

# BISPHENOLS AND THE IMPACT ON THE LEATHER INDUSTRY

THE IULTCS TEAM

12/9/2024



#### WHAT ARE BISPHENOLS?

Bisphenols are widely used chemicals found in everything from food and beverage can linings to thermal paper and used to make polycarbonate plastic as well as epoxy resins.

Bisphenol A (BPA) is the best-known member of this chemical class, but similar compounds (BoSCs) such as Bisphenol S (BPS) and Bisphenol F (BPF) are chemical cousins that are also of concern. When states and companies restricted the use of BPA, many manufacturers turned to these similar and also toxic compounds. Today, the BPA ban extends to the similar BoSC compounds.

In animal studies, researchers have linked developmental exposure to bisphenols to reproductive and developmental harm (Endocrine Disruptors).

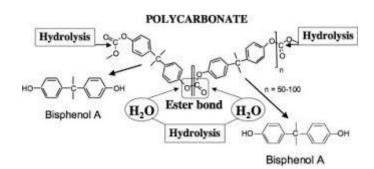


#### BISPHENOL A USES









# Paris 2024: Olympics-themed water bottles recalled in France over harmful levels of banned chemical BPA

A week before the games kick off, authorities recalled the merchandise, which features images of the Olympic rings, flame, and mascot.



[Photo: Paris 2024 Olympics]



#### **BISPHENOL** A

Bisphenol A (4,4'-isopropylidenediphenol) is used in traditional plastics synthesis, most commonly in the manufacture of polycarbonates and epoxy resins. It is also used as a stabilizer and antioxidant in the manufacture of PVC.

Bisphenol A polymers are found in many materials, including common plastics, food can linings, shopping receipts, textiles, toys, and water bottles.

Bisphenol A polymers are not used in the leather industry.

CAS: 80-05-7



#### RECYCLING OF PLASTICS WITH BISPHENOLS

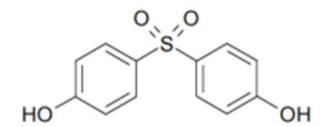


Plastics containing Bisphenol A do not have their own classification and are classified as OTHERS (7)

All plastics containing Bisphenol A are in category 7, but not all those in category 7 contain Bisphenol A



#### **BISPHENOL S**



The Bisphenol S (dihydroxyphenyl sulfone) is used in the traditional synthesis of aromatic synthetic tannins, whether based on sulfones or phenolic condensates. A certain amount of Bisphenol S monomers remains at the end of the reaction.

Bisphenol S has low reactivity, remaining in the finished polymer.

Synthetic tannins based on Bisphenol S are widely used to produce white leathers, have excellent filling power and are essential for the transformation of wet white into leathers because they have tanning power.

CAS: 80-09-1



#### BISPHENOL F

The Bisphenol F (methylene diphenol) is produced by secondary condensation reactions of phenol with formaldehyde.

Bisphenol F is not used directly as a material to produce synthetic tannins for the leather industry

Bisphenol F is not formed when Bisphenol S is polymerized, only by the condensation of phenol with formaldehyde CAS 620-92-8



#### BISPHENOLS OF SAME CONCERN (BoSC)

Substances	Index No	EC No	CAS No
4,4'-isopropylidenediphenol (Bisphenol A)	604-030-00-0	201-245- 8	80-05-7
4,4'-(1-methylpropylidene)bisphenol (Bisphenol B)	N/A	201-025-	77-40-7
4,4'-sulphonyldiphenol (Bisphenol S)	N/A	201-250- 5	80-09-1
4,4'-methylenediphenol (Bisphenol F)	N/A	210-658- 2	620-92-8
4,4'-[2,2,2-trifluoro-1- (trifluoromethyl)ethylidene]diphenol (Bisphenol AF)	N/A	216-036- 7	1478-61- 1



