DETOXING WET-END CHEMICAL AND LEATHERS, READY TO REALIZE IT!

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ABSTRACT

This presentation offers a selective representation of several innovative and successful developments carried out in our company to detoxify wet-end leather products, ensuring high performance on leather while minimizing negative impacts on both human health and the environment.

One of our studies highlighted the ecological and toxicological advantages of using the tanning agent **sodium p-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzenesulphonate** compared to glutaraldehyde and Cr(III) salts. As a chrome-free tanning agent, it eliminates the risk of generating carcinogenic Cr(VI).

Another project demonstrated the application benefits of a resin structurally similar to **melamine resins**. This polymer, synthesized through aromatic nucleophilic substitution of triazine derivatives—rather than traditional condensation of melamine with formaldehyde—eliminates free melamine and formaldehyde in both products and leather, while enhancing retanning performance.

The presentation also shows a patented discovery: the use of **rice husk in leather retanning.** This product not only delivers superior results compared to conventional syntans and vegetable tannins, but also avoids the risks associated with bisphenols and formaldehyde.

Lastly, we present an example of process optimization aimed at reducing the free content of SVHCs such as **Cyclotetrasiloxane (D4), Cyclopentasiloxane (D5), and Cyclohexasiloxane (D6) in waterproofing agents.**

GC-MS analysis confirmed that, through the use of suitable thin-layer evaporators and precise control of temperature and pH during emulsification, the content of free D4, D5, and D6 was reduced from thousands of ppm to just a few tens of ppm in the final formulations.

Keywords: chrome and aldehyde-free tanning, retanning agent, melamine-type resin, rice husk, cyclomethicones.

1. Introduction

The large number of eco-toxicological tests conducted each year to enhance human and environmental protection has significantly increased awareness of the unintended harmful properties of certain chemical products. In some cases, by-products of chemical synthesis—despite the positive intentions behind their invention—have raised serious environmental and health concerns.

This growing awareness, combined with evolving legislation and regulatory pressure, has driven our company to develop and innovate a wide range of wet-end leather chemicals with improved eco-toxicological profiles.

This presentation offers a curated overview of key developments in the wet-end leather sector. It highlights successful efforts to detoxify leather products by re-evaluating and redesigning chemical formulations, aiming to preserve performance while reducing their impact on health and the environment.

2. Material and Methods

OECD 301F Ready Biodegradability; OECD 209 Activated Sludge; OECD 203 Fish, Acute Toxicity Test; OECD 201 Alga, Growth Inhibition Test; OECD 202 Daphnia sp. Acute Immobilization Test; OECD 211 Daphnia Magna Reproduction Test; EU Method C.3; FIFRA Giudeline No: 72-3.

OECD 423 Acute Oral Toxicity; OECD 402 Acute Dermal Toxicity; OECD 439 In Vitro Skin Irritation; OECD 405 acute eye irritation corrosion; GARDair In vitro respiratory sensitization assessment; OECD 414 Prenatal developmental toxicity study; OECD 422 Combined Repeated Dose Toxicity Study. BS EN ISO 20200: 2015 (modified); Eurofins TerrAttesT; REAL CCS v3.1.

GPC**:** Agilent Technologies 1260 Infinity; Detector: RID; Solvent: Solution of Sodium nitrate 0,2 M and Sodium Dihydrogenophosphate 0,01M to pH 9; Columns: Agilent PL acquagel-OH 5 µm; Agilent PL aquagel-OH 20 5 µm 300 X 7,5 mm; Agilent PL aquagel-OH 20 5 µm 300 X 7,5 mm; Temperature: 35°C; Flow: 0,5 ml/min; Injection: 20 ml; Sample conc.: 5 mg/ml; Data processing: Agilent GPC/SEC Software Vers A.02.01; Calibration data points: PEG with MW 19720, 14360, 8460, 3890, 1490, 1030, 620, 435, 238, 194.

ISO 13320:2020 particle size analysis; ISO 105-A02 Tests for colour fastness; ISO 105-B02 Tests for colour fastness - Part B02: Colour fastness to artificial light: Xenon arc fading lamp test; ISO 23649:2025 Determination of cyclosiloxanes (D4,D5,D6) by GC-MS ; ISO 20200 Modified for Leather: Disintegration and Biodegradability Testing, FTIR-ATR Agilent Resolution Pro.

