

Bisphenol Reduction in Syntans and Examples for Extraction and Migration of Bisphenols from Leather Articles

by

Jochen Ammenn*

Production Support, Stahl, Benzstrasse 11, 70711 Leinfelden-Echterdingen, Germany

Abstract

Bisphenol S and F play a major role in the synthesis of syntans. Bisphenol S can be a starting material or undesired side product, while bisphenol F can form as an undesired side product. They can be found in basically all syntans in a range from close to the detection limit up to several thousand parts per million and can be detected in most leather articles by extraction or by migration. 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 After a public consultation, ECHA has temporarily withdrawn the restriction proposal and wants to re-work it.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 and migration from leather articles down to detection limits will be outlined in this article.

Introduction

Bisphenol A (BPA) is common building block in the chemical industry, especially for plastic materials and is on 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 leather 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 were 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 parts per million (ppm) as the sum of all bisphenols for both leather chemicals and leather articles for a period of five years after the resulting regulation would come into

force. After that time a limit of 10 ppm was proposed for the sum of all bisphenols in leather chemicals and leather articles. In case these values could not be met, a migration value of 0.04 mg/L as the sum of all bisphenols was proposed for leather. 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 finalize a restriction proposal for the European Commission, that would have entered the legislative process in the EU. However, as a result of the public consultation, ECHA has temporarily withdrawn the restriction proposal and wants to re-work it, as announced end of August 2023.

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. Reprotoxic 1B means that animal studies have clearly shown reproductive effects and that it is suspected to have a similar effect on humans. This classification in the EU requires BPS to be mentioned in the safety data sheet of a chemical if the concentration exceeds 1,000 ppm and to label the whole product with a hazardous warning notice if the concentration is larger than 3,000 ppm.

Experimental

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 1.

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 1, dominantly depends on the amount of formaldehyde added and indicates that the structure inside the parenthesis is repeated “n” times. It can be measured in a size exclusion chromatography and

Some data of this Technical Note was presented at the IULTCS conference in Chengdu, China, October 18-20, 2023, as a PowerPoint presentation, subsequently converted to this manuscript and significantly extended with recent data, including migration results.

*Corresponding author email: jochen.ammenn@stahl.com Phone: +49-174 1878217
Manuscript received February 29, 2024, accepted for publication March 4, 2024.

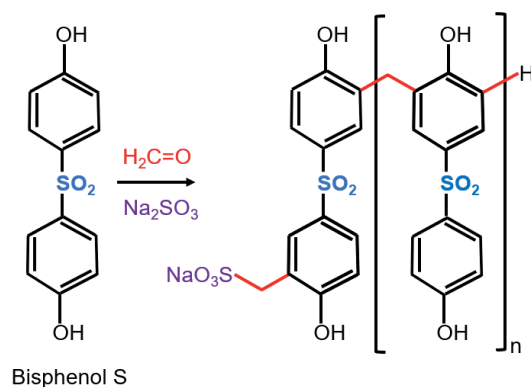


Figure 1. Synthesis of sulfone syntans

related to a standard or reference compound.⁵ This value is important to maintain in the optimization of existing products, otherwise performance properties like fullness, softness, and grain tightness could change significantly.⁶ BPS levels of the sulfone syntans in the market range from several hundred to several thousand ppm, depending upon reaction conditions. In case this chemistry is carried out in the presence of phenol, BPF can be detected in this chemistry as well. The products are analyzed for BPS and BPF via calibrated high pressure liquid chromatography (HPLC) analog to DIN EN ISO 11936.

In phenolic syntans, phenol is partially sulfonated and condensed with formaldehyde.⁷ The synthesis is depicted in Figure 2. 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. Synthesis of the syntans described here were carried out in reactors between five tons and twenty tons.

Re-tanning was carried out with wet blue, obtained from the treatment of pickled pelt with 6-8% chromium sulfate. In a typical example, 100 g of wet blue of southern German origin with a strength of 1.7 mm was treated in a 3.5 L tanning drum with 100 g water, 1.2 g sodium formiate and 0.3 g sodium bicarbonate and the drum was turned for 90 minutes. The resulting float had a pH of 4.5. Approximately 6 g of the retanning agent referring to active material were added and turning of the drum was continued for 90 minutes. The float was discharged and the leather washed with 200 g water. Subsequently, the leathers were treated with three percent of a standard brown dye and with two percent of a standard fat liquor in 200 g water for 90 minutes, before the float was acidified with 0.7 g 85% concentrated formic acid and the drums were turned for 20 minutes. The float was discharged and the leathers were dried via hang drying over night without vacuum at room temperature and subsequently stacked.