Name	Bisphenols with endocrine disrupting properties for the environment and their salts
EC Number	-
CAS Number	
Submitted by	Germany
Scope	Restricting the placing on the market of mixtures and articles where concentration is equal to or greater than 10 ppm (0.001 % by weight).  The first condition shall not apply to mixtures and articles where the bisphenols in the scope of the restriction are either covalently bound to any type of matrix (e.g. via functioning as a cross-linker) or are used as intermediates in the manufacture of polymers, and for which  i. contact to aqueous media in any form can be excluded during their reasonable and foreseeable use throughout their service life or  ii. the migration limit in the respective mixtures and articles does not exceed 0.04 mg/L over the entire service life.
Information note on restriction report	
Restriction report	Annex XV report
Restriction report annexes	Annex Annex H
Consultation on restriction report	Give Comments
Start of consultation on Annex XV report	21/12/2022
1st deadline for comments on Annex XV report	25/01/2023
End of consultation on Annex XV report	22/06/2023



#### **BISPHENOL S**

The **Bisfenol S** was classified as SVHC (Substance of Very High Concern) on January 17, 2023

https://echa.europa.eu/candidate-list-table

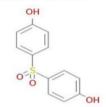
Substance name 🗘	EC No. 🗘	CAS No.	Date of inclusion 🧅	Reason for inclusion 🗘
<b>4,4'-sulphonyldiphenol</b> Process related name: <b>Bisphenol S</b>	201-250-	80-09-1	17-Jan-2023	<ul> <li>Toxic for reproduction (Article 57c)</li> <li>Endocrine disrupting properties (Article 57(f) - environment)</li> <li>Endocrine disrupting properties (Article 57(f) - human health)</li> </ul>

- Art.57.c: Toxic for Reproduction
- Art.57.f: Endocrine Disruptor substances that may present similar risks to humans and the endocrine environment



#### **BISPHENOL S**

Structural formula:



Substance Name: 4,4'-sulphonyldiphenol

EC Number: 201-250-5 CAS Number: 80-09-1

MEMBER STATE COMMITTEE SUPPORT DOCUMENT FOR IDENTIFICATION OF

4,4'-SULPHONYLDIPHENOL

AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS TOXIC FOR REPRODUCTION (ARTICLE 57C), ENDOCRINE DISRUPTING PROPERTIES (ARTICLE 57(F) - ENVIRONMENT), ENDOCRINE DISRUPTING PROPERTIES (ARTICLE 57(F) - HUMAN HEALTH) PROPERTIES

Adopted on 28 November 2022

**CLASSIFIED AS SVHC ON JANUARY 17, 2023** 

Table 1: Substance identity	
EC number:	201-250-5
EC name:	4,4'-sulphonyldiphenol
CAS number (in the EC inventory):	80-09-1
CAS number:	80-09-1
IUPAC name:	4-(4-hydroxybenzenesulfonyl)phenol
Index number in Annex VI of the CLP Regulation	604-098-00-1
Molecular formula:	$C_{12}H_{10}O_4S$
Molecular weight range:	250.27 g/mol

4,4'-sulphonyldiphenol	201-250-5	80-09-1	Toxic for reproduction
			(Article 57c): Endocrine disrupting
			properties (Article 57(f) -
			environment);
			Endocrine disrupting
			properties (Article 57(f) -
			human health)



#### **BISPHENOLS REGULATION**

#### **INITIAL PROPOSAL 2023**

#### WHAT HAS BEEN WITHDRAWN (TEMPORARILY):

Bisphenols of Similar Concern (BoSC) envisaged a limit of 500 mg/kg BPS/BPF for leather by 2025 and a further reduction of this limit to 10 mg/kg by 2030. The Federal Office for Chemicals (BfC), the German authority for REACH, has decided to temporarily withdraw the dossier without further information.

