



Preserving agents in the leather production process

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Due to extended times in transport and storage, leathers in the wet blue and wet white condition need protection against bacterial and fungal contamination. This is provided by synthetic preserving agents. However, triggered by new regulations, these agents and their use in the leather production process have become the focus of a number of chemical safety and consumer health issues.

This paper provides an overview of basic leather preservation, the most common ingredients, and the current situation regarding use of these products.

Microbiological action on leather and its precursors: aspects to consider

The most obvious reason to stop microbiological degradation of leather, is the fact that leather articles are expected to be durable under normal conditions of use and storage. If such conditions exclude an excessive amount of moisture, the tannage itself is capable of fulfilling this demand and no added preserving agent should be necessary in the finished leather.

Lately, a number of leather processing industries have started to request more than this. On one side, some upholstery applications would like to distinguish themselves, offering protection of the leather even under unlikely usage conditions. On the other side, some shoe and garment applications want to go even further, and in addition protect the consumers skin by agents included into the leather. In both cases, the advantages have to be carefully weighted against the potential side effects.

Bacteria as well as fungi prefer to settle on the well accessible portions of the hide and/or skin, nourishing on the collagen. This can result in directly visible damage such as a destroyed grain structure, or in more indirect effects like veininess, looseness, or uneven dyestuff affinity. And for the leather producing industry, the question of microbiological damage of the intermediates is as important, since it can greatly effect the quality of the leather. These actions may all lead to a down-

grading of the finished leather and a loss in value.

Last but not least, there are the direct health effects of the microorganisms. Fungal spores are among the most prominent allergens known today. Some mould species are pathogenic themselves, that is dangerous to human health, because they can produce strong toxins. This is not only a problem for workplace safety at the tannery, but also for consumer protection. Even if the superficial mould is completely removed during processing, spores and toxins can remain within the leather structure and will survive even harsh treatment conditions.

Any single one of those aspects is reason enough to avoid a situation as shown in *Panel 1*:

Leather production and preservation requirements

The requirements for leather production can be divided into two sections

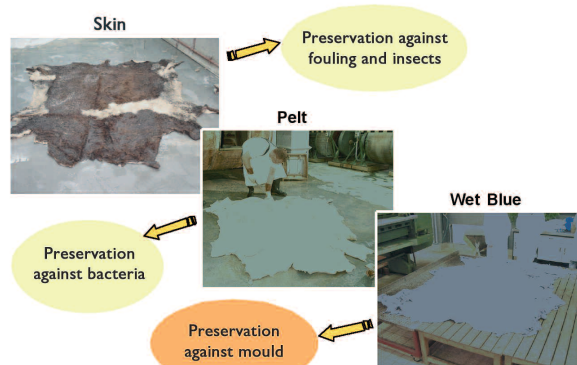
1) LEATHER PRODUCTION: HIDE/SKIN TO WET BLUE

The role of preservatives is illustrated in *Panel 2*:

Panel 1: Wet blue with bacterial and fungal contamination



Panel 2: Preservation needs: rawskins to wetblue



Today, in most regions of the world, the production of leather is an industrial process. The output of local slaughter houses cannot fulfil the demand of normal size tanneries for raw materials. Therefore, even before starting the tanning process, the hides and/or skins have to be protected against rotting and insect attack during storage and transport. For short time-periods this



can be achieved by cooling, but the most common method is to apply about 30% of common salt (*sodium chloride*) on hide weight, sometimes spiked with some insecticide and/or bactericide.

This salt and other agents have to be removed before the tannage can start, together with all the dirt attached to the hides, using detergents and water. However, the soaking process, with its neutral pH and slightly elevated temperatures, offers ideal growth conditions for bacteria. The hide may be thus damaged within hours, so bactericides are employed to prevent this. Apart from questions of workplace safety, such products are of no concern to the consumer. The active agents can be selected so that they will be completely and reliably destroyed through the subsequent steps of leather production.

After removal of the hair - under conditions which by themselves are sterilising - the pelt is acidified during the tanning, thereby shifting into the pH range of fungal activity. Chrome tanned "wet blue" and free of chrome "wet white" intermediates then are stored and shipped all over the world. The moisture content of these leathers is about 50%, so resistance against mould attack is required for weeks or months.

