



“Formaldehyde-free leather” – a realistic objective?

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There is an increasing demand for “formaldehyde-free” leather. No legal regulation presently exists for this chemical in the EU, but in many areas of application the amount of formaldehyde contained in leather is limited by technical specifications or eco-labels^{1,2,3}.

Formaldehyde is used in large quantities as a starting material for the production of synthetic aromatic and resin-tanning agents. During the production of these compounds formaldehyde acts as a condensation agent, helping to develop larger molecules. The resulting condensation products have different levels of hydrolytic stability, so are potential sources of formaldehyde. In addition, some dyeing auxiliaries, fatliquors and finishing products are also able to release formaldehyde.

However, high quality leather requirements cannot be met unless a wide range of tanning and retanning agents, dyeing auxiliaries and fatliquors are used. It therefore appears necessary to develop a leather-producing technology that meets high quality demands and guarantees a minimal risk of formaldehyde release from the finished product.

Attempts to bind free and releasable formaldehyde in leather with scavenging compounds have been reported⁴ and the modification of some technological steps has also been investigated⁵.

However, another way to reduce the formaldehyde content of leather is to select the recipe components on the basis of their potential to release formaldehyde. Even so, an adequate analytical method to determine the free formaldehyde in tanning agents and auxiliaries had not been previously developed.

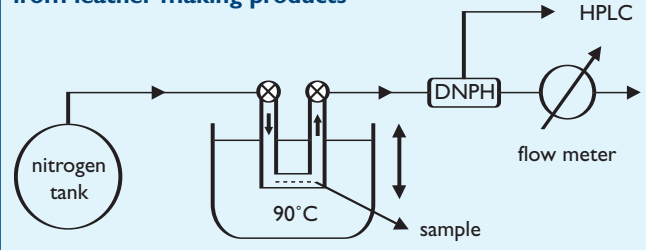
Within this investigation the development and validation of such a method was therefore essential. Furthermore, it was important to take into account that the interaction between chemicals and the leather matrix might generate synergistic effects. Also the ageing process of leather could involve formaldehyde release. Finally, several compounds needed testing regarding their suitability as formaldehyde scavengers.

A test method for the determination of free formaldehyde

On the basis of preparatory work within the TEGEWA-group¹⁵, a dynamic diffusion method (in-house LGR-method) was developed to determine free formaldehyde in products used in leather manufacture. This sampling mode ensures that no hydrolysis occurs.

In principle, the sample is placed in a U-tube and is heated to a temperature of 90°C using an oil bath for 30 minutes. Released free formaldehyde is swept continuously, with a stream of nitrogen gas, into a cartridge containing dinitrophenylhydrazine (DNPH), where it is collected. On completion, the formaldehyde is analysed by High Performance Liquid Chromatography (HPLC) as indicated in the schematic outline in Panel 1.

Panel 1: The release and collection of formaldehyde from leather making products



The development of this new procedure included the optimal sampling, and conditions for sample preparation, so determined:

- The most effective way to collect free formaldehyde from the sample (*static or dynamic*)
- The flow rate of the inert carrier gas
- The optimisation of the washing steps with inert gas
- The heating duration
- The heating temperature
- The optimal elution conditions of the formaldehyde-derivative from the collection cartridge
- The stability of the analyte on the collection medium and in the final measuring solution
- The formaldehyde content of all reagents and auxiliaries used in the method

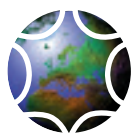
The statistical evaluations of both the sampling and analytical methods were performed in accordance with DIN 32625⁶, DIN 38402 part 51⁷, and specialised literature^{8,9,10}. The calibration used an external standard over the range 0.5-50 µg/10 ml. Initially, the calibration was made over the whole procedure, but trials showed this to be unfeasible in routine. In consequence, ready-prepared commercial formaldehyde hydrazone solutions were used.

The internal validation experiments were followed by external ones. Several inter-laboratory trials on solid and fluid samples helped to improve both the robustness of the procedure and the standard operating procedure.

