Bisphenol & Glutardialdehyde:

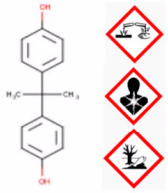
Will old chemicals become a new issue in leather manufacture?

M. Kleban; S. Niven; J. Fennen; D. Tegtmeyer

Date: 04/11/2021

What is a Bisphenol

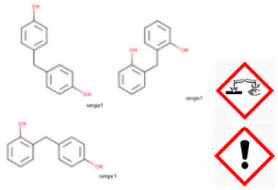
Bisphenol A



> 1.000.000 t/a

- Monomer high performance plastics
- Raw material resins
- Color developer thermoprint paper

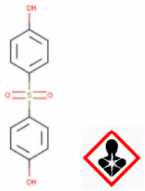
Bisphenol F



> 1.000 t/a

- Raw material resins
- Impurity synthetic tannins

Bisphenol S



> 10.000 t/a

- Monomer high performance plastics
- Monomer synthetic tannins

Bisphenol: Points of Concern

Bisphenol A

- Shows acute toxicity and corrosiveness typical for phenol-type substances.
- Has been demonstrated to be a low potency reprotoxin to mammals and fish.
- The reprotoxic effect is likely to be based on an endocrine mechanism
- Some tests with other hormonal receptors indicate effects

Bisphenol A has been listed as SVHC candidate substance under REACh

BUT: Decision has been passed not to prioritize BPA for Authorization

- Ban against the use in plastics for baby-bottles (regulation on food contact materials)
- REACh **Restriction** against the use as color developer in thermoprint papers
- Announced **Restriction** on BPA and **similar substances** in consumer Articles

Bisphenol A (BPA): Announced Restriction

Restriction on Bisphenol A and structurally related bisphenols of similar concern for the environment

- Announced by German Authorities in October 2020. Background paper:
  - List of "similar substances" including **BPS** & **BPF** in particular, all BPs in general
  - Threshold for chemicals used in Europe, unless strictly controlled conditions
  - Threshold for consumer articles imported to / manufactured in Europe
  - Migration test method and threshold

Publication of Draft re-scheduled from 10/2021 to 4/2022. Points of concern:

- Is **BPS** in scope? Environmental effects different from BPA
- **BPF** and "true BPs" as one group: few studies, future read across to **BPA** ? 
- Strictly controlled conditions vs. industrial conditions ?
- Threshold for chemical formulations vs. consumer articles ?
- Test method for leather / textiles / chemicals ?

Expected Finalization: 4/2023 or later

Expected Implementation: 4/2025 or later

What is Glutaraldehyde?

C5
(Glutaric acid, Glutaminic acid, Glutamate ...)

Glutaraldehyde

–CHO
(Formaldehyde, Acetaldehyde ...)

Glutaraldehyde

- Shows acute toxicity and corrosiveness typical for aldehyde-type substances.
- Is sensitizing by inhalation and skin contact
- **Has been extensively demonstrated NOT to be cancerogenic, mutagenic or reprotoxic (no CMR)**

Glutaraldehyde Legal Limits

Legal limits exist for the concentration of GA at the workplace:

- Limits are different from country to country
- Within one country, often different types of limits:
  - OEL: Time weighted average (typically 8h)
  - STEL: Short Term Exposure Limit (typically 15 min)
  - Ceiling (0 min)

	OEL (8-h)	STEL (15-min)	Ceiling
AT^	0.2 mg/m3	0.2 mg/m3*	0.2 mg/m3
DE^	0.2 mg/m3	0.4 mg/m3	n.d.
IT^	0.2 mg/m3*	0.2 mg/m3*	0.2 mg/m3
ES^	0.2 mg/m3*	0.2 mg/m3	n.d.
CH^	0.2 mg/m3	0.4 mg/m3	n.d.
UK^	0.2 mg/m3	0.2 mg/m3	n.d.

^: all inhalation, no dermal limits set
*: values not officially defined, but indirectly applicable due to ceiling value or STEL
n.d. : not defined

ECHA – REACH dossier

	DNEL (8-h)	DNEL (15-min)
Inhalation	0.2 mg/m3	0.4 mg/m3
Dermal	6.25 mg/kg bw/day	n.d.

Odour threshold of GA < 0.001 ppm
⇨ **If you don't smell it, you are well below any limits!**

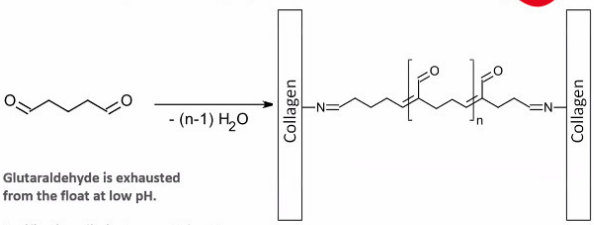
With proper equipment (ventilation) and handling these limits can be kept quite easily

How does Glutaraldehyde Tan?

Glutaraldehyde reacts not only with collagen, but also with itself

Values from pickle to crust
4% of pretanning agent used in 50% float

Process	Content of glutaraldehyde
offer	16 000ppm
pretanning float, 8h/pH3	1400 ppm
Basifying float, pH 4,2/4h	847 ppm
After 0,3% Sodium metabisulfite	400 ppm
On wet white	Not detectable to 60ppm
On crust	Not detectable to 5ppm



Glutaraldehyde is exhausted from the float at low pH.

Basification eliminates most the GA. At pH=4.2 to pH=5, a small change of pH can have a big impact on the residual GA of the float.

Scavengers like sodium metabisulfite can reduce the residual mount of GA in float, wet white and crust

With a state of the art process practically no glutaraldehyde is detectable in the crust

Regulatory Risks: SVHC Candidate & Sensitizer Restriction

SVHC Candidate

- Glutaraldehyde has been included in the SVHC Candidate List in 7/2021 as inhalation sensitizer.
- Articles need to be notified to ECHA if residual concentration exceeds 1000 mg/kg
  - ➢ Potential traces in leather are much lower
- Prioritization for authorization unlikely

Restriction on Skin Sensitizers in Textiles and Leather

- Glutaraldehyde part of master list of technically relevant substances
- Planned threshold for maximum residual concentration similar to free formaldehyde
  - ➢ State of the art tanning process makes sure value will not be exceeded

Expected Finalization: 2022 or later
Expected Implementation: 2025 or later

Epicutaneous Test on Humans

Patches of chromium-free leather were wetted and applied to the skin of test participants

Ca. 50% of the test participants were already suffering from different types of skin rashes (psoriaris vulgaris, atopic excema etc.)

These test conditions can be considered especially tough

The material was tolerated by all participants without any visible reactions

- **"The chromium-free leather is a skin friendly material, with which even skin-sensitive people may come into direct, prolonged skin-contact. The materials have no potentially sensitizing properties."**

SUMMARY

Bisphenol-type chemicals are in the focus of developing regulations, mainly because of their property as low potency reprotoxin with a potentially hormonal activity.

In leather industry, Bisphenol F can be an impurity in synthetic tannins, while Bisphenol S is a monomer that is used to manufacture synthetic tannins, which can lead to residues in the final product.

Scope and impact of regulations are under discussion and not yet clear but will not come into force before 2025.

Glutaraldehyde pre-tanning is a proven and efficient technology.
It can be done economically and reliably in tanneries equipped with current machinery.

There is no ban to the use of glutaraldehyde as a pre-tanning agent, and with proper processing there is no detectable glutaraldehyde in the final leather that would be subject to a restriction.

Chrome-free leather pre-tanned with glutaraldehyde is a skin-friendly material with no potentially sensitizing properties.