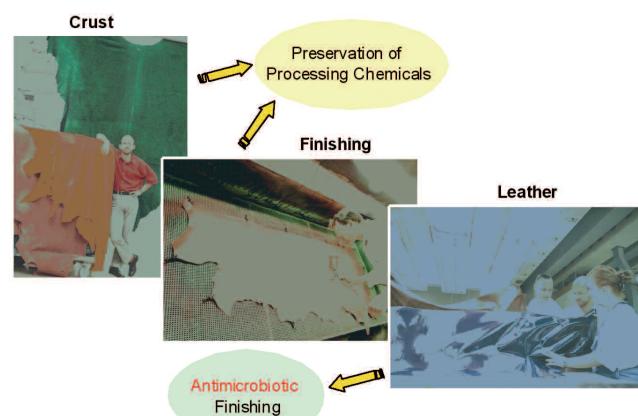
This is the most crucial step of leather production regarding preservation needs due to the long storage periods, high moisture content and convenient pH-value for microbiological attack. Although at the typical pH of about pH 4 fungal growth should be predominant, cases have been reported in which bacteria as well as fungi have been found on wet blue. This is shown in *Panel 1* as red spots of bacterial growth.

This can happen due to sub-optimum process conditions, for example, an elevated surface pH, or if the metabolism of one microorganism changes the environment to become more advantageous for another species.

2) LEATHER PRODUCTION: CRUST TO FINISHED LEATHER

The role of preservatives is illustrated in *Panel 3*:

Panel 3: Preservative needs: crust to finished leather



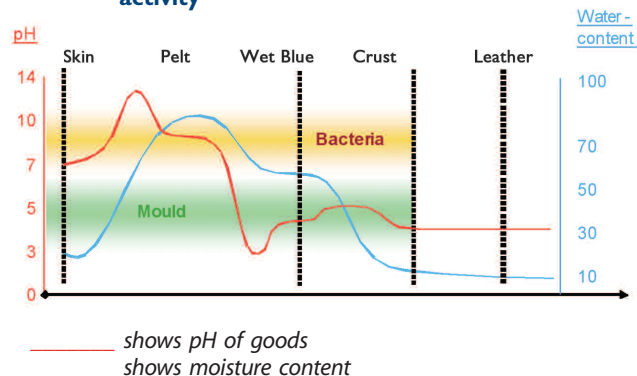
After the wet blue or wet white have returned to the drum for retanning, the focus for preservation turns towards the process chemicals which are used to complete the leather production. Due to their chemical structure, retanning polymers, fatliquors or finishing binders are generally less susceptible to microbiological decomposition than collagen. But supply chain considerations require them to be stable for at least six-months and up to two years.

If transport chemical containers are (*semi*-)transparent, growth of algae has to be considered: this demands a different formulation of the "in-can" preservative package.

Combined with the fact that the process chemicals are only used in the percentage range based on the leather weight (*or even less*), this is the reason why such preservatives should only play a minor role when evaluating the properties of a finished leather. The addition of antimicrobial finishes to the leather article is limited to a small number of applications and are not discussed in this paper. ^[Legend 1]

The conditions during leather processing and the microorganism activity are summarized in *Panel 4*, where it is shown that microorganisms can become active whenever the pH (*red line*) is in their respective window, and the water content (*blue line*) above 20%.

Panel 4: Process parameters and micro-organism activity



Fungal growth prevention is the most crucial aspect during the production, if leather intermediates (*wet blue / wet white*) is not processed immediately but shipped and/or stored.

Fungicides and their mode of action

Compared to the loss in value associated with damage, the cost of fungicidal treatment is relatively low. Within the chemicals for

Panel 5: Process parameters and micro-organism activity

Market Share	Thiocyanomethylthiobenzothiazole (TCMTB)
	o-Phenylphenol (OPP)
	p-Chloro-m-cresole (PCMC)
	n-Octylisothiazolinone (OIT)
	Methylen-bis-thiocyanate (MBT)
	Carbendazim (BCM)
	Diodomethyltolylsulfone (DIMTS)



the wet end, however, fungicides are among the most highly priced ones on a per kg base. This cost element, combined with the fact that use in leather production often involves uncommon conditions for biocide application requiring a lot of application research and formulation development, means there are only a very limited number of active substances available in Europe. The most common products are listed in *Panel 5*.

