Bisphenols: examples for successful reductions in products and leather articles

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Abstract

Bisphenol S and F are starting materials or undesired side products in the synthesis of syntans. They can be found in basically all syntans in a range from close to the detection limit up to several thousand parts per million. They can be detected in most leather articles by extraction. In an initiative by the European Chemicals Agency (ECHA) to drastically reduce bisphenols in consumer goods and in the environment, challenging limits were proposed in 2022. These limits would have had a strong impact on syntan portfolios of the leather chemical manufacturers and on many leather articles. After a public a consultation, ECHA has temporarily withdrawn the restriction proposal and wants to re-work it. Examples for reductions of both bisphenols in leather chemicals and the impact on extractions from leather articles made with these chemicals will be outlined in this article.

Keywords: syntans, bisphenol S, bisphenol F, re-tanning of leather, extraction of bisphenols from leather

1. **Introduction**

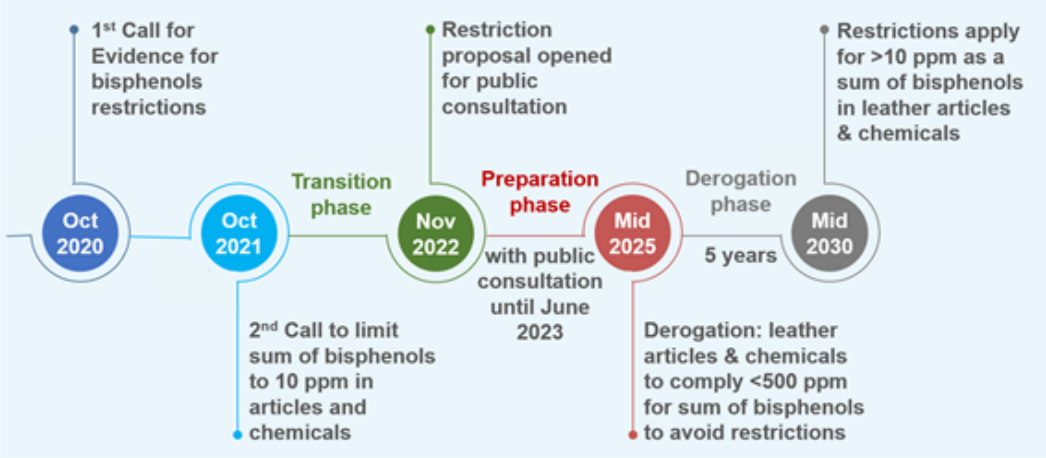
Bisphenol A (BPA) is common building block in the chemical industry, especially for plastic materials and is in the ECHA list of substances of very high concern since 2017 due to its toxicity for reproduction[1]. Other studies about the toxicity of bisphenol A have been published abundantly[2]. BPA is seldomly found in leathers articles and leather chemicals.

In 2020 efforts were started in the EU to restrict BPA further and to prevent substitution of bisphenol A with similar structures, called bisphenols of similar concern (BosCs) including bisphenol S (BPS) and bisphenol F (BPF). Both play a major role in syntan synthesis. In 2020 and 2021 two calls for evidence where run by national affiliates working on behalf of ECHA for BPA and BosCs restrictions.

After the end of the second call for evidence, ECHA published a restriction proposal with a limit of 500 ppm as the sum of all bisphenols for both leather chemicals and leather articles for a period of five years after the resulting regulation comes into force. After that time a limit of 10 ppm was proposed for the sum of all bisphenols in leather chemicals and leather articles. These timelines are depicted in Figure 1.

This proposal was published end of 2022 and open for public consultation until the end of June 2023. With the input of this consultation, ECHA wanted to formulate a restriction proposal for the European Commission, that would have entered the legislative process in the EU. However, as a result of the public a consultation, ECHA has temporarily withdrawn the restriction proposal and wants to re-work it, as announced end of August 2023.