For the extraction of BosCs from leathers, the DIN EN ISO 11936 was applied. For this, one gram of leather was cut into small pieces and extracted with 20 mL methanol at 60°C for one hour in an ultrasonic bath, which provided agitation. The extraction solutions

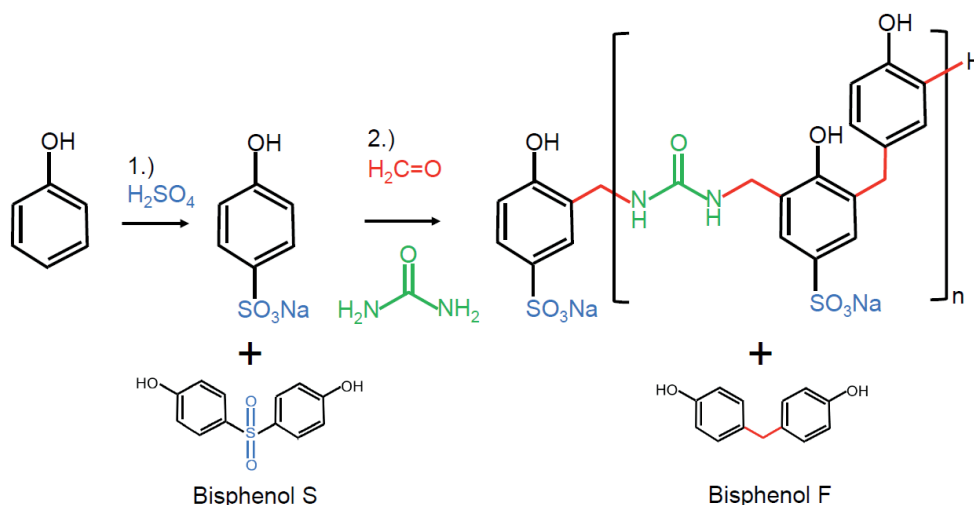


Figure 2. Synthesis of phenolic syntans

were analyzed via calibrated HPLC. This is also applied for the determination of the bisphenols in the products for which they are dissolved in water. The latter modification of DIN EN ISO 11936 can also be used for the analytics of bisphenols in the application floats.

For the migration of BosCs from leathers, the DIN EN ISO 11641 was applied. This procedure derives from color migration tests in which the textile soaked in an artificial sweat solution is pressed on a piece of leather for 3 h at 37°C. For migration the sweat solution was analyzed for BosC's via calibrated HPLC analog to this step in extraction assays via DIN EN ISO 11936.

For leather application evaluation the softness can be quantified according to DIN EN ISO 17235, or via haptics. Grain tightness and fullness were evaluated via haptics. Bleaching and dye penetration were evaluated after application with a brown dye. The lightfastness and heat ageing properties were determined via Xeno test in a Suntester according to DIN EN ISO 105-B06.

Results and Discussion

Examples of bisphenol reductions in syntans

In the sulfone syntans BPS is the starting material and remains as a rest monomer. Through process optimization, changing the parameters like equivalents of starting materials, time, pressure, and pH, the BPS content in sulfone syntan 1 could be reduced from 25,000 ppm in the old version down to 2,700 ppm. The product contained also BPF. Results are depicted in Table I. With a sum of 5,400 ppm bisphenols in syntan 1 the intended level of 500 ppm was still clearly exceeded. For further improvements the chemistry of syntan 1 was changed from sulfone chemistry to phenolic, leading to syntan 1.LB, in which "LB" stands for low bisphenols. In extensive application trials the maintenance of the

performance on leather of syntan 1.LB compared to syntan 1 and syntan 1 old were positively tested. Evaluation included fullness, softness, grain tightness, dye penetration, bleaching, as well as fastness properties. The only measurable differences between the "LB" version, the current or the old version of syntan 1 are the bisphenol contents. The content of the sum of bisphenols could be lowered by more than 99% from syntan 1 to syntan 1.LB. These products are spray dried powders with dry matter equal or larger than 95 percent. Due to the high BPS content syntan 1 old is not marketed anymore.