Unfortunately, none of these molecules give a uniform protection against all families of fungi commonly found in a tannery environment. The combination of biocides is a state of the art process. Moreover, blending suitable actives together into one single product is subject to limitations. This is based on substance stability and mode of action, to which respect the fungicides can be broadly divided into two groups:

1) BIOCIDES MECHANISM: ELECTROPHILIC REACTIVE

The following products are employed for protection during soaking and tanning:

For soaking: Carbamates, Benzisothiazolinon (BIT)

For tanning: TCMTB, Isothiazolinones, MBT

These agents are characterised by irreversible chemical reaction

of the electrophilic actives with nucleophilic centers within the microbes cell, and with other nucleophilic agents (*eg. process chemicals*). Nucleophilic reaction partners within the cell can be amino- or thio-groups of amino acids, protein, or DNA. This has the following consequences:

- Actives are consumed by chemical reaction. Long term protection effect can vary.
- High acute toxicity (*Classification T or T+*), high requirements to workplace safety (*see Panel 7*).
- Typically recommended offer about 500 ppm (*wet blue*).
- Addition to the tanning preferably towards the end of the process to minimize decomposition.

2) BIOCIDES MECHANISM: MEMBRANE ACTIVE

The following products are employed for protection:

For tanning: OPP, PCMC

These products are characterised by reversible, physical adsorption of the active molecules to the outer cell membrane, and subsequent penetration and interaction with the cytoplasmic-membrane. This causes interruption of nutrients transport, damage to inner cell membrane, leading to death of the mould cell.



The actives of these agents are re-liberated after cell destruction, so consequently:

- The actives are not consumed. Provides constant long term effect.
- Low acute toxicity (*classification Xn or Xi*).
- Authorisation for use in cosmetics, food packages etc.
- Typically recommended offer for wet blue about 1200 ppm.
- Addition to the tannage preferably towards the start of the process for better distribution and uptake.

The majority of the active substances of both of these two groups have been extensively reviewed, by the suppliers and/or independent institutions (*Lederinstitut Gerberschule Reutlingen*). The focus of those reviews lay on the evaluation of the performance during the intermediate state. ^[Legend 2] Lately this has shifted to give a higher priority to the amount of fungicide that can be found in the finished leathers. Values (*ie. mg fungicide per kg of finished leather*) from literature resulting from an adequate protection of the intermediates are listed in *Panel 6*:

Panel 6: Amount of preserving agent required in leather (results from adequate protection of intermediates)

Active	Experience	Published	Reference
TCMTB	0 - 800	480; 630;	1, 2
OPP	200 - 1200	330; 660; 1170; 650;	1, 2, 3, 3
PCMC	300 - 1200	490; 950; 790;	1, 2, 3
OIT	0 - 400	140;	1

1. Emission of Fungicide from furniture leather : C. Hauber, E. Hurlow; JSLTC; **2005**; 210 - 213.
2. Leather Preservation - the current Situation in Europe : O. Kretschick; LGR Infotagung; **2005**
3. Kurzstudie zum Emissionsverhalten von Fungiziden in chromfreien M obelledern; C. Hauber; FGL e. V. (Hrsg.); **2006**.

In general, it can be noted that free of chrome "wet white" leathers require a higher amount of preservation to achieve the same stability as chrome tanned leathers. Among the wet white processes, an extensive study conducted at the Lederinstitut Gerberschule Reutlingen^[Legend 3 and 4] showed, that leathers pretanned using tetrahydroxymethylphosphonium sulfate (*THPS*) were most difficult to stabilize against fungal attack.

Due to their mode of action, the concentration of substances from the "electrophilic, reactive" mechanism group found in the leather can vary over a wide range - even within one production batch. Accordingly, the recommended offer has to be higher than strictly necessary for immediate activity if long term protection is required.

Product formulations and classification

No products are sold with 100% active ingredients. For reasons of stability, solubility, or handling formulations are prepared with concentrations ranging from 20 to 50 % of actives.

Some detailed information can be found in Chapter 3 of the material safety data sheet (MSDS) "information on composition". Since all substances are classified as more or less hazardous this will lead to a labelling of the product if contained in any useful concentration. The classifications in detail are given in *Panel 7*:

Panel 7: Summary of classification and labelling requirements

Active	Classification	Risk Phrases
TCMTB	T ⁺ , N	R: 22-26-36/38-43-50/53
OPP	Xi, N	R: 36/37/38 -50
PCMC	Xn, N	R: 21/22 -41-43-50
OIT	T, N	R: 22-23/24-34-43-50/53
MBT	T ⁺ , N	R: 25-26-34-43-50
BCM	T, N	R: 46-60-61 -50/53

Classification letters: Risk Phrases:

<i>Xi</i> : Irritant	<i>R</i> 21: harmful at skin contact
<i>Xn</i> : Harmful	<i>R</i> 22: harmful when swallowed
<i>T</i> : Toxic	<i>R</i> 23: toxic when inhaled
<i>T+</i> : Very toxic	<i>R</i> 24: toxic at skin contact
<i>N</i> : Harmful to the environment	<i>R</i> 25: toxic when swallowed
	<i>R</i> 26: very toxic when inhaled
	<i>R</i> 34: causes burns
	<i>R</i> 36: irritating for the eyes
	<i>R</i> 37: irritating for the respiratory tract
	<i>R</i> 38: irritating for the skin
	<i>R</i> 43: sensibilisation possible via skin contact
	<i>R</i> 46: may cause heritable genetic damage
	<i>R</i> 50: very toxic for aquatic organisms
	<i>R</i> 53: may cause long-term adverse effects in the aquatic environment
	<i>R</i> 60: may impair fertility
	<i>R</i> 61: may cause harm to the unborn child

BCM or Carbendazim has only recently been evaluated as mutagenic and reprotoxic. For this reason it has been listed for new classification under the 29th revision of the European directive for classification, labelling and packaging of dangerous substances (ATP 29).

Existing regulations and limitations to the use of certain biocides

In 1998 the European Union passed directive 98/8/EC known as the Biocidal Product Directive (BPD). Under the BPD, every active substance of a biocide formulation has to be evaluated for its performance and side effects in any of the applications it is recommended for.

After preregistration, priority lists have been formed to define deadlines until when a completed dossier has to be delivered to the European authorities. If an organisation had to start without any information, the costs for toxicological testing and evaluation of the test results will easily sum up to several million Euro per substance.



In case of leather preservatives, the deadline will be October 2008, when a complete dossier must be filed to the authorities. All the major active ingredients have been preregistered for the use in "fibres, leather, rubber and polymers" grouped in PT 09. (> PT = "Product Type") and given in Panel 8:

Panel 8: Overview on PT 09 pre-registration (and some selected additional application areas)

Pre-Registration:	TCMTB	OPP	CMK	OIT	MBT	BCM
PT 09 fibre, leather, rubber, polymers	—	—	—	—	—	—
PT 06 in-can conservation	—	—	—	—	—	—
PT 01 human hygiene products	—	—	—	—	—	—
PT 02 private and public health area	—	—	—	—	—	—
PT 03 veterinary area	—	—	—	—	—	—
PT 04 food and feed area	—	—	—	—	—	—

Products will only remain marketable in Europe after the deadline if a complete dossier is delivered in time. While this seems to be a reasonable safe assumption to make for the "big four" in the list of active ingredients, there is some doubt related to BCM.

Self regulation

Regarding voluntary self restrictions, the - "Blue Angel" RAL UZ 117: Low emission upholstered furniture - has played an important part in many discussions regarding leather preservation during the last few years^[Legend 5]. The German "Umweltbundesamt" (UBA) - author of the "blue angel" environmental mark - argues that:

"according to the consumer protection act, no consumer must be put at risk by any article, and especially not by any toxic component or impurity within".

In case of leather preservation, this puts the burden of proof on the shoulders of the article producer or his chemicals supplier. They need to show that any preservative labelled as hazardous in its pure form will not put the consumer at risk when used for the production of leather in a suitable way (or at least will have a positive performance/side effect ratio, if no better alternative is available).

For the phenolic ingredients OPP (classified "irritant", Xi) and PCMC (classified "harmful", Xn) this has already been shown when the label was installed in 2004, also the reactive NOIT (classified "toxic", T). However, based on the sparseness of data regarding emissions of those substances from leather, the UBA set thresholds for their use that made complying to the environmental sign difficult at best.

Extensive additional investigations followed, and in 2007 the requirements were reviewed. Accordingly, the threshold for the fungicides already permitted have been increased to a more workable level. In addition, the reactive TCMTB (classified "very toxic", T+) has been added to the list based on its good fixation to the leather matrix and low volatility. The thresholds now can be summarized as given in Panel 9:

Other substances classified as T or T+ must not be used during production as defined in the general specifications of the RAL UZ 117. Although not mentioned explicitly in the list of products that should be avoided (because no validated analytical method has been presented), this includes BCM and MBT. A declaration of

Panel 9: "Blue angel" RAL UZ 117: Low emission upholstered furniture

Preserving agents must only be used for intermediates protection for transport and storage.

The following threshold values apply for the finished leathers:

PCMC	<	600 mg / kg *
OIT	<	250 mg / kg *
OPP	<	1000 mg / kg *
TCMTB	<	500 mg / kg

The following actives must not be present. Thresholds of detection are:

MBT	<	5 mg / kg
Polychlorinated phenols	<	1 mg / kg e. g. PCP, TCP
Polybrominated phenols	<	1 mg / kg e. g. Tribromo phen

(* PCMC 300 – 600 mg/kg, OPP 500 – 1000 mg/kg, OIT 100 – 250: contro emission)

compliance has to be given by the leather producer.