Figure 1: Restriction timelines proposed by ECHA before public consultation

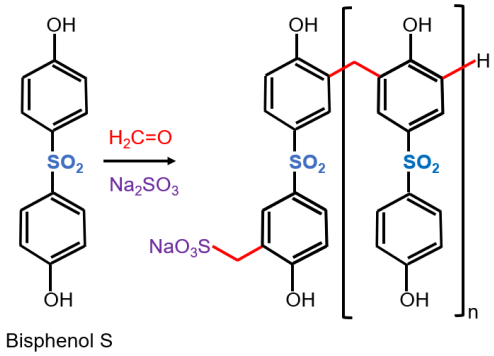


In leather chemicals BFS and BPF are not used as BPA substitute. Several studies about the reproductive toxicity of BPS have been published, more recent ones also include BPF[3]. While BPS is already classified reprotoxic 1B in the EU, this process is still in preparation for BPF. In this article examples will be given how BPS and BPF could be reduced significantly through process optimization, maintaining the performance properties of the optimized syntans on leather. Additionally, this article will focus on results of extractions of bisphenols from leather. Examples will be shown how optimized syntans contribute to leathers with significantly reduced extractable levels of bisphenols down to detection limits.

2. **Chemistry of Syntans**

In the synthesis of syntans two chemistries are applied: phenolic syntans starting from phenol and sulfone syntans starting from BPS. In the latter BPS is condensed with formaldehyde leading to a poly-condensate, as can be seen in Figure 2. The condensation can be carried out either in presence or absence of naphthalene or phenolic chemistry. In either case, BPS remains as a rest monomer in the product, due to the low reactivity of BPS[4].The chain length of the poly-condensate, reflected by “n” in Figure 2, dominantly depends on the amount of formaldehyde added and indicates that the structure inside the parenthesis is repeated n times. BPS levels in these products in the market range from several hundred to several thousand ppm, depending upon reaction conditions. Provided that the chemistry is not carried out in the presence of phenol, BPF can not be detected in this chemistry.

Figure 2: Synthesis of sulfone syntans

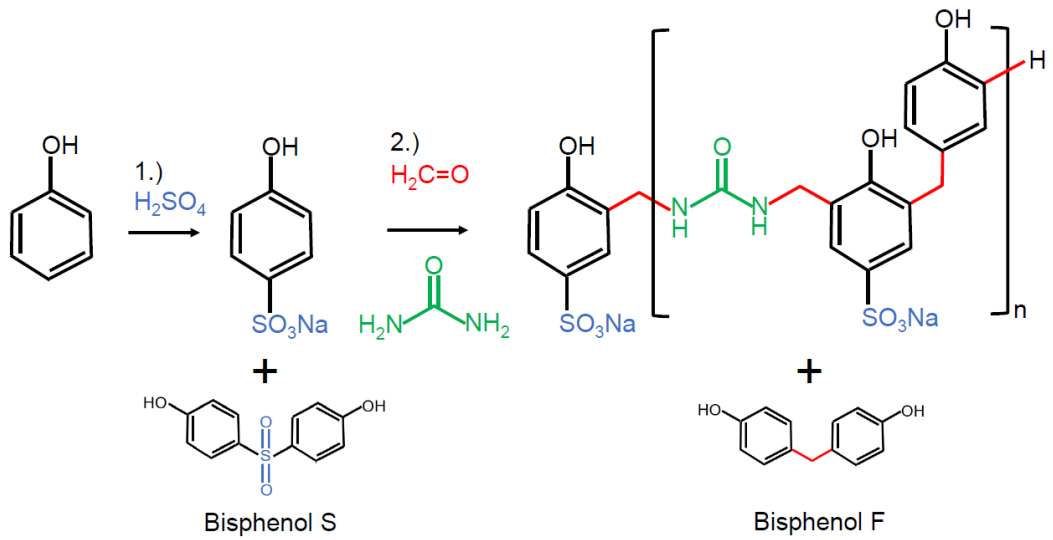


Bisphenol S

In phenolic syntans phenol is partially sulfonated and condensed with formaldehyde[5]. The synthesis is depicted in Figure 3. Here BPS forms as a side product in the first step, the so called sulfonation, in a range between double digit ppm and several hundred ppm, depending on reaction conditions. Many products from this chemistry in the market have 200 – 500 ppm BPS. BPF is the reaction product of unreacted phenol and formaldehyde and can form between below detection limit and above 10.000 ppm,

again depending upon reaction conditions. The chain length of the poly-condensate, indicated by “n” in *Figure 3*, is mainly determined by the equivalents of formaldehyde used and can be measured in a size exclusion chromatography and related to a standard or reference compound[6]. This value is important to maintain in the optimization of existing products, otherwise performance properties like fullness, softness, and grain tightness could change significantly[7].