Materials for assessment and scope of the investigation

The most important products used in upholstery leather manufacturing were tested and their content of free and, under the conditions of the method, releasable formaldehyde determined using the newly developed procedure¹¹.

Two recipes—for chrome and chrome-free tanning—that gave a certain formaldehyde content served as a basis for the scavenger investigations. This enabled a study of the potential of different inorganic and organic substances to bind the available formaldehyde in the leather matrix to be carried out. ➤



In each investigation, three different concentrations (1%, 2.5%, and 5%) of the potential scavenger were applied. To allow a comparison, leather produced by the same recipe, but without the final addition of a scavenger, was used. In addition, leather properties such as touch and appearance were also considered.

Starting with South Germany raw hides, wet blue and wet white were produced. After testing the auxiliaries and assessing their formaldehyde release potential, recipes for the production of crust were developed.

The resulting crusts and leathers were tested according to four different analytical procedures. Two extraction procedures (*draft DIN 53315 A and B¹²*) and two gas phase methods (*VDA¹⁶ 275¹³ and LGR-method*).

On the basis of the studies, two upholstery leathers (*chrome and chrome-free*) with the lowest formaldehyde content were chosen. Four artificial ageing test series with different conditions of temperature, relative humidity and time were performed. All samples were conditioned (23°C/50% Relative Humidity) immediately after the test for 48 hours and analysed according to the same analytical procedures.

Furthermore, two leathers (*chrome and chrome-free tanned*) with a somewhat high formaldehyde content were tested, at four-week intervals, according to these test procedures. During the whole period, the leathers were stored in well-defined conditions (23°C/50% relative humidity).

Determination of free formaldehyde in tannins and auxiliaries

Using the described technique, free formaldehyde was determined in more than 70 chemicals typically used for the production of upholstery leather (*Panel 2*). These values were based on the product as used in manufacture and not the dry weight as this reflects their use in practice.

Panel 2: Free formaldehyde in different product classes

Tanning and retanning agents	30	< 0.5 - 73
Fat-liquoring + waterproof agents	16	< 0.5 - 939
Preservatives	5	< 0.5 - 280
Dyes and dyeing auxiliaries	5	< 0.5 - 12
Beamhouse auxiliaries	5	< 0.5
Finishing materials	8	< 0.5 - 220
Other auxiliaries	6	< 0.5 - 51

Reliable quantification limit (RQL) 0.5 mg/kg product.

As expected, the findings show a large spread of results. It is noted that the formaldehyde content of a given product also varies from one container to another, and can alter during storage.

It was also found that the analytical method was inappropriate with tannins based on glutaraldehyde. Under the sampling conditions this aldehyde becomes volatile, reacts with DNPH, and exhausts the capacity of the cartridge (75 µg carbonyl compounds).

The production of formaldehyde-free leather

THE USE OF FORMALDEHYDE SCAVENGERS

The formaldehyde content in leather can be reduced by using selective reacting substances as scavenging agents in manufacture. The role of these products is well-known, and was confirmed

once more by the experiments performed.

For chrome tanned leather the following potential scavenging agents were tested:

- **Inorganic compounds and products:** Sodium dithionite, sodium perborate, sodium disulphite, and Auxiliary A
- **Organic compounds and products:** Melamine, dicyandiamide, mimosa, and Auxiliary B

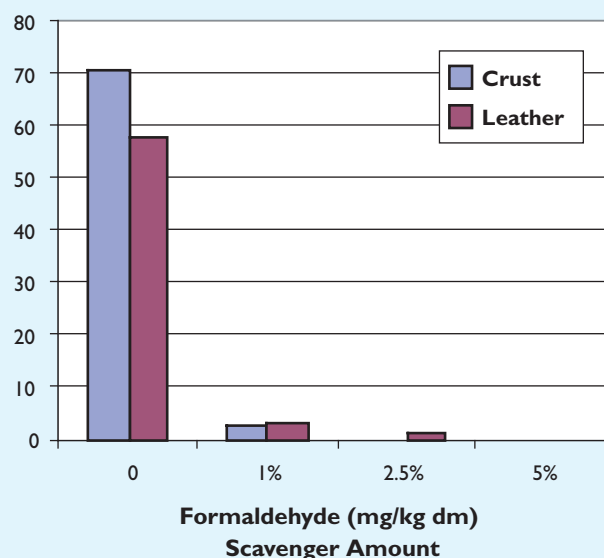
The findings from the use of three of these products is given in *Panels 3, 4 & 5*.