With the review of the threshold values, the quality sign -

"Golden M", RAL GZ 430: Upholstered furniture

- authored by the "German federation for quality furniture" (Deutsche Gütegemeinschaft Möbel DGM) has adopted the same requirements on preserving agents starting January 2008.

Based on judgements by the German governments institute for environmental protection (UBA), if certain thresholds are complied with, even if the consumer is exposed to direct skin contact as with furniture upholstery, the following products can be safely used for the production of leather:

- TCMTB
- OPP
- PCMC
- OIT

Changes in regulations

The California Safe Drinking Water and Toxic Enforcement Act - a local regulation often referred to as "Proposition 65" - in 1998 listed OPP to be a substance which presence has to be labelled on articles and goods it is used for, for example, for the protection of citrus fruits. However, in 2002 a very conservative "No Significant Risk Level" was proposed by industry at a daily uptake of 170 microgram: no labelling is necessary if this threshold can be guaranteed. Various investigations have proven this to be the case for a potential exposure via OPP in leather.

With the listing on "Proposition 65", the Öko-Tex Standard 100 for textiles had declared OPP as a singled-out unwanted substance. Again in 2002, acknowledging the no significant risk level, and the facts that even textile auxiliaries have to receive an "in-can" preservation, OPP is among the best actives regarding performance/side effect ratio. Accordingly, the Öko-Tex Standard was modified to permit up to 100 ppm of OPP (based on textile weight), which is sufficient to cover for left-over traces from the in-can preservation.

One major sport shoe producer included these textile standard values into his internal quality requirement for leather. Given the latest development on the RAL UZ 117, and the reasoning behind the existing thresholds, it can be hoped threshold values



for leather articles may be implemented in the future which are suitable for the protection of the leather matrix, and not only for "in-can" preservation residues.

PCMC is widely used for a variety of different applications besides leather whenever a product with low acute toxicity and excellent performance and no side effects are needed. However, based on its chemical nature, it can contribute to the adsorbable organic halogens (AOX) value in the waste water. If local waste water regulations exclude the presence of such substances, its use has to be avoided or the waste water subjected to a suitable processing before being disposed of. Since phenolic ingredients like PCMC are readily biodegradable at neutral pH, this can be eliminated, for example, in a biological waste water treatment step.

Summary of information

- Given the globalised nature of industrial leather production, the use of preserving agents to protect the intermediates cannot be avoided.
- There are suitable products available and state of the art processes to use them which exclude any risk to the customer. This applies even if the preserving agent remains partially in the leather of the consumer article.
- Product formulations and application processes are under continuing development. However, completely new active ingredients are not to be expected in the near future.
- New voluntary self restrictions within the leather processing

industry or by consumer groups should be checked beforehand for practicability. Help is needed by these respective suppliers or competent consultants.

Acknowledgements:

Dr. Oliver Kretschik and Mr. Hartmut Rehbein for help on technical questions and in the preparation of the manuscript, and Dr. Gerd-Friedrich Renner and Dr. Klaus Stroeck for valuable input.

Legend

- 1) Information is given in the paper *Microbiological testing of leather*, M. Wuertz, *World Leather*, 2006, 31- 32.
- 2) *Studies of fungicide application in chrome tannage and its distribution in wet blue*, C. Hauber, H-P. Germann; *Das Leder*, 1996, 189 - 195).
- 3) *The resistance of wet-white pre-tanning systems to mould growth when supported by various fungicides*, C. Hauber, H-P. Germann: *World Leather*, 2006, 31 – 32.
- 4) *Wet-White Verfahren unter der Lupe*, C. Hauber, H-P. Germann: *Leder & Häute Markt*, 2006, 20 - 22).
- 5) The RAL-UZ *** "Blue Angel" environmental label gives manufacturers and retailers an opportunity to clearly, simply and credibly label low-emission, environmentally friendly products. By using this widely recognized environmental label, businesses can significantly and lastingly enhance the competitive potential of their products. In the context "Blue Angel" RAL UZ 117: Low emission upholstered furniture, RAL is a norming organisation similar to DIN, UZ an abbreviation of "Umwelt-Zeichen", an environmental sign/label, 117 the category number.
- 6) It should be noted that the information in this article is given in good faith but without warranty and may be not exhaustive.