



# Glutaraldehyde: Proven technology for white metal-free leathers

## Part 1 of 2: Pre-tanning with modified glutaraldehyde

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### 1. The theory and practice of glutaraldehyde tanning

Glutaraldehyde first received attention as a tanning agent in the 1960s. For monoaldehydes, the higher homologous species are progressively less effective tanning agents than formaldehyde. In general, the same applies to dialdehydes in relation to the smallest example glyoxal. However, glutaraldehyde is an exception to this rule as it is a very efficient tanning agent.<sup>1</sup>

The mechanism of glutaraldehyde tanning has since been investigated in depth. Aldehydes react with amines to form Schiff's bases as shown in *Panel 1*.

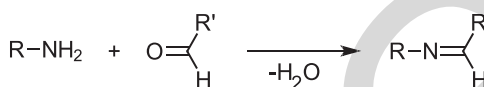
In this situation, the aldehyde tanning agents will bind to amino groups in the lysine side chains of collagen. It may appear that the bifunctional glutaraldehyde can react with lysine side chains of two collagen molecules and one molecule may thus form a crosslink, but this has been shown not to be the case. Instead, it is important to consider that glutaraldehyde will, under the conditions of tanning, not only react with collagen, but also with itself, undergoing a so-called aldol reaction as shown in *Panel 2*.

This reaction can lead to a polymerisation of monomeric glutaraldehyde, and this also has a decisive influence on the character of the tanned leather. Other reactions take place as well, and finally a very wide variety of different structures are formed during the tanning step. On average, three molecules of glutaraldehyde react with each lysine amino group; this statistically means six molecules per crosslink. However, there is no evidence that crosslinking is even taking place.<sup>2</sup>

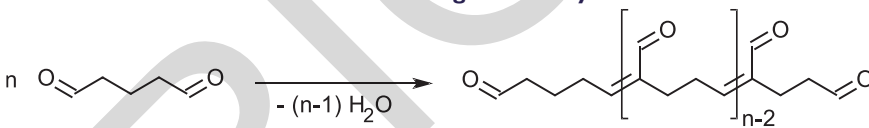
#### 1.1 TANNING WITH MODIFIED GLUTARALDEHYDE

Tanning with glutaraldehyde only gained industrial relevance with the introduction of so-called "modified

**Panel 1: Reaction of aldehydes with amines to Schiff's bases**



**Panel 2: Aldol condensation reaction of glutaraldehyde**



glutaraldehyde" about 25 years ago.<sup>3</sup> The role of the modification is a moderation of the reactivity of the aldehyde towards collagen. This vastly improves the reliability and robustness of the tanning process in comparison to the very reactive unmodified form.

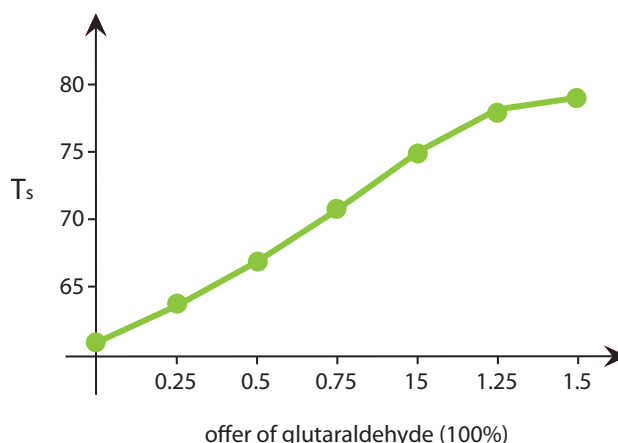
Since the introduction of this technology, the volume of chromium-free leathers produced in this way has steadily increased. This is especially so in the field of automotive leather where the market share for this type of leather has now reached 25%.

From a practical point of view, small amounts of glutaraldehyde are sufficient to achieve a significant tanning effect. The results of tanning trials with a typical modified glutaraldehyde<sup>4</sup> in varying amounts is shown in *Panel 3*.

Industrial processes are usually carried out with an offer of around 3-4% of product with a concentration of 20-25%, corresponding to about 0.75-1% glutaraldehyde. The typical shrinkage temperature obtained is in the range from 72-75°C.

The main control parameter during a

**Panel 3: Shrinkage temperature  $T_s$  in °C as a function of glutaraldehyde offer**



**NOTE:** The measurements were performed after basification to pH 5.0.



tanning process with glutaraldehyde is the pH. The reactivity towards collagen as well as the reaction rate of the aldol condensation is increased when the pH is raised from pH 3.0 to pH 4.2-5.0 during basification. Other parameters, such as temperature, also need to be kept within certain limits, but as some deviations are tolerable, technical requirements are low.

Due to the technical experience and control required with chromium tanning, tanneries are adapted to controlling the pH and other parameters. Accordingly, a robust and reliable wet white tanning process based on glutaraldehyde can easily be implemented in a standard tannery. The formation of covalent bonds in the tanning reaction is irreversible, and the polymeric nature of the polymerised tanning agent explains the softening and filling effect of glutaraldehyde tanning.