Figure 3: Synthesis of phenolic syntans



3. **Results and Discussion**

Examples of bisphenol reductions in syntans

In the sulfone syntans BPS is the starting material and remains as a rest monomer, due to low reactivity. Through process optimization, changing the parameters like equivalents of starting materials, time, pressure, and pH, the BPS content in sulfone syntan A could be reduced from 25.000 ppm down to 2.700 ppm. The products were analyzed for BPS via calibrated HPLC. Results are depicted in Table 1. In extensive application trials the maintenance of the performance on leather of syntan A new compared to syntan A old were positively tested, including fastness properties. The only noticeable difference between the old and the new product is the BPS content.

Table 1: BPS in sulfone syntan A

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

In phenolic syntans BPS forms as a side product in the sulfonation. BPF is the major side product in the formaldehyde condensation of un-sulfonated phenol. In a major phenolic product called here syntan B, we measured about 3.360 ppm BPF in the regular production and aimed for improvement.

After a first production trial had reached an about five fold improvement in BPF, it was possible to reduce the level of BPF in a second production trial further to 210 ppm, as depicted in Table 2. With a sum of 340 ppm for BPS plus BPF, this second production trial of syntan B new was below 500 ppm that were stated in the restriction proposal by ECHA. Compared to the initial syntan B, this reflects a sixteen fold improvement

in BPF levels. Like with syntan A it was important to maintain the performance of the syntan B and syntan B new in all retanning aspects as well as on heat and light fastness properties to enable tanners to provide the same leather articles.

Table 2: BPF and BPS in phenolic syntan B

	BPF [ppm]	**BPS [ppm]**	**SUM of BPS + BPF**
Syntan B (phenolic)	3.360	150	**3.510**
1st production Syntan B new	670	90	760
2nd production Syntan B new	210	130	**340**

Extraction results of BosCs from retanned leather

For the extraction of BosCs from leathers, the DIN EN ISO 11936 is applied. For this one gram of leather is cut into small pieces and extracted with 20 mL methanol at 60°C for one hour in an ultrasonic bath, which provides agitation. We approached two research institutes, FILK in Freiberg, Germany and CTC in Lyon, France to extract our leathers. We extracted the leathers ourselves as well and compared the results. 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. As can be seen in Table 3, the approximately tenfold reduction of BPS in the product syntan A new is reflected in the BPS extraction values from leather made with sulfone syntan A new in retanning. Measurements at three different sites, FILK, CTC, and our lab, came out within a reasonable and realistic margin of error, showing that leathers with below 200 ppm BPS can be achieved, with optimized products like syntan A new. For the theoretical amount available in crust, it was taken into account that six percent of syntan A was used on wet blue for retanning. It was again assumed that wet blue has about a fifty percent water content and that it takes therefore two grams of wet blue to obtain one gram of crust. This leads to the maximal calculated amount of twelve percent syntan inside the crust. In this calculation, depicted in the third column of Table 3, it is assumed that all the syntan is taken up and none remains in the float. This gives rise to a recovery rate of about 30% for syntan A and 38% for syntan A new. In the light of the fact that not all syntan is taken up from the float, the recovery rate should be higher with measured float exhaustion.

Table 3: Extraction from leathers made with 6% sulfone syntan A in retanning

	Measure-ment in product	**Calculated extractable from crust (= 12%)**	**Measurement after extraction from leather**		
	BPS [ppm]	**BPS [ppm]**	**BPS [ppm]**		
HPLC measurement at	Stahl	calculated	Stahl	FILK	CTC
Syntan A old (Sulfone)	25.000	3.000	860	1.100	730

	Measure-ment in product	Calculated extractable from crust (= 12%)	Measurement after extraction from leather		
Syntan A new (Sulfone)	2.700	320	130	150	80