Extraction results of bisphenols from re-tanned leather

For the extraction of BosCs from leathers, we approached two research institutes, FILK in Freiberg, Germany and CTC in Lyon, France to extract our leathers. The leathers were made with 6% of the syntan as a powder. We extracted the leathers ourselves as well and compared the results. Measurements at three different sites, FILK, CTC, and our lab, came out within a reasonable and realistic margin of error. The values for the sum of bisphenols ranged from 970 ppm to 1,230 ppm. As can be seen in Table II, the approximately tenfold reduction of BPS in the product from syntan 1 old to syntan 1 is reflected in the BPS extraction values from leathers re-tanned with these products. With syntan 1 a BPS level of 150 ppm and 100 ppm BPF were extracted at the FILK institute leading to 250 ppm as the sum of bisphenols extracted. This is identical to what was extracted in Stahl and 80 ppm higher than the level extracted at CTC institute. This is showing that with optimized products like syntan 1 leathers with below 500 ppm bisphenols extracted can be achieved. Since the level of all bisphenols in the product in syntan 1 with 5,400 ppm clearly exceeded the initially proposed limit of 500 ppm, work continued to develop syntan 1.LB. Here a level of 35 ppm BPF was achieved while the BPS level was below a detection limit of 10 ppm. At the FILK institute less than the detection limit of twenty ppm of BPS and BPF could be extracted from crust made with syntan 1.LB.

Table I
BPS and BPF in syntan 1

	BPS [ppm]	BPF [ppm]	Σ (BPS + BPF) [ppm]
Syntan 1 old (until 2020)	25,000	2,700	27,700
Syntan 1 (since 2020)	2,700	2,700	5,400
Syntan 1.LB (LB = low bisphenols, since 2024)	< 10	35	< 45

Table II
Extraction from leathers made with 3 types of syntan 1 in re-tanning (6%)

	Measurement in product at Stahl [ppm]	DIN EN ISO 11936 measurement in [ppm] after extraction from leather at:		
		Stahl BPS / BPF (S = BPS + BPF)	FILK BPS / BPF (S = BPS + BPF)	CTC BPS / BPF (S = BPS + BPF)
Syntan 1 old	25,000 / 2,700 ($\Sigma = 27,700$)	860 / 140 ($\Sigma = 1,000$)	1,100 / 130 ($\Sigma = 1,230$)	730 / 140 ($\Sigma = 970$)
Syntan 1	2,700 / 2,700 ($\Sigma = 5,400$)	130 / 120 ($\Sigma = 250$)	150 / 100 ($\Sigma = 250$)	80 / 90 ($\Sigma = 170$)
Syntan 1.LB	< 10 / 35 ($\Sigma = < 45$)		< 20 / < 20	

For the theoretical amount extractable from crust, it was taken into account that six percent of a syntan was used on wet blue for re-tanning. 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, which is the relevant amount for extraction. This leads to the maximal calculated amount of twelve percent syntan inside the crust. In this calculation, depicted in the third column of Table III, it is assumed that all the syntan is taken up and none remains in the float. We wanted to determine the recovery rate of BPS and BPF in extraction and analyzed extracting the same crust three times. As can be seen in Table III, the amount BPS collected after the first extraction with 150 ppm BPS and 150 ppm BPF corresponds to 46 percent of the calculated amount of 324 ppm of each bisphenol. A second extraction still accesses 49 ppm BPS and 37 ppm BPF. The sum of the two extractions collected

199 ppm BPS and 187 ppm BPF. This corresponds to 61% recovery rate for BPS and 58% for BPF after two extractions. A third extraction of the same crust showed BPS and BPF below detection limits of 20 ppm, as given by the FILK institute for these HPLC measurements. The third extraction did not contribute to raise the 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.

