Overcoming the Bisphenol hurdle

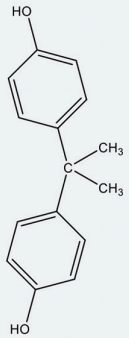
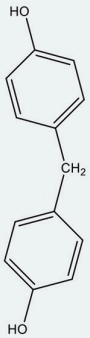
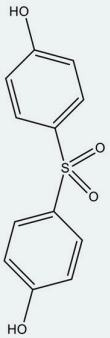
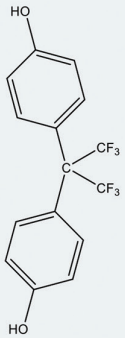
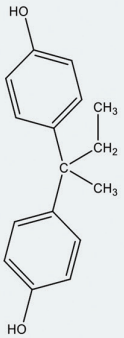
Abstract

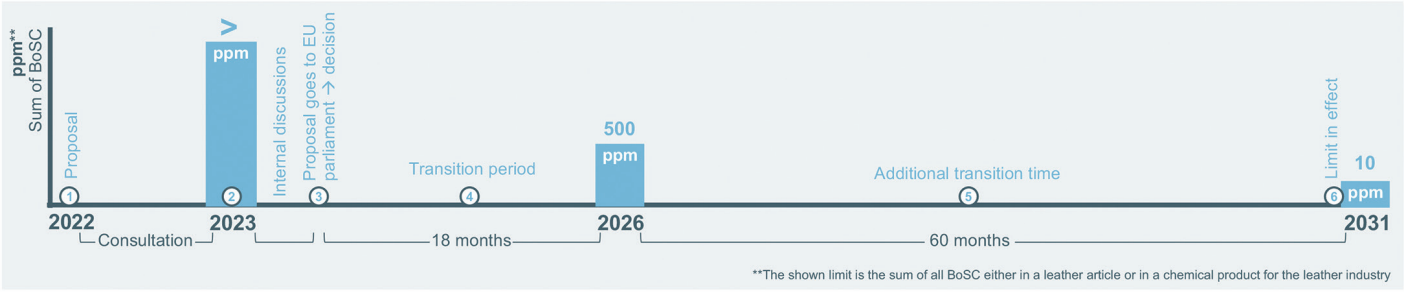
The European Chemical Agency (ECHA) has recently proposed a new regulation for the placing on the market of mixtures and articles containing bisphenols. If the draft is implemented without changes, this will – after various transition times – result in very low limits for these chemicals in leather auxiliaries and leather articles. When it comes to syntans, bisphenols are raw materials and unwanted side products, respectively. State-of-the-art production technologies for syntans might not succeed in lowering bisphenol content to the proposed limits, though. As syntans play an essential part in the production of almost all of today's leather articles, the new regulation will lead to a disruptive change in the selection of chemicals in common recipes. Zschimmer & Schwarz has anticipated this issue and presents the first solutions to achieve completely bisphenol-free leather.

In December 2022, ECHA published a new proposal to regulate the use of Bisphenol A (BPA) and all similarly structured chemicals known as BoSC (Bisphenols of Similar Concerns – see Figure 1). Bisphenol A is a well-known molecule because of its former usage in polycarbonate drinking bottles for babies and children. Due to its known effect as an endocrine disruptor, it was banned from such uses.[1] Nevertheless, most polycarbonate plastics which are not used in products meant for babies or children as well as many epoxy resins are still based on Bisphenol A.

Although not used in leather manufacturing itself, Bisphenol A still has an impact on the tanning industry: due to their structural similarity to BPA, Bisphenol S, F – which are frequently found in leather chemicals – and other bisphenols are now proposed to be regulated as well. On October 7, 2022, the German Bundesamt für Arbeitsschutz und Arbeitsmedizin (BAuA) submitted a restriction proposal to the ECHA. On December 21, 2022, it was published on the ECHA's website, and the official public consultation started.[2] This restriction takes into account the endocrine-disrupting effects known so far (similar to those of oestrogen or other hormones) as well as the structural similarity of the substances and thus proposes a limit for leather auxiliaries and leather articles. This means that the restriction is based on a precautionary, hazard-based approach – a risk-based approach, which would take exposure into account, might have led to a different outcome.

Figure 1: Structural comparison of the five bisphenols which are affected by the restriction and their relevance for the leather industry.

