used (Lathe1956). Calibration was achieved with polyacrylates of defined molecular sizes. The bisphenol levels in the product were measured via calibrated HPLC. From lab scale we went straight to multi ton production scale, once the consistent performance on leather was achieved with the lab sample.

2.2 Re-tanning with Syntans

The re-tanning was carried out on bovine wet blue with two millimeters strength after neutralization with six percent active material in float lengths of two hundred percent, based on wet blue weight. Subsequently, the leathers were treated with one percent of a standard brown dye and with two percent of a standard fat-liquor in a separate float. After re-tanning, the leathers were dried and stacked. The comparison was run with a standard syntan, subjected to the same procedure. The softness can be quantified according to DIN EN ISO 17235, or via haptics. Grain tightness and fullness were evaluated via haptics. Goal was that after process optimization with lowering of bisphenols the performance of the products on leather stayed the same.

2.3 Extraction of Bisphenols from Leather

For the extraction of leathers, ten grams of crust were cut into ten by ten millimeter pieces and extracted with hundred milliliters methanol, for 60 minutes at 60°C, with mechanical stirring in a 250 mL round bottom flask. Decreasing the time to 30 minutes as well as switching from methanol to ethanol did not change the results to a significant extent.

We approached two research institutes offering this extraction assay to compare the results. The FILK leather research institute in Freiberg, Germany cuts leather samples into three by five millimeter pieces and extracts one gram of these pieces with ten milliliter methanol for 60 minutes at 60°C in an ultrasonic bath. CTC in Lyon, France used methanol for 60 minutes at 60°C. The extraction solutions were analyzed via calibrated HPLC. Remaining bisphenols in the floats were analyzed via calibrated HPLC, as for the determination of the bisphenols in the products.

3. Results and Discussion

3.1 Chemistry of Syntans concerning Bisphenols

In the first set of poly-condensates, the sulfone syntans, BPS is condensed with formaldehyde, as can be seen in figure 1. The condensation can be carried out either in presence or absence of naphthalene or phenolic chemistry.

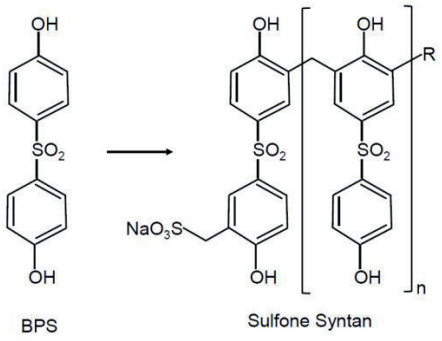


Fig. 1. Chemistry of sulfone syntans; for n = 1: R = H; for n > 1: R means that the structure inside the parenthesis is repeated n times

In either case, BPS remains as a rest monomer in the product, due to the low reactivity of BPS (Reich1963). The chain length of the poly-condensate, reflected by "n" in figure 1, dominantly depends on the amount of formaldehydeadded. Provided that the chemistry is not carried out in the presence of phenol, BPF can not be detected in this chemistry.

In the second set of poly-condensates, phenol is partially sulfonated and condensed with formaldehyde. This leads to the so called phenolic syntans. The final structure is depicted in figure 2. Here BPS forms as a side product in the sulfonation in a range between double digit ppm and several hundred ppm, depending on reaction conditions of the sulfonation. BPF is the reaction product of unreacted phenol and formaldehyde and can form between below detection limit and above 10.000 ppm, depending upon reaction conditions, chosen for the desired performance. The chain length of the poly-condensate, indicated by "n" in figure 2, is mainly determined by the equivalents of formaldehyde used.