3. Results and Discussion

3.1 Sodium p-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzenesulphonate as a tanning agent

In leather production, the tanning process plays a crucial role in determining the properties and quality of the final product. Among the various tannings known in the art, i.e. mineral, vegetable and synthetic, chrome-based tannage is the most conventional and widely spread way of tanning and glutaraldehyde is primarily used as an alternative to chrome tanning in the leather industry, particularly for producing chrome-free leathers. Both chrome and glutaraldehyde are highly versatile tanning agents, known for producing leather with excellent performance, appearance, flexibility, and durability. However, their use also raises specific environmental and health concerns that must be carefully considered.

One of our study led to the invention of a non-metal tanning system of outstanding quality based on sodium p-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzenesulphonate as a tanning agent which also allow to omit a pickling as conventionally carried out before chrome tanning or aldehyde tanning.

Several tests reported in Table 1 showed the ecological and toxicological advantages of this tanning agent in comparison to the glutaraldehyde for the production of wet white, and in comparison to Cr(III) salts avoiding the risk of carcinogenic Cr(VI) formation.

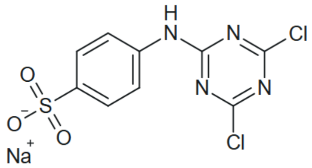

Figure 1. sodium p-[(4,6-dichloro-1,3,5-triazin-2-yl)amino] benzensulphonate structure

TEST	TYPE	RESULT	METHOD	CLASSIFICATION
Acute oral toxicity	LD 50	>2,000 mg/kg	OECD 423 - Acute Oral Toxicity	Not classified
Acute Dermal Toxicity	LD50	>2,000 mg/kg	OECD 402 - Acute Dermal Toxicity	Not classified
Skin sensitization		>1%	Guinea pig maximisation test and Human Repeated Insult Test	Skin Sens. 1. H317: may cause an allergic skin reaction
Respiratory sensitization		Not sensitizing	GARDair In vitro respiratory sensitization assessment	Not classified
Skin Irritation/Corrosion		Not irritating	OECD 439 - In Vitro Skin Irritation	-
Eye irritation/corrosion		Irreversible effects on the eyes	OECD 405 - Acute Eye Irritation/Corrosion	Eye Damage 1 H318: causes serious eye damage
Specific target organ toxicity (STOT-SE)		No human evidence of respiratory tract irritation	-	-
Preliminary prenatal development toxicity study in rats			OECD 414- Prenatal developmental toxicity study	Not classified
Developmental toxicity/Teratogenicity			OECD 422 - Combined Repeated Dose Toxicity Study	Not classified
Biodegradability		55.1 %	OECD 301F Ready Biodegradability	Not easily biodegradable
Toxicity to microorganisms	NOEC	320 mg/L	OECD 209- Activated Sludge	No inhibitory effect up to 320 mg/L
Toxicity to microorganisms	EC50	>1000 mg/L	OECD 209 - Activated Sludge	No inhibitory effect up to 320 mg/L.
Short-term toxicity to fish	LC0	143 mg/L	OECD 203 - Fish, Acute Toxicity Test	Not classified
Short-term toxicity to fish	LC50	>> 143 mg/L	OECD 203 - Fish, Acute Toxicity Test	Not classified

Toxicity to aquatic algae	NOEC	143 mg/L	OECD 201 - Alga, Growth Inhibition Test	Not classified
Toxicity to aquatic algae	EC50	> 143 mg/L	OECD 201 - Alga, Growth Inhibition Test	Not classified
Short-term toxicity to aquatic invertebrates	EC50	> 100 mg/L	OECD 202 - Daphnia sp. Acute Immobilization Test	Not classified
Long-term toxicity to aquatic invertebrates (on reproduction)	NOEC	143 mg/L	OECD 211 - Daphnia Magna Reproduction Test	Not classified

Table 1. Eco-toxicological test results.

The leather industry uses harmless Cr(III) salts, that could be oxidized to highly harmful Cr(VI) species, during leather manufacturing, in finished leather, wastewater and slurries.(Chandra et al.2022) Cr(VI) is classified as a group 1 carcinogen by the World Health Organization (WHO) and by the International Agency for Research on Cancer (IARC) since it is known to increase the risk of several types of cancers and is also being recognized as neurotoxicant.(Wise at al.2022)

Glutaraldehyde, according to the harmonized classification and labelling approved by the European Union, is fatal if inhaled, is toxic if swallowed, causes severe skin burns and eye damage, is very toxic to aquatic life, is toxic to aquatic life with long lasting effects, may cause an allergic skin reaction, may cause allergy or asthma symptoms or breathing difficulties if inhaled and may cause respiratory irritation. It is a substance of very high concern (SVHC) and it is included in the candidate list for authorization.(ECHA)

The tanning system based on sodium p-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzensulphonate is proposed as a more sustainable tanning system.

