Research Project

Preservatives in Leather Production

In a cooperative research programme under the leadership of the German Leather Research Accociation (Forschungsgemeinschaft Leder e.V.), the Test and Research Institute Pirmasens (Prüf- und Forschungsinstitut Pirmasens e.V., PFI) and the Research Institute of Leather and Plastic Sheeting (Forschungsinstitut für Leder und Kunststoffbahnen, FILK) have completed a research project entitled «Studies on the Sustainable Use of Antimycotic Agents in Leather Production». The IGF project (18368 BG) was funded by the German Federal Ministry of Economics and Energy (BMWi) through the German Federation of Industrial Research Associations (AiF) within the IGF programme for promoting industrial cooperative research and development.

Background

Owing to a highly fragmented process chain, leathers and semi-finished leathers are frequently kept in storage for several months or transported all around the globe. Semi-finished goods, leather, and leather products often have to be transported over wide distances and through various climatic zones. Temperature and humidity fluctuations, condensation phenomena on packaged goods during transport, and storage over prolonged periods all mean that not only semi-finished products but also leather and leather goods can develop mould. The use and making available on the market of biocides in Europe are subject to the currently valid Biocides Regulation (EC 528/2012). The principal objectives of the Biocides Regulation are first of all to reduce the application concentration of the active agents and secondarily not to permit the general approval of biocides but to make approval dependent upon product groups and areas of application. Assessment and approval of commercially available preservatives have yet to be concluded. Depending upon the nature of the product, different transition periods apply for preservatives currently on the market.

Table 1: Typical leather preservatives

Abbreviation	Name	CAS No.
TCMTB	• Thiocyanomethylthiobenzothiazole • (Benzothiazol-2-ylthio)methyl thiocyanate	21564-17-0
CMK	• 4-Chloro-3-methylphenol • Chlorocresol • PCMC	59-50-7
OPP	• ortho-Phenylphenol • 2-Phenylphenol	90-43-7
OIT	• 2-Octylisothiazolone	26530-20-1

Treatment of moist semi-finished products with a number of preservatives to prevent mould infestation is permissible. Nevertheless, mould fungi still repeatedly cause damage and in many cases the material affected is no longer suitable for further processing to leather. In contrast to moist semi-fished goods, finished leathers are dry and hence less susceptible to attack by mould. However, if leather becomes wet during transport or storage it can also develop mould. In such cases total loss of the goods may result because it is not always possible to refurbish mouldy leather. This leads to huge annual economic losses. Use of increased amounts of preservatives already during in tanning process with the goal of assuring subsequent leather preservation is not permissible. In addition, subsequent treatment of leather and leather products with biocides as protection against mould infestation is regulated by the Biocides Regulation. If, for example, finished leathers are treated with preservatives or if leather samples are found to contain large amounts of preservatives presumably originating from the production process, then these leathers must be designated accordingly.

It is important for importers and shippers of leather and leather articles to be aware of the kinds of climatic conditions under which finished leather goods become susceptible to mould infestation for any assessment and selection of appropriate measures. Transport through different climate zones in overseas containers is of particular importance in this respect. Various transport conditions were therefore simulated in the research project and the leathers conditioned in that way examined to establish the content of preservatives and susceptibility to attack by mould fungi. These laboratory simulations provided preliminary information permitting a risk-orientated appraisal of measures suitable for protection of leather during transport.

Objectives of the Research Project

- Semi-finished goods require optimum protection against mould. Minimum concentrations of the investigated biocides should therefore be established in the project.
- In the interests of the end user, leather should not be contaminated with biocides. To this end, the climatic condition under which leather becomes vulnerable to mould infestation should be established in this project.
- Biocides found in leather as a consequence of the preservation of semi-finished goods may be hazardous to human health. Release of biocides from leather on skin contact should be determined in order to assess possible consumer exposure.

Experimental

FILK produced semi-finished materials (Wet Blue, Wet White) and corresponding crust leathers with various mixtures of the preservatives TCMTB, OIT, CMK, and OPP. The preservative contents of the semi-finished goods and crust leathers were determined at different sampling times, both without storage and after four weeks' storage, under simulated climate conditions (storage at 20 °C and 40 °C and 95 % relative humidity in a climate cabinet).