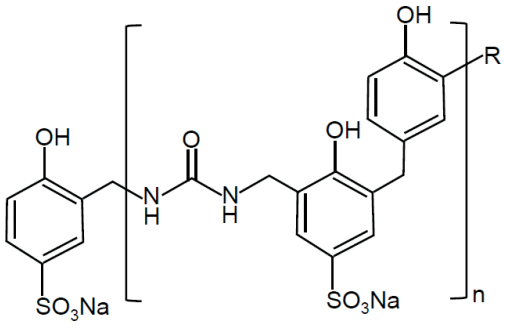


Fig. 2. Chemistry of phenolic syntans; for n = 1: R = H; for n > 1: R means that the structure inside the parenthesis is repeated n times

Both chemistries of syntans were developed to replace natural tanning agents partially and - in some cases - entirely. In the latter case the term replacement syntan is commonly used. Due to the higher fastness properties of the syntans compared to most natural tanning agents, leather articles with superior fastness and ageing properties could be made (Heidemann1993). Syntans also have a strong influence on the properties of the final leatherarticle like softness, fullness, and tightnessof thegrain. Another role of the syntans is to lead to a better uptake and a more even distribution of other leather chemicals like dyes, fat-liquors, and natural tanning agents, making the process and the use of these chemicals more efficient. Due to these advantages, the clear majority of leather articles worldwide are made with syntans.

3.2 Examples of Bisphenol Reductions in Syntans

In the first set of poly-condensates, BPS is the starting material and is condensed with formaldehyde in a closed system resulting in sulfone syntans. Some quantities of BPS remain as a rest monomer, due to low reactivity. Several projects wereand are run to minimize the rest monomeric BPS content. Through process optimization, changing the parameters like equivalents of starting materials, time, pressure, and pH, we could reduce the BPS content from 25.000 ppm down to 2.700 ppm BPS in one of our major sulfone syntan, here named as syntan A. Results are depicted in table 1.

	BPS [ppm]
Syntan A old (Sulfone)	25.000
Syntan A new (Sulfone)	2.700

Table 1: BPS reduction in syntan A (sulfone)

In the second set of poly-condensates, phenol is partially sulfonated and condensed with formaldehyde, leading

to phenolic syntans. Here BPS forms as a side product in the sulfonation in a range between double digit ppm and several hundred ppm, depending on conditions during sulfonation. A value of 60 ppm BPS was the lowest we achieved. Many products from this chemistry in the market have 200 – 500 ppm BPS.

BPF is the major side product in the formaldehyde condensation of phenol and is formed in a range from below detection limit up to more than one percent within this chemistry, depending on reaction conditions. In a major phenolic product called here syntan B, we measured about 3.000 – 4.000 ppm in the regular production and aimed for 500 - 600 ppm BPF in an optimization effort. On a lab scale basis, we reached this value, maintaining the performance of the product in re-tanning. In a first production trial it was possible to reach the level of the lab protocol. A second production trial brought further improvement to a BPF level of 200 ppm, as depicted in table 2.

	BPF [ppm]	BPS [ppm]
Syntan B (phenolic)	3.360	150
Lab rial for Syntan B new	620	170
1st production Syntan B new	670	90
2nd production Syntan B new	210	130

Table 2. BPF and BPS in syntan B (phenolic)

Over all, we achieved a sixteen fold reduction of the BPF level in syntan B on production scale. A reduction in BPS was not attempted in this effort, due to low levels to start with.

3.3 Extraction Results of BosCs from Re-tanned Leather

For the extraction of bisphenols from leathers, we started with leathers obtained from re-tanning with our optimized syntan A to evaluate if the optimization in the product was in line with the results obtained from the extraction of leathers, both internally and with two research institutes. As can be seen in table 3, the approximately ten fold reduction of BPS in the product is reflected in the BPS extraction values from leather. Measurements at three different sites come out with a reasonable and realistic margin of error, showing that leathers with below 200 ppm BPS can be achieved, with optimized products.

	Measurement in product	Measurement after extraction from leather		
	BPS [ppm]	BPS [ppm]		
HPLC measurement at	Stahl	Stahl	FILK	CTC
Syntan A old (Sulfone)	25.000	860	1.100	730
Syntan A new (Sulfone)	2.700	130	150	80

Table 3: BPS reduction in syntan A and results after extraction form letaher

In a subsequent set of experiments, we wanted to analyze, if repeated extraction would increase the quantities of extractable bisphenols. For this we worked with leathers obtained from re-tanning with syntan A. The amount of BPS extractable from this leather was 3.000 ppm.