It is classified as a low hazard substance with an LD50 value greater than 2000 mg/kg by both dermal contact and oral ingestion, may cause an allergic skin reaction, causes serious eye damage, and it has a negligible environmental toxicity profile, not being classified for short-term fish toxicity, toxicity to aquatic algae, short-term and long term toxicity to aquatic invertebrates and showing no inhibitory effect to aquatic microorganisms up to 320 mg/L.

A further significant advantage offered by this tanning system is the possibility of reusing the leather shavings, precisely for their eco-toxicological profile.

The levels of chemicals found in the compost obtained from leather shavings tanned with CAS 4156-21-2 Sodium 4-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzenesulfonate were comparable to those found in the negative control and were not of concern.

Tomato seedlings grown in the compost containing leather shavings obtained with CAS 4156-21-2 Sodium 4-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzenesulfonate performed better than the control samples. Growth was measured in terms of top growth, plant height and number of leaves.

The correlated reduction in chemicals, energy and water consumption obtained with this tanning system and, in addition, the suitability of producing biogas from shavings confirmed by preliminary studies, constitute further environmental and socio-economic benefits.

3.2 Synthesis of safer melamine-type resin for retanning products

Melamine resins are widely used as retanning agents in the leather industry due to their ability to improve leather's physical and aesthetic properties. Conventionally, these resins are synthesized through the condensation of melamine and formaldehyde. However, concerns over residual free formaldehyde and melamine - associated with adverse health and environmental effects- have driven considerable research into safer alternatives. Recent advancements have focused on developing formaldehyde-free melamine resins.(Zhang2024)

In the present study, we propose an alternative synthetic route for melamine-type resins based on cyanuric chloride, diethylenetriamine, and sodium sulfanilate. This novel approach completely eliminates the use of both melamine and formaldehyde. The resulting polymer was characterized through Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC).

FTIR spectrum exhibits all the characteristic peaks of a melamine-type resin:

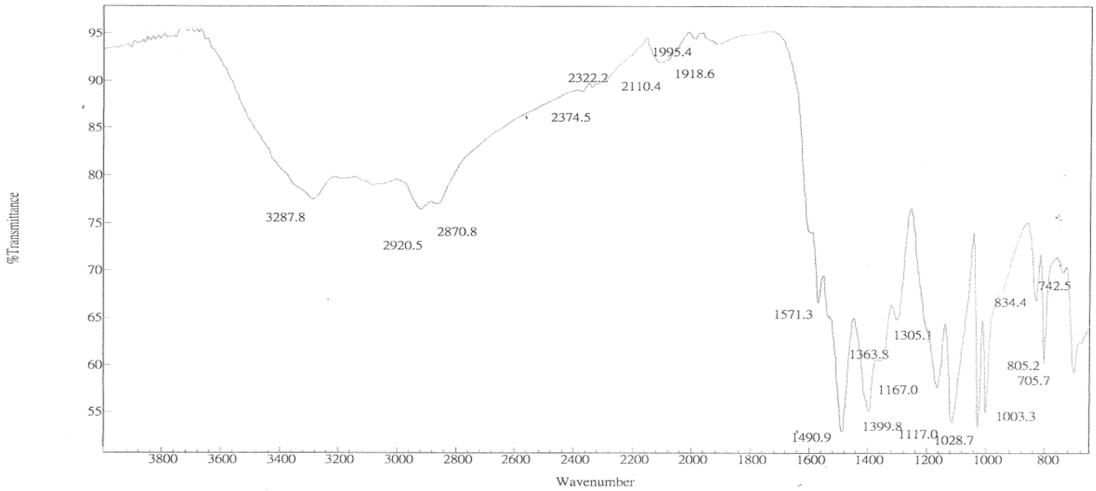

Figure 2. FTIR spectrum of the new melamine-type resin.

The GPC chromatogram shows three peaks and the corresponding molecular weight data are shown below:

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	4672	3379	4950	7340	10422	6938	1.465
Peak 2	654	621	635	648	659	646	1.023
Peak 3	140	115	132	142	150	141	1.148

Table 2. Molecular weight data of the new melamine-type resin.

A comparative study was carried out to evaluate the performance of the newly synthesized resin relative to a commercial melamine-based reference product. The assessment focused on physical properties, tactile characteristics, and finishing behavior under standardized application conditions, on bovine hides wet blue tanned.

Both resins delivered comparable overall physical performance, demonstrating adequate mechanical strength and dyeing uniformity. However, distinct differences emerged in the tactile and surface properties. The novel resin imparted a firmer handle and produced a slightly tighter grain structure, resulting in a more structured and well-defined leather surface. Both products ensured good uniformity and leveling during the dyeing phase.