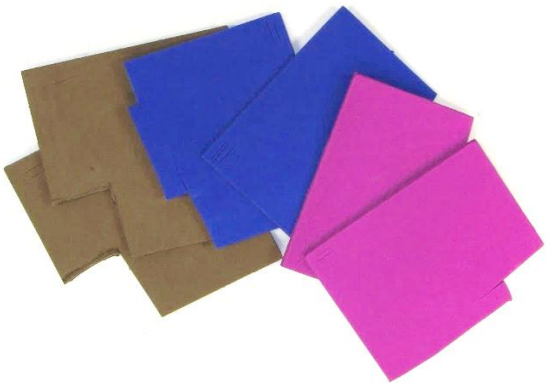

Figure 1: Crust leathers produced for and investigated in the project

Influence of Storage

The climate prevailing during transport and storage affects not only fungal growth in the semi-finished goods but also the migration behaviour and evaporation of the preservatives and thus the mould resistance of the semi-finished goods. The results of the four-week storage test at 20 °C or 40 °C demonstrate the enormous influence of storage and transport conditions on the biocide contents of the semi-finished goods and thus on their mould resistance. Moderate temperatures higher than 20 °C over a period of four weeks were sufficient to reduce the contents of the semi-volatile biocides CMK and OPP by up to an average of 40 %. Storage temperatures of 40 °C over four weeks led to evaporation of, on average, between 80 % and 90 % of the preservative (except OIT) from the semi-finished goods and there was no longer any protection against mould infestation. Owing to the wide range of variation of the preservative contents determined in the semi-finished goods and in view of the effects of climate during their storage and transport it is only possible to derive guideline values. The concluding report will provide a detailed account of the effect of climate on the retention of residual preservatives from the preservation process.

About 50 % of the preservatives used were lost during further processing of the semi-finished goods to crust leather. Four weeks' storage of the crust leather under controlled climatic conditions resulted in a further biocide loss of 40 % to 70 %. In contrast to the semi-finished materials, the average drop in preservative content of the crust leathers was only slightly greater at 40°C than that at 20 °C. The temperature did not have any decisive influence on biocide migration during the storage of crust leathers as against the storage of semi-finished products.

Influence of Time of Addition and Distribution

The distribution of preservatives in a semi-finished hide and the influence of the time of addition of the preservatives were examined in further experiments. The time of addition of the preservative was found to have a pronounced effect on the concentration of preservative attained in the semi-finished product at any given time. The highest concentration of preservative could be measured on addition of preservative at the pickling stage and after addition of tanning agent. Determination of the preservative concentration at different sampling points of the hide confirms the influence of the fat content and the texture of the semi-finished material on the uptake of the preserving agent.

Mould Resistance

The mould resistance of each semi-finished product and each crust leather was checked for each climatisation level. During the experiments the extreme difficulty of determining the minimum concentration of preservative necessary for protection of semi-finished materials during storage and transport became apparent. It proved impossible to attain a specific concentration of active agent necessary to protect the semi-finished goods against mould on addition of a defined amount of preservative. In spite of constant experimental parameters and multiple repeat experiments, the measured preservative concentrations showed considerable scatter, particularly in the case of semi-finished chrome leather. Although process preservation of semi-finished leathers is viewed as the sole desirable approach, it was nevertheless important to keep track of the whereabouts of residual preservatives in leather and leather products, which may vary depending upon the high temperatures and high humidity that can occur during transport and storage. Investigations of the influence of climate during the storage of crust leathers showed the temperature to have a negligible influence on migration of the preservative. The decrease in biocide concentration of between 40 % and 70% could be ascribed to the humidity. OIT migrated hardly at all in leather during storage. Studies on the mould resistance of crust leathers showed that in spite of high residual contents of biocides (partly in excess of 1000 mg/kg) protection against

mould was still incomplete. The risk of mould infestation increased with increasing atmospheric humidity and the resulting moisture in the leather.

Customary Industry Limit Values

In some cases over half of the preservatives were lost during the production of crust leathers from preservative-treated semi-fished materials. Nevertheless, the residual concentrations exceeded the customary limit values stipulated by the «Blue Angel» (Blauer Engel), the «SG Requirements», and the «Leather Standard by OEKO-TEX». This is possibly due to the rapid succession of measuring cycles in the project after a maximum storage period of one month. On longer storage of the leather for up to a year, as is customary in the industry, the preservative contents in the final product leather would probably be much lower and compliance with the customary industry limit values would be expected.

Table 2: Comparison of resulting preservative concentrations in leather with industrial limits for preservatives

		Limits for preservatives [mg/kg]		
Preservative	**Content in the test leathers**	**SG leather 2017**	**Oekotex leather Product class II**	**"Blue Angel" for leather**
TCMTB	737 – 1091	300	500	500
CMK	355 – 1920	300	300	600
OPP	588 – 2490	750	750	1000
OIT	225 – 300	100	100	250

Table 2 shows that rather high concentrations of preservatives were measured in leather – despite losses during production and storage – and compliance with the customary limit values for the industry was seen only in some cases for CMK. This indicates a discrepancy between an intended mould resistance of the semi-finished products and compliance with the limit values for the leathers produced therefrom. Compliance with the limit values can only be attained if mould-resistant semi-finished materials are subjected to additional long washing cycles during leather production.