	1st extract.	2nd extract.	3rd extract.	**total**
BPS [ppm]	3.000	1.100	370	**4.470**
BPS [%]	67	25	8	**100**

Table 4: BPS after repeated extraction

As can be seen in table 4, the amount BPS collected after the first extraction corresponds to 67% of the total amount obtained after three extractions. A second extraction still accesses 25% of the extractable amount. This corresponds to a bid more than a third of the amount obtained in the first extraction. In the third extraction still about 8% of the total quantity extracted could be obtained. From a scientific view this is important to realize that the extraction will not be complete with first attempt. From a practical view, repeated extraction is less feasible for large throughput.

In a further study the amount of BPS in the re-tanning, fat-liquoring floats, and washing floats were analyzed to investigate to which extent the BPS can be found in the floats and to which extent BPS can be washed out of the leather. After the re-tanning with six percent of an un-optimized sulfone syntan, the float was collected and analyzed. The un-optimized sulfone syntan had a BPS content of

20.000 ppm. The leather was washed once with two hundred percent float. Subsequently, the fat- liquoring was carried out with two hundred float length and analyzed. Finally, the crust thus obtained was washed twice with two hundred float length with cold water. All three washing floats were collected and analyzed. The amount of BPS extractable from this leather was 3.300 ppm.

	Re-tanning float	1st wash	Fat-liquoring float	2nd wash	3rd wash	**total**
BPS [ppm]	240	160	150	90	50	**690**
BPS in percent [%]	35	23	22	13	7	**100**

Table 5: BPS analyzed in re-tanning and fat-liquoring floats as well as three washing floats

As can be seen in table 5, about one third of the amount BPS collected in floats came from the re- tanning float, while two thirds came from the fat-liquor floats and three washes. In the first wash about as much BPS was found as in the fat-liquoring float. In the second and third wash only 13% and 7% of BPS were collected. Out of the 690 ppm BPS in the floats, 300 ppm were found in the three washing floats. Compared to the 3.300 ppm BPS in the leather, these 300 ppm represents 9%. With 690 ppm BPS in the combined aqueous floats and 3.300 ppm BPS extractable from the leather, about 20% of the BPS is not taken up by the leather or washed out.

For the phenolic syntans both BPS and BPF are relevant, but as described earlier, BPS only to a minor extend. The optimization with the first production batchof a major phenolic syntan B revealed a 5 fold reduction of BPF in the product as well as in the re-tanned leather, as depicted in table 6. This work is still ongoing, this is why extraction datafrom leather of the subsequent production batch is still missing, while in the product a further improvement by factor 3 could achieved in that second production, adding up to 16 fold reduction of BPF, compared to the original syntan B.

	Measurement in product		Measurement after extraction from leather	
	BPF [ppm]	BPS [ppm]	BPF [ppm]	BPS [ppm]
Syntan B (phenolic)	3.360	150	750	75
1st production Syntan B new	670	90	170	30
2nd production Syntan B new	210	130	no data yet	no data yet
Syntan C (phenolic)	below det. limit	60	< 20	< 20

Table 6: BPS and BPF reduction in phenolic syntans and after extraction from leather

Our best and already optimized products for the second set of poly-condensates show BPF below detection limit and BPS of 60 ppm. These are represented by syntan C. After re-tanning with syntan C, extractable bisphenols from leather were below the detection limit of 20 ppm, as depicted in the bottom row of table 6.

4. Conclusion

Through process optimization we could optimize a major sulfone syntan and lower the BPS level by factor ten in the product. This reduction is also reflected by a corresponding reduction of BPS after extraction from leather. For a major phenolic syntan the BPF levels could be reduced by factor five both in the product and on leather with the first out of two production batches. A simple extraction of leather with methanol does collect the whole quantity of bisphenols inside the leather but resembles the current state of the art for this analytic. Through washes the quantities of BPS collected reflected only about 10% of the content of bisphenols extractable form leather. With an optimized phenolic syntan we achieved leathers from which less than 20 ppm bisphenols can be extracted from leather.

5. Acknowledgements

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Note