From these results, the new resin, free of melamine and formaldehyde, proved to be a valuable alternative as a retanning agent, combining high performance with non-toxicity and environmental compatibility.

3.3 Rice husk in leather retanning

In recent years some components present in the synthetic tannins have been recognized as reprotoxic substances, 4,4' isopropylidendiphenol (Bisphenol A), 4,4'-sulphonyldiphenol (Bisphenol S) and, o-[(4-hydroxyphenyl)methyl]phenol (Bisphenol F), and as endocrine disrupters, Bisphenol A and Bisphenol S. Bisphenol A and Bisphenol S are SVHC, Bisphenol F has been proposed as SVHC.

These reclassifications and the increased awareness of the associated risks have stimulated our company to seek alternative substances and products.

We have developed a project focused on selecting raw materials of biological origin that do not compete with the use of such raw materials as a food source, giving priority, when possible, to the use of waste streams of biological origin.

Within this research project, it was discovered that rice husk can be applied on leather, such as via an industry standard procedure, for retanning. It was found that leathers treated with rice husk, gave similar or better properties to the leather than syntans or vegetable tannins, concerning softness, fullness, tightness, smoothness, bleaching, light fastness and heat fastness while creating no bisphenol or formaldehyde problem. An analysis of toxic formaldehyde or bisphenols is not even required for these retanning compositions, because none of the ingredients contains or could release formaldehyde or could form bisphenols.

The retanning composition of the study comprises milled rice husk wherein the rice husk is milled and dried to obtain a rice husk powder having a moisture content of around 10 weight % based on the total weight of the powder and an average particle size in the range from 50 µm up to 300 µm, measured according to ISO 13320.

Leathers previously tanned with chromium sulphate or a metal-free tanning product commercially available were retanned respectively with 15% and 20% of rice husk powder, compared with Quebracho and with Mimosa powder. The thickness of the bovine leather was 1,1/1,2 mm for wet blue and 1,0/1,1 mm for wet white.

	Rice Husk	Quebracho	Mimosa
Tightness	3,5	4,0	4,0
Smoothness/Fineness	2,0	2,0	2,0
Softness	3,0	2,0	2,5
Fullness	3,0	2,0	3,0
Fluffiness	3,0	2,0	2,5
Handle/Touch	2,0	2,0	3,0
Uniformity	2,5	2,0	3,0
Shade	2,5	2,0	3,0
Bleaching	2,0	6,0	4,0
Cross section	100%	100%	100%
Average	2,6	2,7	3,0

Table 3. Retanning properties of rice husk, Quebracho and Mimosa on wet blue leathers.

The leathers were evaluated by specialized technicians. Lower numbers indicate better properties.

As reported in Table 3, the leathers retanned with rice husk give an average score that is comparable with the score obtained with the reference retanning agent Quebracho and better than obtained with the reference retanning agent Mimosa.

The leather specimens were used for measuring the light fastness. The leathers were exposed to light in a sun tester for 24, 48 or 72 h., according to ISO 105-B02, also known as Xenotest. After exposure to light, leather samples were evaluated according to blue scale with numbers from 1 to 8. Larger numbers indicate less color change and therefore more resistance to light induced aging.

The leather specimens were also used for measuring the resistance to heat. The leathers were exposed to heat at 80 °C for 72 h., or 100 °C for 168 hours or 120 °C for 168 hours, according to ISO 105-A02. After exposure to heat, leather samples were evaluated according to the grey scale with numbers from 1 to 5. Larger numbers indicate more stability against heat.

	Rice Husk	**Quebracho**	**Mimosa**
Light fastness 24 hours (blue scale)	5,0	4,0	3,5
Light fastness 48 hours (blue scale)	4,0	3,0	3,0
Light fastness 72 hours (blue scale)	4,0	3,0	3,0
Heat fastness 80 °C, 72 hours (grey scale)	3,0	3,0	2,0
Heat fastness 100 °C, 168 hours (grey scale)	3,0	1,5	1,5
Heat fastness 120 °C, 168 hours (grey scale)	2,0	2,0	1,5

Table 4. Light and heat fastness results using rice husk, Quebracho and Mimosa.

As reported in Table 4, the leathers retanned with rice husk gave light fastness scores that were better than the scores obtained with the reference retanning agent Quebracho and also better than the scores obtained with retanning agent based on Mimosa.

The heat fastness results of the leathers retanned with rice husk were somewhat better than scores obtained with the reference retanning agent Quebracho and only little lower than obtained with reference retanning agent based on Mimosa.