Consumer Exposure

In addition to the total preservative content of leather, which can be determined according to DIN EN ISO 13365, great importance attaches to assessment of the preservative with respect to its retention in the leather matrix in order to rule out any risk to the consumer from leather goods. On use of leather products with prolonged skin contact (such as car

seats, footwear, gloves, and upholstered furniture) part of the biocides still present can leave the leather through dissolution in perspiration or through rubbing and be absorbed through the skin, possibly leading to skin irritation, allergies, or other health problems. No method has hitherto been published for determining the extent to which biocides can be transported out of the leather by dissolution in perspiration or by rubbing in the case of the preservatives most commonly used in leather production, i.e. OPP, OIT, CMK, and TCMTB. This precludes any estimation of the amount of migratable preservative, also in relation to the total content of preservative in the leather sample. In order to assess the possible consumer exposure to preservatives remaining in the leather, a method for determining the amount of soluble preservative was developed as part of the project. The preservative content of the selected leathers was first determined according to DIN EN ISO 13365. In order to simulate a possible transfer of the preservative under physiological conditions the leather was subsequently subjected to various treatments such as migration by extraction or Martindale abrasion. Attention was paid to the highest possible preservative contents (600 to 1550 mg/kg) when selecting the leathers for this procedure.

(A) (B)

Figure 2:
(A) Leather being prepared for determination of the soluble preservatives
(B) Starting leather, leather sample after abrasion and cotton cloth with felt underlay according to Martindale

Direct determination of preservatives in extracts from acidic artificial-perspiration solution and purification of the extracts on a solid phase proved unsuccessful owing to the low migration rates of the preservatives. The fundamental suitability of extraction of the sample leather into an acidic artificial-perspiration solution of pH 5.5 followed by liquid/liquid extraction could be demonstrated. The procedure was derived from the standardised method, DIN EN ISO 17072-01: 2011, for determination of heavy metals extractable under physiological conditions with human perspiration. Because it includes two extractions the method is very time consuming and hardly suitable for routine analysis. Moreover, results from the

Martindale procedure showed that only extremely small amounts of preservative migrate out of the leather through mechanical abrasion. Although the leathers selected for the migration and abrasion experiments had high preservative contents, which exceed the usual preservative contents of commercially available finished leathers three- to four-fold, only small quantities of preservative able to migrate under physiological conditions were found. Migration of the tested preservatives is therefore not assumed be pose a risk to the consumer.

Summary of Results

The set goals were largely achieved for the leathers produced in the project, taking experimental variations into account.

Table 3: Preservatives in leather production – Starting situation and project objectives

Starting situation	Project objectives
Protection against spoilage	• Sustainable use of preservatives • Appraisal of mould infestation during storage and transport
Provisions of the Biocides Regulation EU 528/2012	• Legal compliance • Exposure of the consumer

On use of preservatives it is important, on the one hand, to ensure adequate protection against mould infestation during production, storage, and transport and, on the other, to keep the concentrations carried over into the finished leather as low as possible in order to avert possible risks to workers, consumers, and the environment. For semi-finished products it was possible to determine guideline values which just suffice for preservation of wet intermediate products. It is inadmissible to use precautionarily high levels of preservatives during the tanning process with the aim of achieving subsequent leather preservation. This has two main reasons: one is that leather is itself resistant to mould at normal humidity levels, and the other is that the consumer is to be protected against risk of exposure to high levels of preservatives. No mould resistance could be demonstrated for leathers with the preservatives TCMTB, CMK, OIT, and OPP in the concentrations used. Thus, as required by law, there is no sign of precautionary preservation of leather through use of preservatives in the leather production process. Together with the studies on the migration of preservatives under physiological conditions it can be concluded from the results for the investigated preservatives that they pose no hazard to the consumer through contact with leather or leather products under everyday conditions.

Acknowledgement

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Research site 1: Test and Research Institute Pirmasens e.V.
Research site 2: Research Institute of Leather and Plastic Sheeting
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The detailed concluding report is available on request from the Test and Research Institute Pirmasens (PFI), Marie-Curie-Strasse 19, 66953 Pirmasens, Germany, or the Research Institute of Leather and Plastic Sheeting (FILK), Meissner Ring 1 – 5, 09599 Freiberg, Germany.

Further questions will gladly be answered by:

Dr. Ines Anderie
Analytical Chemistry
Tel.: +49-(0)6331 – 2490 712
E-Mail: ines.anderie@pfi-germany.de