For the phenolic syntans both BPS and BPF are relevant, but as described earlier, BPS only to a minor extent. As can be seen in Table IV, the optimization of phenolic syntan 2 revealed a reduction of both BPF and even BPS by 99%. The performance on leather could

Table III
Repeated extraction from leathers made with 6% syntan 1 in re-tanning

	Measurement in product [ppm]	Calculated extractable from crust [ppm] = 12%	1st Extraction [ppm]	2nd Extraction [ppm]	3rd Extraction [ppm]
	BPS / BPF ($\Sigma = \text{BPS} + \text{BPF}$)	BPS / BPF ($\Sigma = \text{BPS} + \text{BPF}$)	BPS / BPF ($\Sigma = \text{BPS} + \text{BPF}$)	BPS / BPF ($\Sigma = \text{BPS} + \text{BPF}$)	BPS / BPF ($\Sigma = \text{BPS} + \text{BPF}$)
Syntan 1	2,700 / 2,700 ($\Sigma = 5,400$)	324 / 324 ($\Sigma = 648$)	150 / 150 ($\Sigma = 300$)	49 / 37 ($\Sigma = 86$)	< 20 / < 20 ($\Sigma = < 40$)

Table IV
Extraction results from leathers made with phenolic syntan 2 and 3 in re-tanning;
values measured internal, as well as at the FILK (Freiberg) and PFI (Pirmasens) institutes

	Measurement in product			Measurement after extraction (8% retanning)		
	BPF [ppm] (source)	BPS [ppm] (source)	Σ (BPS + BPF) [ppm]	BPF [ppm] (source)	BPS [ppm] (source)	Σ (BPS + BPF) [ppm]
Syntan 2	8,400 (Stahl)	400 (Stahl)	8,800	510 (PFI)	15 (PFI)	525
Syntan 2.LB	85 (PFI)	< 5 (PFI)	< 90	< 5 (PFI)	< 5 (PFI)	< 10
Syntan 3	< 10 (Stahl)	60 (Stahl)	< 70	< 20 (FILK)	< 20 (FILK)	
Syntan 3.LB	< 5 (PFI)	< 5 (PFI)				

be maintained in re-tanning in all aspects. The detection limit of ten ppm for both bisphenols was measured with our HPLC. In an extraction measurement at the PFI institute in Pirmasens leathers re-tanned with 8 percent syntan 2.LB had BPS and BPF levels below the detection limit of five ppm leading to less than ten ppm as the sum of bisphenols. This advanced detection limit could be reached through mass coupling (LC/MS) of the identified peak in HPLC. Syntan 2 and syntan 2.LB are spray dried powders with dry matter equal or larger than 95 percent.

Phenolic syntan 3 showed double digit values of BPS and BPF values below the detection limit of ten ppm in the product. This is the detection limit of our HPCL. Extraction from leathers re-tanned with this product came out below detection limit of twenty ppm for both bisphenols. This detection limit was given by the measurements of the FILK institute that conducted the extraction.

In an effort to lower BPS in syntan 3 further, syntan 3.LB was developed. Here BPS levels could be lowered to below five ppm while maintaining BPF below the detection limit. This measurement was carried out at the PFI institute in Pirmasens, where five ppm is the detection limit. For the sum of both bisphenols, a value smaller than ten ppm could be reached for the first time. Again, it was important

to test the performance of syntan 3.LB in all re-tanning aspects as well as on heat and light fastness properties compared to syntan 3 to enable same applications. This was achieved. Note that syntans 3 and syntan 3.LB are liquid syntans with a concentration of forty percent.

Migration results of bisphenols from leather re-tanned with syntans 2 and 2.LB

In the ECHA restriction proposal from 2022 it was envisioned that after a period of five years, in which a limit of 500 ppm BosC’s would be applicable, a new limit of 10 pm of BosC’s would be enforced for the sum of all bisphenols in leather chemicals and leather articles. In case these values could not be met, a migration value of 0.04 mg/L of BosC’s was suggested for leather as the sum of all bisphenols, measured via DIN EN ISO 11641. In this test, a textile soaked in an artificial sweat solution was pressed on a piece of leather for three hours at 37°C. Afterwards, the sweat solution was analyzed for BosC’s that have migrated from leather via calibrated HPLC analog to this quantification step in the extraction assay DIN EN ISO 11936. As can be seen in Table V leathers re-tanned with eight percent syntan 2 showed migration values of BPS and BPF below the detection limit of 0.04 mg/L. This was surprising, since this was the unoptimized version of the product. With the optimized syntan 2.LB, the same results were achieved as well.