The scavenging efficiencies of all of the compounds can be compared very clearly, as shown in *Panel 6*.

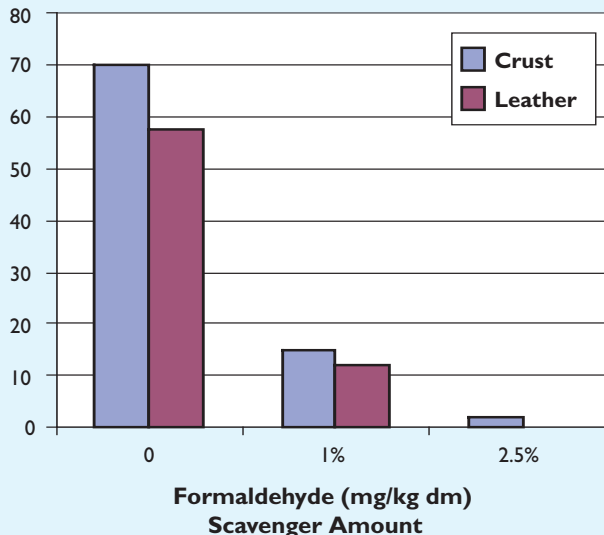
As expected, the oxidant sodium perborate produced a detectable amount of chromium(VI) and accordingly is inappropriate as a scavenging agent. This reaction did not occur when using the other agents.

Chrome tanned and chrome-free leathers were also evaluated

Panel 3: Inorganic compound: effect of sodium disulphite (chrome tanned leather)

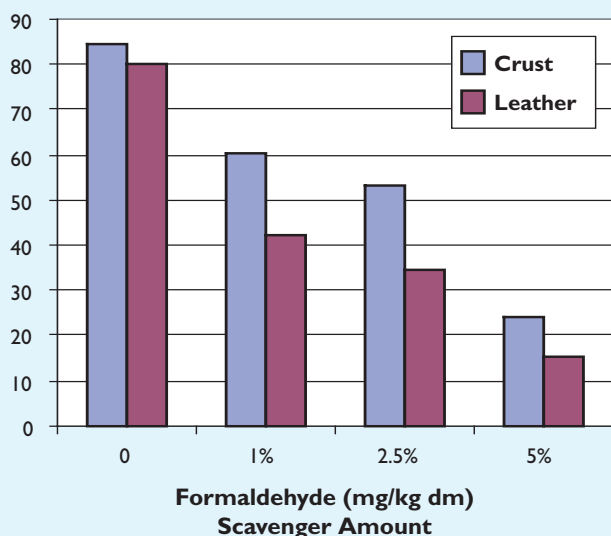


Panel 4: Inorganic compound: effect of Auxiliary A (chrome tanned leather)