	Bisphenol A	Bisphenol F	Bisphenol S	Bisphenol AF	Bisphenol B
Molecular structure					
Name	4,4'-isoprop-ylidenediphenol	4,4'-methylene-diphenol	4,4'-sulphonyl-diphenol	4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene] diphenol	4,4'-(1-methyl-propylidene) bisphenol
CAS number	80-05-7	620-92-8	80-09-1	1478-61-1	77-40-7
EC number	201-245-8	210-658-2	201-250-5	216-036-7	201-025-1
Relevance for syntans and leather production	no	yes	yes	no	no



1. **ECHA proposal published on 21 December 2022** for consultation
2. **Consultation will end on 22 June 2023**
3. After final statements from ECHA and **internal discussions** between national authorities, the proposal will be given to the EU parliament and decided; the whole process will take **6–12 months** if there are no further changes.
4. Then an **18-month transition** period starts during which **no change** in limits for **mixtures and articles** will arise
5. For **leather, an additional** transition time of **60 months** with a **limit of 500 ppm of the sum of BoSC for mixtures and articles** will follow
6. Only after that, a limit for the leather industry of **10 ppm for the sum of BoSC for mixtures and articles** will be in effect → **possibly around June 2031**

Figure 2: Possible timeline and limits according to the restriction proposal of ECHA.

Figure 2 shows the next steps in the regulation process as laid out in the restriction proposal. The proposal is now in the commenting phase, which will end on June 22, 2023. After the usual consultation process in EU legislation, a restriction of the aforementioned bisphenols could come into effect in 2024. This would initiate a transitional period of 18 months without any limits, followed by a 60-month transitional period with limits of 500 ppm in leather auxiliaries and articles, and eventually to a limit of 10 ppm, which currently comes close to a ban of bisphenols in leather. Of the bisphenols to be regulated, BPF and BPS are currently found in nearly all syntans and syntan-containing fillers - in phenol- as well as in sulphone-based products. Thus, the regulation will significantly impact leather making in the future.

Until now, the synthesis based on phenol (including phenol partially sulfonated by sulfuric acid) and/or Bisphenol S with formaldehyde and/or urea has been the latest process for syntan production. Figures 3a and 3b provide an overview of the general reaction pathways: both the intermediate molecule Bis(4-hydroxyphenyl)methane (Bisphenol F) and Bisphenol S can serve as starting material to form the polymeric products. For simplification, only the reaction with formaldehyde is illustrated, but the reaction could be extended by adding urea and other raw materials.

Bisphenol levels in commercial syntans range from <100 ppm to >10,000 ppm. Unfortunately, current technologies offer only limited possibilities to further reduce these values significantly below 50–100 ppm. As a result, these chemicals and the resulting leather articles will fall under the regulation and must no longer be sold in the European Union.

The restriction will thus significantly impact global leather production, as syntans have been used for decades in both the (re)tanning and pretanning of leather: they provide special properties such as grain tightness, fullness, improved lightfastness, heat resistance and better dyeability, and they further stabilise the leather structure. Used in the pretanning of wet-white, for example, classical syntans improve sammying or dehydrating, which simplifies shaving and allows a better thickness control, which, in turn, leads to a greater consistency in terms of quality.[3] All of this makes syntans and syntan-containing fillers allrounders used in

Figure 3a: Simplified reaction pathway towards sulphone-based syntans.

