Exploring biocide residues in leather: a migration study

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The leather making process is a complex and intricate journey involving several steps to transform raw animal hides into high-quality leather. One crucial aspect of this process is the use of biocides, which play a vital role in protecting the leather intermediates from microbial growth and deterioration. However, concerns have been raised regarding the potential risks associated with biocide residues in final leather products and their impact on consumer safety. To address these concerns, a migration study was conducted to evaluate the migration of biocides from leather and assess any potential risks to consumers.

Biocides in the leather making process

Biocides, such as PCMC (4-chloro-3-methylphenol), OPP (ortho-phenylphenol) (2-phenylphenol), OIT (octyliso-thiazolinone), and TCMTB (2-(thiocyanomethylthio)-benzothiazole), are commonly used in the leather tanning process. These chemicals are applied to protect leather intermediates, including wet blue and wet white from microbial attack, decay, and spoilage. Their antimicrobial properties ensure the preservation and longevity of leather during production and storage.

Stringent hazard classifications

Biocides used in the leather making process are subject to stringent hazard classifications due to their potential toxicity and environmental impact. It is important to note that these classifications are generally more rigorous than those applied to other process chemicals. The focus on safety reflects the importance of proper handling, usage, and disposal of biocides to minimise any adverse effects on human health and the environment.

Residues in final leather products

Despite the thorough processing and treatment, the final leather products may contain residual amounts of biocides. The presence of such residues may raise concerns about potential risks to consumers who wear and use leather items like footwear, bags, and garments, and thus have direct skin contact. Therefore, it becomes crucial to investigate whether such biocide residues pose any significant risks to individuals.

Migration study: addressing consumer safety concerns

To provide insights about the migration of biocides from leather products, a comprehensive study was conducted. The study aimed to determine whether biocides leach or migrate out of the leather, particularly under realistic use conditions. Migration testing simulates the conditions that leather products might encounter during their lifecycle.

The findings of the migration study are essential in evaluating the potential risks associated with biocide residues in leather items. By measuring the levels of migrated biocides, researchers can assess the likelihood of human exposure and determine if these levels pose a risk to consumer safety.

Consumer safety: evaluating risk and regulation

Consumer safety is a primary concern when it comes to the usage of leather items containing biocide residues. Regulatory bodies and industry organisations closely monitor and evaluate the potential risks associated with these residues. Risk assessments based on migration studies, toxicological data, and exposure scenarios help establish guidelines and regulations to safeguard consumers.

Methodology

In this study, four different types of leather were produced: automotive leather, shoe upper leather, garment leather, and furniture leather. The wet blue intermediates were preserved with four common biocides:

- PCMC (4-chloro-3-methylphenol),
- OPP (2-phenylphenol),
- OIT (octylisothiazolinone),
- TCMTB (2-(thiocyanomethylthio) benzothiazole).

PCMC and OPP are usually dosed higher due to different modes of action, whereas OIT and TCMTB are usually dosed lower. The dosage chosen for the individual active ingredients in this study was intentionally much higher than the usual and recommended application quantities to demonstrate that even in the worst-case scenario no migration takes place. These quantities will not be reached in commercially available leathers.

Friction tests were conducted following the DIN EN ISO 105-X12 standard, using a sample size of 50 x 140 mm and a reaming length of 104 ± 3 mm. The leather samples and cotton fabrics, saturated with an artificial sweat solution of pH 5.5 according to DIN EN ISO 105-E04, were subjected to 1,000 friction cycles with a friction force of 9 ± 0.2 N.

Analytical determination of the active ingredient content was carried out on the leather samples and cotton fabrics, following the DIN EN ISO 13365-1 and DIN EN ISO 13365-2 standards, respectively.

Table 1: Analytical results for the different types of leather (shoe, garment, automotive and furniture) and for the cotton fabric according to DIN EN ISO 13365 -1 (2020-12) in mg/kg; not detectable=not detectable (detection limit <30 mg/kg);

Active Ingredient Content in mg/kg for the different types of leather				
	OPP	PCMC	OIT	TCMTB
	DIN EN ISO 13365 -1 (2020-12) in mg/kg dry weight	*DIN EN ISO 13365 -1 (2020-12) in mg/kg dry weight*	*DIN EN ISO 13365 -1 (2020-12) in mg/kg dry weight*	*DIN EN ISO 13365 -1 (2020-12) in mg/kg dry weight*
Shoe Upper				
Leather sample	3500	1800	1300	1100
Cotton fabric after rubbing leather grain side	not detectable	not detectable	not detectable	not detectable
Cotton fabric after rubbing leather flesh side	not detectable	not detectable	not detectable	not detectable
Garment Leather				
Leather sample	4600	2000	1600	1300
Cotton fabric after rubbing leather grain side	not detectable	not detectable	not detectable	not detectable
Cotton fabric after rubbing leather flesh side	not detectable	not detectable	not detectable	not detectable
Automotive				
Leather sample	3300	1600	1200	990
Cotton fabric after rubbing leather grain side	not detectable	not detectable	not detectable	not detectable
Furniture				
Leather sample	2700	1500	690	545
Cotton fabric after rubbing leather grain side	not detectable	not detectable	not detectable	not detectable
Cotton Fabric				
before rubbing	not detectable	not detectable	not detectable	not detectable

IMPORTANT NOTE: The doses chosen for the individual active ingredients were intentionally much higher than the usual application quantities to show that, even in the worst case, no migration takes place. These quantities will probably never be reached in commercially available leathers.

Results

The analytical determination of the active ingredient content in the leather samples showed high values for all four biocides due to the deliberate use of high quantities for preservation *(Table 1)*. After the friction tests, the presence of the four biocides in the cotton fabrics soaked in the sweat solution was examined. Of note, all biocides in the cotton fabrics showed levels below the detection limit of 30 mg/kg *(Table 1)*.

Conclusion

The leather making process involves the use of biocides to protect the leather intermediates from microbial degradation. Although biocide residues may be present in the final leather products, migration studies provide valuable insights into the potential risks associated with these residues. Through scientific evaluation, regulatory measures can be implemented to ensure consumer safety while enjoying leather items. As the industry continues to advance, ongoing research and improved manufacturing practices will contribute to minimising any potential risks posed by biocide residues in leather products.

The results of this migration study provide reassurance that there is no detectable migration of biocides from the leather and therefore prove consumer safety. The absence of biocide residues in the cotton fabrics used in the friction tests indicates that consumers can use leather items with confidence, as these finding show that biocide residues in the leather do not pose a risk to their health.

It is important to note that the deliberate use of high quantities of biocides in this study represents a worst-case scenario, which by far exceeds normal usage levels. The findings of the study emphasise the effectiveness of the leather manufacturing process in preventing the migration of biocides and further highlight the industry's commitment to producing safe and high-quality leather products.