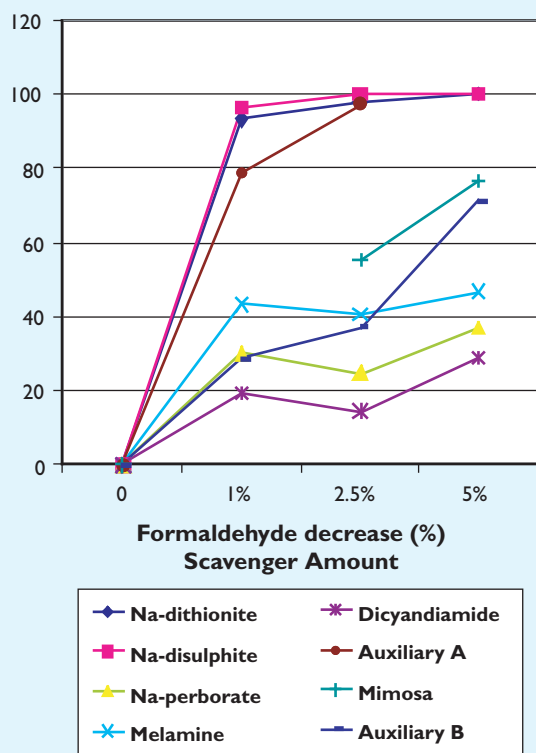




Panel 5: Organic compound: effect of Auxiliary B (chrome tanned leather)



Panel 6: Efficiency of the tested scavengers (VDA 275, chrome tannage)

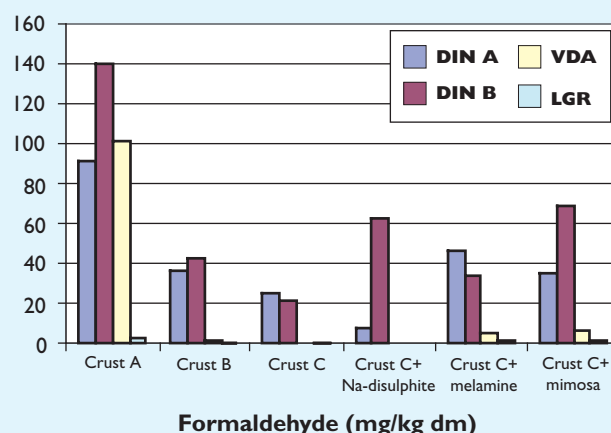


Deviations from the trend of decreasing formaldehyde content were attributed to analytical procedure. Other scattering of results is possible due to differences in thickness and structure between samples.

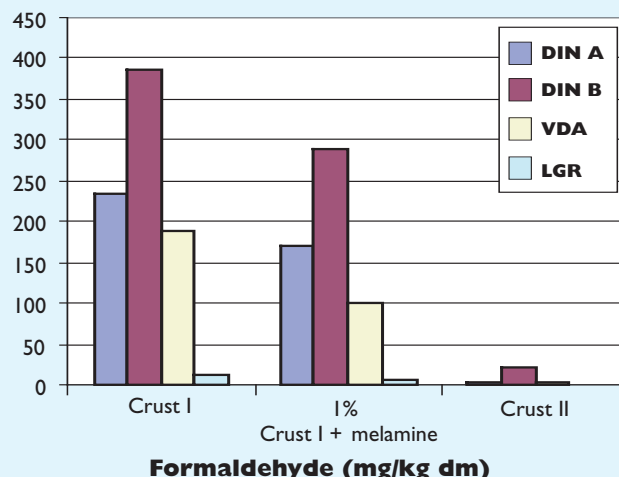
for their appearance and tactile properties. The following observations applied to both leathers:

- Melamine caused a significant deterioration in the handle of chrome-tanned leather.

Panel 7: Development of recipes for low formaldehyde release (chrome tannage)



Panel 8: Development of recipes for low formaldehyde release (chrome-free tannage)



- Several of the scavengers produced colour change upon dyeing. Sodium dithionite caused a change of hue from brown towards green, sodium perborate produced a darkening effect, and auxiliaries A and B gave rise to a slight lightening in colour.

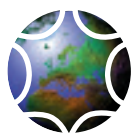
The influence of product selection

WITH REFERENCE TO THE FINDINGS GIVEN IN PANEL 7:

The production of crust leather (*Crust A*) to a known upholstery leather recipe resulted in a considerable increase in formaldehyde content when compared with the raw material as wet blue.

A considerable decrease in the formaldehyde content was achieved by replacing products identified as a source of formaldehyde by similar products but with low formaldehyde release (*Crust B*). However, repeat trials using the same recipe showed variations in formaldehyde release of up to 40% when using extraction procedures DIN 53315 A & B.