The use of rice husk represents a novel non-toxic, renewable alternative retanning agent, sourced from a readily available byproduct of the rice industry, compared to conventional retanning agents in the leather industry sourced from oil based phenol-formaldehyde condensates or from vegetable sources that are less readily available, such as conventional Quebracho obtained from the wood of the Quebracho tree, Mimosa obtained from the bark of the Acacia tree,or Tara obtained from the fruit of the Tara bush.

3.4 D4, D5, D6 reduction in waterproofing products

The final section of this presentation focuses on the challenge of reducing the content of D4, D5, and D6 in wet-end leather chemicals.

Cyclic siloxanes such as D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane), and D6 (dodecamethylcyclohexasiloxane) are volatile, low molecular weight compounds widely used in the past as monomers in the production of silicone polymers and as functional ingredients in various industrial formulations.

Due to their environmental persistence, bioaccumulation, and potential toxicity, particularly to aquatic life, these substances have been identified as Substances of Very High Concern (SVHC) under the

REACH Regulation. Specifically, D4,D5,D6 are considered as both PBT (persistent, bioaccumulative, and toxic) and vPvB (very persistent and very bioaccumulative). In response, the EU adopted Regulation (EU) 2024/1328, restricting the placing on the market of D4, D5, and D6 at concentrations ≥0.1% w/w in most uses, including cosmetics and industrial applications (excluding the use as monomer).(ECHA). Moreover D4 has a harmonized classification as reprotoxic Cat.2.

These regulatory measures have significant implications for industries relying on silicone-based formulations, including the leather chemical sector, where silicone polymers are commonly used as primary components in wet-end waterproofing systems and D4, D5, and D6 may be present in final formulations as residual monomers or synthesis by-products, requiring careful control to ensure regulatory compliance and health and environmental safety.

In this context a study was conducted to implement technological and process improvements on an industrial scale to reduce the levels of D4, D5, and D6 well below the regulatory threshold.

These cyclic siloxanes, being volatile in nature, can be removed through specific post-processing treatments. Two industrial processes are mostly employed to reduce cyclomethicone levels:

- Bulk Stripping: in this method, silicone polymers are heated in bulk vessels under vacuum and with agitation. The combination of heat and reduced pressure facilitates the removal of volatile cyclic siloxanes. This process typically reduces residual levels of D4, D5 and D6 to below 0.1% w/w.
- Wiped Film Evaporator Stripping (WFE): this advanced technique is a specialized type of evaporator that uses a rotating rotor with wiper blades to spread a thin film of silicone polymers liquid onto a heated surface for efficient separation of volatile under vacuum. The increased surface area and efficient heat transfer result in effective removal of volatile components. Cyclomethicone concentrations can be reduced to below 0.01% w/w.

Table 5 shows the concentration of cyclic siloxanes in carboxy silicone oils before and after treatment, confirming the effectiveness of the stripping method.

	D4 (ppm)	**D5 (ppm)**	**D6 (ppm)**
Silicon oil a) before treatment	1668	5059	3852
Silicon oil b) before treatment	1955	4890	4652
Silicon oil a) after treatment (WFE)	5	<5	51
Silicon oil b) after treatment (WFE)	13	7	25

Table 5 . Concentration of D4, D5, D6 in carboxy silicone oils before and after treatment, by GC-MS.

Table 6 reports the concentration of cyclic siloxanes in a production batch of a waterproofing composition containing silicones treated by WFE.

	D4	**D5**	**D6**
	ppm	ppm	ppm
Waterproofing Composition	< 10	<10	<10

Table 6. Concentration of D4, D5, D6 in a waterproofing composition.

Our findings demonstrate that post-polymerization treatments, such as bulk stripping and wiped film evaporation, are effective in significantly reducing residual levels of these substances. These insights emphasize how careful process control can ensure both compliance with regulations, and health - environmental safety of silicone-based waterproofing systems for wet-end leather manufacturing.

4. Conclusion

The ongoing detoxification of wet-end leather chemicals—through sustainable product design, advanced processing technologies, and the integration of bio-based materials—represents a fundamental pillar of modern leather manufacturing. By integrating process intensification techniques and minimizing the presence of hazardous substances such as formaldehyde, bisphenols, glutaraldehyde, Cr(VI), and SVHC-classified siloxanes, the industry is moving toward more sustainable, and high-performance chemical solutions. These efforts not only align with regulatory and environmental expectations, but also support the sustainability and competitiveness of the leather industry, providing benefits for producers, consumers, and the environment.

5. Acknowledgements

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6. References

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