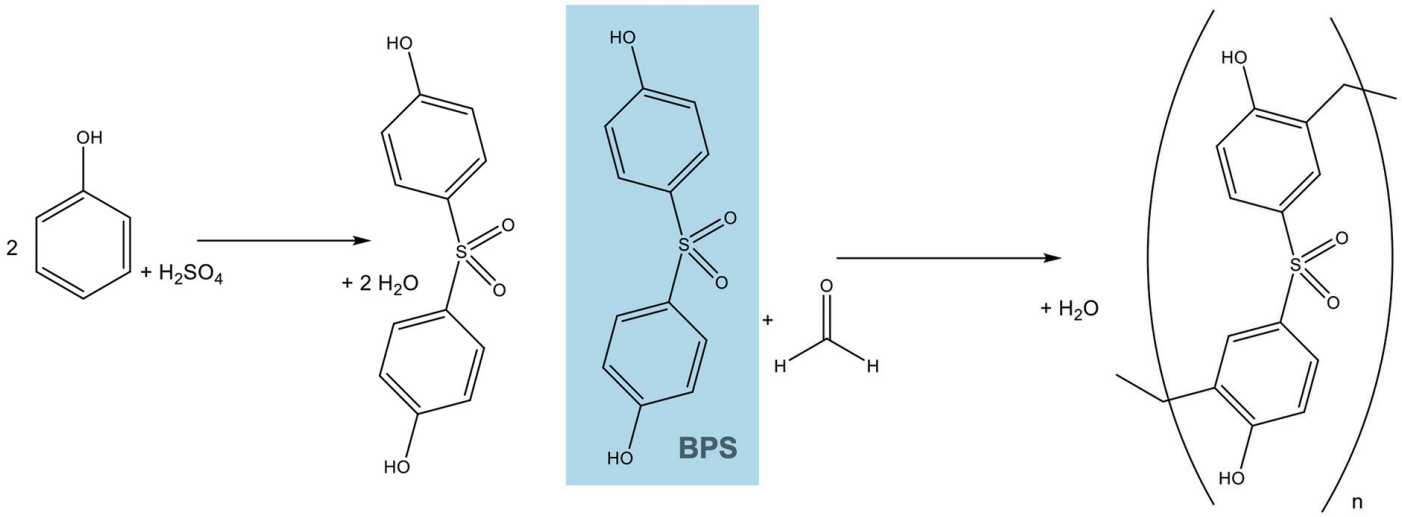
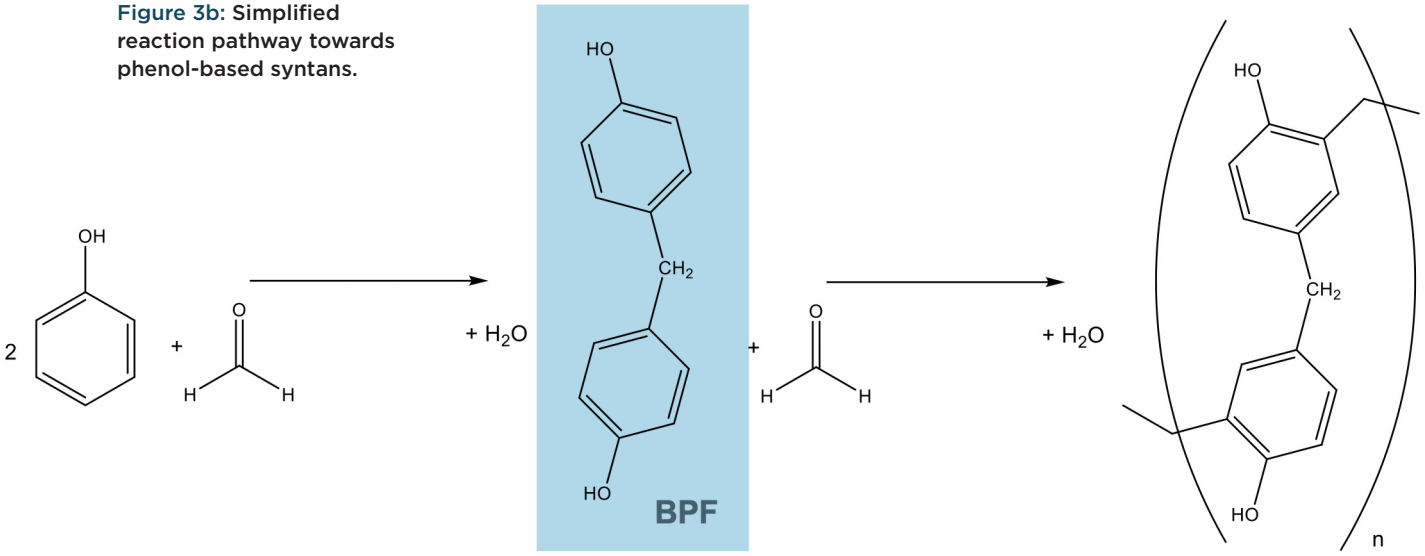


Figure 3b: Simplified reaction pathway towards phenol-based syntans.