After removing all sources of formaldehyde from the recipe, the free formaldehyde of the resulting crust (*Crust C*) was reduced to less than the reliable quantification limit of the two gas phase methods (*VDA 275* and *LGR*). However, part-hydrolytic formaldehyde as determined by DIN 53315 ►



A & B persisted.

Trials to further reduce part-hydrolytic formaldehyde failed. The addition of scavengers caused a considerable increase of the analyte.

For developments based on the chrome-free leather recipe, similar results were obtained as shown in *Panel 8*. Product selection proved to be more effective than the use of formaldehyde scavengers. Even so, the selection of low-formaldehyde products could not fully reduce the hydrolysable formaldehyde in resulting leathers.

At this stage it can be stated that:

- Scavengers proved to be very effective when used with leathers with relatively high formaldehyde values (VDA 275) stemming from the auxiliaries. However, they did not cause a further decrease with auxiliaries that yielded low values of free formaldehyde.
- There is no simple mathematical relationship between the free formaldehyde content of the used leather auxiliaries and that of the ensuing leather. This indicates an existence of synergistic effects.

The influence of ageing

THE EFFECTS OF ARTIFICIAL AGEING

In order to reveal what happens regarding the formaldehyde content during use, two leathers with low formaldehyde content were exposed to artificial ageing. These leathers were from each tanning method, using ageing conditions according to draft IUF 412 14, and shown in *Panel 9*.

The formaldehyde content of the examined upholstery leathers

Panel 9: Artificial ageing parameters

V1	50	38	24	96	168	48
V2	90	38	24	96	168	48
V3	50	50	24	96	168	
V4	90	50	24	96	168	

Panel 10: Results of artificial ageing experiments on chrome tanned leather

V1	14.92	5.34	11.10	3.76
V2	15.48	3.81	10.83	2.95
V3	10.44	2.68	8.80	2.12
V4	10.98	3.39	6.53	2.40

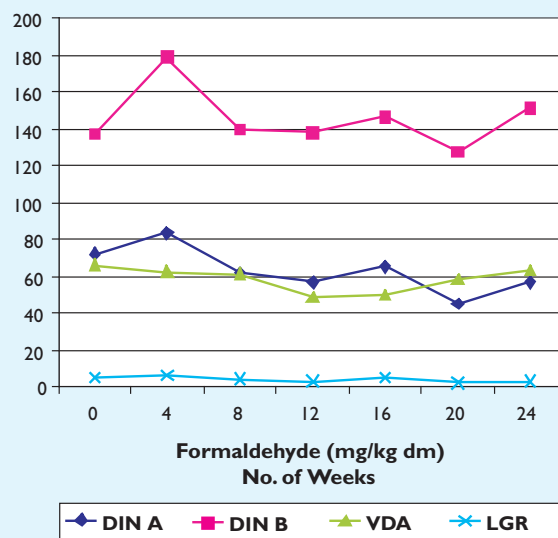
Formaldehyde content according to DIN 53 315
A: 15.86 mg/kg; VDA 275: 5.50 mg/kg

Panel 11: Results of artificial ageing experiments on chrome-free leather

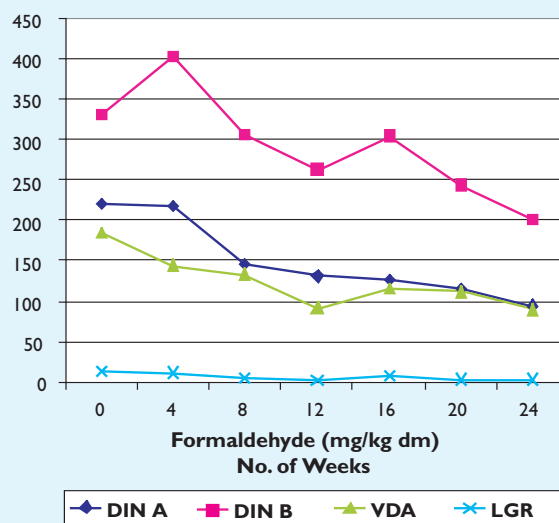
V1	17.12	2.56	16.71	2.63
V2	23.81	1.32	22.35	1.48
V3	17.77	1.75	15.60	1.41
V4	16.32	1.48	21.52	1.39