## 2. Ecological and toxicological aspects

Producing leather involves chemicals, and these are under continued and ever increasing scrutiny concerning their ecological and toxicological profile. The same is true for the final product as leather following chemical processing.

Tanneries therefore need to know that the technologies they are employing are safe. This is not only from today's point of view, but also within the foreseeable future. Any technology used in a leather making process, whether it is new or established, therefore needs to be continuously re-evaluated based on up-to-date data.

An advantage of glutaraldehyde tanning is that it forms an organic bond, with no inorganic materials such as metals, halogens, etc., added to the natural collagen structure of the hide. The resulting leather can be composted<sup>5</sup> and unlike chromium tanned leather, there is no issue if it is incinerated.

### 2.1 FOCUS ON ALDEHYDES

Glutaraldehyde as a chemical is often looked upon with some uncertainty by tanners. This is because it is an aldehyde, and other aldehydes such as formaldehyde are classified as "CMR" substances (*carcinogenic, mutagenic, reprotoxic*).

There is, however, a misunderstanding. Aldehydes are omnipresent in our food – not because the food is contaminated with chemical residues, but because the aldehydes are an integral part of many food items. Very often they provide the characteristic smell or taste of a particular fruit or vegetable.

This is, for example, the case for vanillin

### Panel 4: Natural content of aldehydes in food items

| Food item      | Aldehyde contained | Concentration up to | Health risk of aldehyde                              |
|----------------|--------------------|---------------------|------------------------------------------------------|
| Coffee         | Furfural           | 250 ppm             | Carcinogenic (low potential)                         |
| Bread          |                    | 14 ppm              |                                                      |
| Ginger         | Citral             | 13,500 ppm          | No health risk                                       |
| Lemon peel oil |                    | 130,000 ppm         |                                                      |
| Vanilla pods   | Vanillin           | 23,200 ppm          | No health risk                                       |
| Cinnamon       | Cinnamaldehyde     | 30,000 ppm          | Potentially mutagenic/<br>carcinogenic (data needed) |
| Fruit          | Acetaldehyde       | 400 ppm             | Genotoxic                                            |

**NOTE:** The listed health risk refers to the pure aldehyde, not to the food item.

(*in vanilla pods*), cinnamon aldehyde (*in cinnamon bark*) and citral (*in lemon and lime*). These and some other examples, together with the content that can be expected and an approximate description of the risk potential,<sup>6</sup> are shown in *Panel 4*.

From these examples, it is clear that the risk potential of aldehydes cannot be generalised. On the contrary, each substance has to be assessed individually, and the type of exposure and the dosage have to be considered as well.

### 2.2 FOCUS ON GLUTARALDEHYDE

With regard to glutaraldehyde, it needs to be emphasised that it is not classified as a carcinogen or as an *in vivo* mutagenic or reprotoxic substance.<sup>7,8</sup> This immediately shows that glutaraldehyde must not be compared to formaldehyde regarding its risk potential.

The labelling of a typical glutaraldehyde-based pre-tanning agent with a concentration of 20-25%, according to the GHS system, is shown in the form of three pictograms in

### Panel 5.

The leather making process involves many chemicals that need to be handled with adequate precautions due to their irritant or toxic properties. Tanneries have to know how to handle substances like formic acid or even sodium sulphide. Any tannery working under proper conditions is therefore able to take the necessary measures to address the irritant and corrosive nature of glutaraldehyde. The sensitising properties of the substance are reflected in rather low occupational exposure limits, which vary from country to country as shown in *Panel 6*.<sup>9</sup>

Limits are often expressed as the average value measured over a defined time period, which can be 8h for the so-called TWA (time-weighted average) limit, or 15 min for the STEL (short term exposure limit). Within these time frames, peak values may exceed the given limits, again depending on local regulations. A ceiling value may not be exceeded for any period of time.

It is important to note that the odour

### Panel 5: GHS labelling of a typical pre-tanning agent based on glutaraldehyde (20-25%)



- The first "irritant" pictogram is related to the hazard statements H302 (Harmful if swallowed), H332 (Harmful if inhaled) and H335 (May cause respiratory irritation),
- The second "corrosive" pictogram is related to the statement H314 (Causes severe skin burns and eye damage)
- The third "health hazard" pictogram is related to H317 (May cause an allergic skin reaction) and H334 (May cause allergy or asthma symptoms or breathing difficulties if inhaled).



threshold of glutaraldehyde is below 0.001 ppm, more than 50 times below the strictest limit. In general, tanneries will be able to respect these limits, especially if dosing is done automatically. Under special conditions, such as spillages or leakages, individual protection may be required.

### 2.3 GLUTARALDEHYDE AS A PRE-TANNING AGENT

An outline formulation for a pre-tanning with glutaraldehyde following lime splitting, deliming and bating, is given as *Panel 7*.

During application, the concentration of glutaraldehyde originally offered is quickly reduced by exhaustion of the float, which in turn further reduces the risk of exposure. The typical values for the glutaraldehyde content in the float and the pelt/leather at different stages of the tanning process is shown in *Panel 8*.