Operation	Product	[°C]	[min]	Sample 1
	Water	35		100%
	PROVOL S-LX		20	1%
	NOVALTAN S-VF			2%
	Sodium formate		10	1%
pH 5.2	Sodium bicarbonate		60	0.8%
	Drain the float			
	Water	30		50%
	PROVOL S-LX		30	5%
	NOVALTAN S-VF			4%
	DOLATAN TA			6%
	SINCAL MS			2%
	Sodium bicarbonate		30	0.2%
	NOVALTAN S-VF			4%
	DOLATAN TA			6%
	TAFIGAL HFB			4%
pH 5.4	Sodium bicarbonate		30	0.2%
	NOVALTAN S-VF			4%
	DOLATAN TA			6%
	Sodium bicarbonate			0.2%
pH 5.3	Leather dyestuff		150	4%
	Water	50	10	100%
	PROVOL S-LX		60	4%
	Formic acid		30	2%
pH 3.5	Formic acid		60	2%
	Drain the float			
	Water	50	10	300%
	Drain the float			
	Water	20	10	300%
Drain the float				
Horse up				
Vacuum dry at 45 °C / 2 min				
Condition				
Stake				
Mill 180 min				

Figure 4: Recipe for a bisphenol-free automotive wet-white crust leather.

the leather industry, and they are part of almost every recipe in present-day tanning.

Importance of syntans

The critical importance of syntans for the leathermaking process and the proposed restriction of bisphenols will inevitably lead to the development of alternatives to products which fall within the restriction limits of the ECHA and thus replace classical syntans. Zschimmer & Schwarz has made the first step in this endeavour to rethink retanning and filling agents. The Germany-based chemical company has developed three new products: Tafigal HFB, Tafigal S-TF and

Method	Bisphenol-free crust
Formaldehyde VDA 275 [ppm]	Not detectable
Fogging grav. [mg]	1.3
Fogging reflect [%]	91
Haze	4
Bisphenol A [mg/kg]	< 5
Bisphenol F [mg/kg]	< 5
Bisphenol S [mg/kg]	< 5
Heatyellowing 120 °C 6 h 0–5	3.66
Heatyellowing 120 °C 6 h 0–5	3.60
Suntest 72 h 0–5	1.56
Tear force A (DIN EN ISO 3377-1) [N]	22
Tensile strength (DIN EN ISO 3376) [N]	95
Break.-elong. [%]	57
Stitch tear force (DIN EN ISO 23910) [N]	69.1

Figure 5: Properties of the crust leather produced with the recipe shown in Figure 4.

Novaltan S-VF do not contain any potentially harmful bisphenols and thus allow to produce completely bisphenol-free leathers. Tests on several leathers have shown that the leather qualities achieved with the help of these products are comparable to those achieved using formulations based on classical syntans. With a high amount of renewable biobased materials and good biodegradability/absorbability, two of these novelty products even meet the requirements of the S-Range, a particularly sustainable product range of the Leather Auxiliaries Division of Zschimmer & Schwarz.

The recipe for a bisphenol-free automotive wet-white crust leather (Figure 4) and the resulting properties (Figure 5) show that a completely bisphenol-free article can be achieved which fulfils all necessary leather requirements. The products have already been tested in pilot plants and are available for sampling and testing at the customer's site.

The planned restriction proposal of ECHA will undoubtedly have a significant impact on the entire leather industry in the near future. Further alternatives to the products containing the restricted substances have to be developed, and they must not compromise the quality and variety of leathers as we know them today. In addition to the retanning and filling agents described above, Zschimmer & Schwarz continues its R&D activities. The globally active company plans to develop further products which successfully meet upcoming requirements and tackle this and other challenges which lie ahead. ❙

References

1. 2011/8/EU: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32011L0008. Last retrieved on 7 February 2023. EU regulation 10/2011: https://eur-lex.europa.eu/eli/reg/2011/10/oj. Last retrieved on 7 February 2023. EU regulation 321/2011: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32011R0321. Last retrieved on 7 February 2023.

2. Restriction proposal: 4,4'-isopropylidenediphenol (Bisphenol A) as well as other bisphenols and bisphenol derivatives with endocrine disrupting properties for the environment. https://echa.europa.eu/de/registry-of-restriction-intentions/-/dislist/details/0b0236e1853413ea. Last retrieved on 23 January 2023.

3. Faber, K; Bibliothek des Leders, Umschau Verlag, (1990) Frankfurt, Band 3, 53–60.
Moog, G.E.; Der Gerber: Professionelle Lederherstellung, Eugen Ulmer KG, (2005/2016), 93–97.
Stather F., Gerbereichemie und Gerbereitechnologie, Akademie-Verlag Berlin, (1951), 274–295.

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