Since the extracted amount was significantly lower than the theoretically calculated, another set of experiments was initiated to analyse, if repeated extraction would increase the quantities of extractable bisphenols. Additionally, BPS levels in the floats were quantified to get more realistic results for the theoretical extractable amount. For this goal, leathers were made with another sulfone syntan with higher quantities of BPS. That product in solid stage had a BPS content of 60.000 ppm. Given that six percent of this product was used in retanning and again assuming that two grams of wet blue would result in one gram crust, the theoretical extractable amount of BPS from one gram crust was twelve percent of 60.000 ppm leading to 7.200 ppm. While this crust was made in three steps with a retanning float in the first step, a washing float as the second step, and a fatliquoring float in the final step, we analyzed all these floats and found combined 540 ppm BPS in these floats. We subtracted that from the total extractable amount of BPS in that crust, leading to 7.200 ppm minus 540 ppm, equaling 6.660 ppm BPS extractable form leather.

Table 4: Repeated extraction from leathers

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

As can be seen in Table 4, the amount BPS collected after the first extraction with 3.000 ppm corresponds to 67 percent of the total amount obtained after three extractions. A second extraction still accesses 25 percent of the extracted amount. In the third extraction still about 8 percent of the total quantity extracted could be obtained. Compared to the theoretically extractable amount of 6.660 ppm BPS an amount of summed-up in three consecutive extractions of 4.470 ppm BPS corresponds to 68 percent recovery rate. From a scientific view this is important to realize that single extraction leads only to a partial and lower recovery rate. From a practical view, repeated extraction is less feasible for large throughput. With smaller amounts of extractable bisphenols, the recovery rate increased.

	Measurement in product			Measurement after extraction (8% retanning)		
All production trials	**BPF [ppm]**	**BPS [ppm]**	**SUM BPS + BPF**	**BPF [ppm]**	**BPS [ppm]**	**SUM BPS + BPF**
Syntan B (phenolic)	3.360	150	3.510	750	75	825
1st trial Syntan B new	670	90	760	170	30	200

	Measurement in product			Measurement after extraction (8% retanning)		
2nd trial Syntan B new	210	130	340			
Syntan C (phenolic)	< 10	60	< 70	< 20	< 20	
Syntan C.LB (phenolic) optimized (LB = low bisphenols)	< 10 (Stahl HPLC) < 5 (PFI HPLC)	< 10 (Stahl HPLC) < 5 (PFI HPLC)				

Table 5: Results and extraction with phenolic syntans

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 batch of a major phenolic syntan B revealed a five fold reduction of BPF in the product and a 4,4 fold reduction of BPF extracted from the retanned leather, as depicted in Table 5. While the sum of bisphenols extracted from leathers retanned with this first trial batch was with 200 ppm well below the proposed limit of 500 ppm, the sum of bisphenols in the product was with 760 ppm clearly above the proposed limit. This is why it was important to lower this sum to 340 ppm in the second trial batch of syntan B new in the product, as depicted in column 4 in Table 5.

Phenolic syntan C showed double digit values of BPS and BPF values below the detection limit of 10 ppm. This is the detection limit of our HPCL. Extraction from leathers retanned with this product came out below detection limit of 20 ppm. This detection limit was given by the measurements of the FILK institute that conducted the extraction.

In an effort to lower BPS in syntan C further, the first production batch, syntan C.LB, came out below a detection limit of 10 ppm for both bisphenols, measured with our HPLC. In a measurement at the PFI institute in Pirmasens the product had BPS and BPF levels below the detection limit of 5 ppm. This advanced detection limit could be reached through mass coupling (LC/MS). With this syntan C.LB the limits of below 10 ppm as the sum of both bisphenols could be reached for the first time. Again, it was important to test the performance of syntan C in all retanning aspects and on heat and light fastness properties compared to syntan C to enable same applications. This was achieved.

4. **Conclusion**

Through process optimization we could improve a major sulfone syntan and lowered 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 by factor four point four on leather with the first out of two production batches and later by factor sixteen in the product with the second batch. A single extraction of leather with methanol does not collect the whole quantity of bisphenols inside the leather but resembles the current state of the art for this analytical method. With phenolic syntan C we achieved leathers from which less than 20 ppm bisphenols could be extracted. In the optimized syntan C.LB bisphenol S and F levels were brought to below detection limit in the product, maintaining the performance of syntan C with syntan C.LB on leather.

5. **Acknowledgements**

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