*Panel 8* shows that at pH 3.0, where the reactivity of glutaraldehyde towards collagen is still relatively limited, more than 90% of the product is exhausted from the float after eight hours. During basification to pH 4.2, the residual concentration in the float is then halved again. Additional trials have shown that basification to a slightly higher pH, for example pH 4.5, will significantly decrease this value.

The final user of the leather article will of course be mainly interested in the residual amounts of glutaraldehyde in the leather article. Contrary to formaldehyde, there are practically no relevant restrictions on the content of glutaraldehyde in leather, but eco-labels may require the total detectable amount of aldehydes to be under a certain level. In any case, the values in *Panel 8* demonstrate that low amounts of glutaraldehyde are often, but not always, detectable in the wet white, and in the crust the concentration is negligible.

A clinical epicutaneous test on humans came to the conclusion that this type of leather is "a skin friendly material, with which even skin-sensitive people may come into direct, prolonged skin-contact. The materials have no potentially sensitising properties".<sup>10</sup> 50% of the participants of the test group were already suffering from different types of skin rashes (psoriasis vulgaris, atopic eczema, etc.), therefore the test conditions can be considered especially tough.

Some confusion was caused within the leather industry by the fact that some tanneries in the EU have to replace

**Panel 6: Occupational exposure limits for glutaraldehyde in different countries**  
**TWA=Time-weighted average, STEL=Short term exposure limit.**

| Country                 | TWA (8h) | STEL (15min) | Ceiling  |
|-------------------------|----------|--------------|----------|
| Netherlands, Belgium    |          |              | 0.06 ppm |
| United Kingdom, Austria | 0.05 ppm | 0.05 ppm     |          |
| Germany                 | 0.05 ppm |              | 0.2 ppm  |
| France                  | 0.1 ppm  | 0.2 ppm      |          |
| Russia                  |          | 1.2 ppm      |          |

**Panel 7: Pre-tanning with glutaraldehyde**  
**Bovine hides lime split to 2.5 – 2.8mm**

| Process            | %       | Product                                       | Time    | Required    |
|--------------------|---------|-----------------------------------------------|---------|-------------|
| <u>Pickle</u>      |         |                                               |         |             |
| Add                | 50      | Water 20°C                                    |         |             |
| Add                | 6.0     | Common salt                                   | 15 min  |             |
| Add                | 1-2     | Natural/synthetic fatliquor <sup>(1)</sup>    |         |             |
| Add                | 0.5     | Formic acid (1:10 dilution)                   | 45 min  | pH 3.0-3.2  |
|                    | 1.0     | Sulfuric acid (1:10 dilution)                 | 180 min | pH 3.0-3.2  |
| <u>Pre-tannage</u> |         |                                               |         | Cut BCG     |
| Add                | 3.0     | Highly masked glutaraldehyde <sup>(2)</sup>   | 5 min   | 100% yellow |
| Add                | 0.1     | Preserving agent                              | 480 min | pH 3.0      |
| Add                | 0.3 x 4 | Sodium Bicarbonate <sup>(a)</sup>             | 180 min |             |
| Add                | 3.0     | Liquid synthetic tanning agent <sup>(3)</sup> | 90 min  | pH 4.2      |
|                    |         | Drain, wash off, pile                         |         |             |

Products - (1) Coripol® SLG, (2) Sellatan® WL-G, (3) Sellatan RLS

(a) make 4 additions in total each at 0.3% offer

**Panel 8: Glutaraldehyde content during tanning process.**

**Values based on 4% pretanning agent and 50% float (full substance hide).**

| Process step                        | Content of glutaraldehyde |
|-------------------------------------|---------------------------|
| Offer                               | 16000 ppm                 |
| In the pretanning float (pH 3 / 8h) | ~ 1500 ppm                |
| After basification (pH 4.2 / 4h)    | ~ 800 ppm                 |
| On the wet white                    | Not detectable to 60 ppm  |
| On the crust                        | Not detectable to 5 ppm   |

glutaraldehyde by other substances if it is used as a biocide. This is due to the fact that currently all biocides are undergoing a revision process. Substances with respiratory sensitising properties are candidates for substitution, but the EU committee that is responsible still

recommends approving glutaraldehyde as a biocide for all the applications that are still under revision.

It is therefore very important to note that the whole revision process only applies to the use as a biocide. It should not be mistaken as a ban or a restriction of



non-biocidal applications. This is because a substance that is used as a biocide has to remain in the article it is supposed to protect. A certain concentration is required to provide the biocidal effect and the product needs to be bioavailable.

This is not the case if glutaraldehyde is used as a tanning agent. There are no relevant levels of the substance remaining in the leather article as shown in *Panel 8*. 🌐

### Part 2 of 2: The versatility of glutaraldehyde in leather making

Part 2 of this paper will be published in *World Leather* in the coming months. It will discuss the flexibility and advantages of leathers pre-tanned with glutaraldehyde, including the processing of full substance materials, heat ageing in comparison with chrome tanned leathers, and waterproofing. Based on the outline pre-tanning system given in Part 1 (*Panel 7*) formulations will be presented for the retannage of automotive and shoe upper leathers.

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