Formaldehyde content according to DIN 53 315
A: 17.12 mg/kg; VDA 275: 0.97 mg/kg

Panel 12: Chrome tanned leather: Variation of formaldehyde content during storage



Panel 13: Chrome free leather: variation of formaldehyde content during storage



was determined according to DIN 53315 A and VDA 275, and the results are given as *Panels 10 & 11*.

This indicates that—for the tested recipes, at least, and under the applied conditions of humid heat—the formaldehyde release potential of recipe components does not increase.

THE EFFECTS OF STORAGE

The effect of storage was investigated using two leathers with relatively high formaldehyde content. The formaldehyde values of these leathers showed slight variations during the testing time period, but no noteworthy increase. In the case of chrome-free leather there was an obvious tendency for the formaldehyde content to diminish. These results are shown in *Panels 12 & 13*.

Conclusions

The results of the investigations may be summarised as follows:

- The analytical procedure for the determination of free



formaldehyde in products used in leather manufacturing provides reproducible results.

- The method can identify formaldehyde sources within the recipe.
- By selecting recipe chemicals on the basis of free formaldehyde content determined with the LGR-method leathers with considerably low formaldehyde contents were produced.
- However, the part hydrolytic-releasable formaldehyde could not be completely eliminated.
- In addition, synergistic effects in the leather matrix exist.
- The efficiency of formaldehyde-scavengers is also dependent upon the initial formaldehyde content of the leather.
- The artificial ageing of leathers with a low formaldehyde content caused no significant increase of the measurable formaldehyde.
- The analysis of leathers with a relatively high formaldehyde content stored in standard climate conditions over a period of six months did not find any significant increase of the analyte. 

References:

1. Wood, B.: *Is the level of environmental testing for leather necessary?*, *Leather*, April 2001, p. 98.
2. Lampard, G.: *Formaldehyde – the final straw?*, *Leather International*, November 2001, p. 65.
3. Cory, N. J.: *An update on environmental constraints*, *JALCA*, 97, 2002, p. 496.
4. Allsop, T. F.: *Scavenging of analysable formaldehyde in woolskins tanned with phosphonium compounds*, *Proceedings XXVI IULTCS-Congress, Cape Town, 2001, 07.03.01 – Session 2*.
5. Wolf, G., Hueffner, S. und Pabst, G.: *Bildung von Formaldehyd im Leder - Ursachen und Vermeidung*, *Leder- & Häutemarkt*, 9-2002, p. 25.
6. DIN 32 625: *Nachweis-, Erfassungs- und Bestimmungsgrenze* (1994).
7. DIN 38 402, Teil 51: *Kalibrierung von Analysenverfahren* (1986).
8. Funk, W., Damann, V. and Donnevert, G.: *Qualitätssicherung in der Analytischen Chemie*, VCH Verlagsgesellschaft, Weinheim, 1992.
9. Doerffel, K.: *Statistik in der analytischen Chemie*, VEB Deutscher Verlag für Grundstoffindustrie, 1966.
10. DIN 38 402, Teil 42: *Auswertung von Ringversuchen* (1984).
11. LGR-intern SOP: *Determination of free formaldehyde content of leather auxiliaries*.
12. DIN 53 315, draft: *Bestimmung des Formaldehydgehaltes in Leder* (1996).
13. VDA 275: *Bestimmung der Formaldehydabgabe – Messverfahren nach der modifizierten Flaschen-Methode* (1994).
14. IUF 412, draft: *Fastness tests – Change in colour with accelerated aging*, (2002).
15. *Abbreviation for the association of producers of chemicals for the manufacturing of textiles, leather, paper, detergents, auxiliaries for cosmetics and for pharma-products*.
16. *Abbreviation for the association of the automotive industry* (Verband der Automobilindustrie).