#### WHAT REMAINS:

For chemicals (synthetic tannins containing BPS) (EUROPE ONLY):

Reporting in the safety data sheet (MSDS):

If the BPS content is above 0.1%, this must be reported in section 3 of the MSDS If the BPS content is above 0.3%, the entire product (synthetic tannin) is classified as toxic for reproduction (H360FD), category 1B



#### **BISPHENOLS REGULATION**

...INITIAL PROPOSAL

WHAT REMAINS:

#### For Leather:

Inform ECHA if the article (leather) they produce contains an SVHC material (in this case BPS) in a concentration higher than 0.1% (by weight) and if the quantity of this substance exceeds one tonne per producer/importer per year.

The obligation to submit a notification (SCIP) applies to all articles placed on the market in the European Community that contain a substance from the Candidate List SVHC in a concentration higher than 0.1% (by weight)

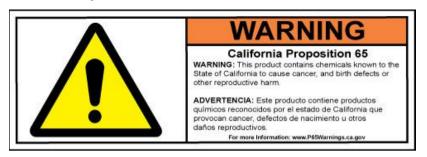


#### BISPHENOL S AND PROPOSITION 65

In the United States, Bisphenol S (BPS) has been listed as a "reproductive toxicant" under California's Proposition 65 (Prop 65). The requirement to provide a warning for significant consumer exposure to BPS from leather goods will go into effect in December 2024.

The Proposition 65 listing requires consumers who purchase an item to be informed that it contains BPS, such as: "WARNING: This item can expose you to chemicals, including BPS, which are known to the State of California to cause birth defects or other reproductive harm.

https://oehha.ca.gov/proposition-65/crnr/bisphenol-s-bps-added-proposition-65-list-following-2023-meeting-developmental





#### BISPHENOL S AND PROPOSITION 65















Proposition 65 Bisphenol S (BPS) Added to Proposition 65 List ...

#### Bisphenol S (BPS) Added to Proposition 65 List Following 2023 Meeting of the Developmental and Reproductive Toxicant Identification Committee

Jan 23, 2024

#### Bisphenol S Listed as Reproductive Toxicant

Effective December 29, 2023, the Office of Environmental Health Hazard Assessment (OEHHA) has added bisphenol S (BPS) to the Proposition 65 list as a reproductive toxicant (female reproductive endpoint). This listing was done via the "State's Qualified Experts" mechanism, based on the Developmental and Reproductive Toxicant Identification Committee's (DARTIC) determination that this chemical was clearly shown to cause female reproductive toxicity.

The warning requirement for significant exposures to BPS will take effect on December 29, 2024.





## RESTRICTED SUBSTANCES LISTS (RSLs) AND BISPHENOLS

Brands are independently implementing their own Restricted Substances Lists (RSLs) not only ahead of any legislation, but with values that may be even stricter, forcing tanneries to comply with low BPA limits (or no BPA at all) in the leather they supply.

Nowadays, some brands are demanding zero Bisphenols in the leather.



## ISO/IULTCS METHOD TO DETERMINE BISPHENOLS IN LEATHER



#### ISO 11936:2023 | IULTCS/IUC 42

Leather — Determination of total content of certain bisphenols

Published (Edition 1, 2023)

Bisphenols A, B, S and F

**Detection limits:** 

10 mg/kg by LC-MS/MS and 100 mg/kg by LC-UV



### ISO/IULTCS METHOD TO DETERMINE BISPHENOLS IN SYNTHETIC TANNINS



Bisphenols A, AF, B, S and F

#### **Detection limits:**

10 mg/kg by LC-MS/MS e LC/MS and 100 mg/kg by LC-UV



#### HOW TO PLAN FOR THE FUTURE?

- ❖ It is unlikely that in the future we will have fewer regulatory restrictions on the presence of Bisphenols and BoSC in leather
- Low BoSC synthetic tannins are a temporary solution. The goal will be to have new products with zero BoSC (without possibility of forming or decomposing to produce BoSC)
- More restrictions will come from brands and legislation, restricting quantities or requiring "zero" BoSC in leather
- The new generation of synthetic tannins will be more expensive and may compromise properties, opening the opportunity for new chemistries or process changes



## THANK YOU ON BEHALF OF IULTCS