Table V
Results of BosC's migration from leathers made with phenolic syntan 2 and 2.LB measured at PFI institute

	Measurement in product			Migration measurement (8% retanning)		
	BPF [ppm] (source)	BPS [ppm] (source)	Σ (BPS + BPF) [ppm]	BPF [mg/L]	BPS [mg/L]	Σ (BPS + BPF) [mg/L]
Syntan 2	8,400 (Stahl)	400 (Stahl)	8,800	< 0.04	< 0.04	< 0.08
Syntan 2.LB	85 (PFI)	< 5 (PFI)	< 95	< 0.04	< 0.04	< 0.08

Conclusions

Through process optimization we improved a major sulfone syntan and we lowered the BosC's level by 99 percent by changing from sulfone chemistry to phenolic condensation. This reduction is also reflected by a corresponding reduction of BosCs after extraction from leather. The performance of the product concerning fullness, softness, grain tightness, dye penetration, bleaching, as well as fastness properties remained unaffected even after the change from sulfone to phenolic chemistry.

A single extraction of leather with methanol does not collect the whole quantity of bisphenols from leather but resembles the current state of the art for this analytical method.

For a major phenolic syntan the BosC's level could be reduced from 8,800 ppm to smaller than 90 ppm as the sum of bisphenols. The performance on leather of this syntan remained the same, but the extracted BosC's levels declined from 525 ppm to below detection limit. In migration the limit of smaller than 0.04 mg/l was even achieved with the unoptimized version of syntan 2.

With phenolic syntan 3 we achieved leathers from which less than 20 ppm bisphenols could be extracted. In the optimized syntan 3.LB bisphenol S and F levels were brought to below detection limit in the product, maintaining the performance of syntan 3 with syntan 3.LB on leather.

Acknowledgements

I want to thank Roberta Gamarino (Stahl, Palazzolo, Italy) and her team for their lab trials, production scale trials, for analytical support, and their impressive dedication. I am obliged to Marcus

Breulmann, Debora Spengler, and Cenk Basoglu for their support with application. I wish to express my gratefulness to my collaboration partner Markus Kalt (BASF, Ludwigshafen, Germany) and his team for the production scale trials in Ludwigshafen. Ute Morgenstern and Ines Stachel from the FILK institute I want to acknowledge for their work to optimize the extraction methods. Special thanks go to Ines Anderie and Oliver Haubrich from PFI institute for analytical support.

References

1. Srivastava, S.; Dhagga, N.; Dose exposure of Bisphenol- A on female Wistar rats fertility, *Hormone Molecular Biology and Clinical Investigation*, vol. **38** (2), p. 20180061, 2019.
2. Eladak, S.; Grisin, T.; Moison, D.; Guerquin; M.J.; N'Tumba-Byn, T.; Pozzi-Gaudin, S.; Benachi, A.; Livera, G.; Rouiller-Fabre, V.; Habert, R.; A new chapter in the bisphenol A story: bisphenol S and bisphenol F are not safe alternatives to this compound, *Fertil Steril.*, **103**(1), 11–21, 2015.
3. McDonough, C.M.; Shibo Xu, H.; Guo, T.L.; Toxicity of bisphenol analogues on the reproductive, nervous, and immune systems, and their relationships to gut microbiome and metabolism: insights from a multi-species comparison, *Critical Reviews in Toxicology*, **51**(4), 283–300, 2021.
4. Reich, G.; Hebestreit, J.; *J. f. Prakt. Chemie*, **19**, 303–308, 1963.
5. Lathe, G. H.; Ruthven, C.R.J.; The Separation of Substance and Estimation of their Relative Molecular Sizes by the use of Columns of Starch in Water, *Biochem J.*, **62**, 665–674, 1956.
6. Ammenn, J.; Huebsch, C.; Schilling, E.; Dannheim, B.; Chemistry of Syntans and their Influence on Leather Quality, *JALCA*, **110**, 349–354, 2015.
7. Heidemann, E.; Fundamentals of leather Manufacturing, Eduard Roether KG Darmstadt, p 380f, 1993.