

Dimethyl fumarate – the background

By BLC Leather Technology Centre Ltd

Introduction

Fungicides and mould inhibiting chemicals play an important role in the production and distribution of leather and leather products. Standard leather-processing fungicides, such as TCMTB (2-(Thiocyanatomethylthio)-1,3-benzothiazole), OPP (ortho-phenyl phenol) and OIT (2-n-octyl-4-isothiazolin-3-one) are added to prevent mould growth during the wet-blue stage. These chemicals are added and are present in the substrate itself, and allow for transport of the wet-blue without the associated risk of mould growth. In general, fungicides interfere with the germination and penetration process of mould into leather or inhibit fungal growth and reproduction. More specifically, fungicides may interfere with cell division, may inhibit the activity of certain enzymes, or may alter the function of cell membranes.

Dimethyl fumarate, also known as DMF, has good antifungal properties, and has been associated with mould inhibitor sachets used in finished footwear and furniture. Recently, DMF has been highlighted as being an allergenic sensitizer causing eczema at low concentrations.

Dimethyl fumarate – properties

Dimethyl fumarate is a methyl ester of fumaric acid, with a chemical structure of $C_6H_8O_4$. This white crystalline solid is a chemical with preservative properties that diminish over time.

DMF has good antifungal properties, and as such has been used as a mould inhibitor within sachets in finished leather products. Like all living organisms, moulds need certain basic requirements to grow and multiply; a source of moisture and a source of nutrients. In wet-blue leather the source of moisture is clear. In finished leather the level of moisture is much lower and, therefore, the growth of mould is less. However, when transporting leather between different climates, or if the leather is stored in an inappropriate manner, moisture build up in certain areas, such as inside packaging, can readily lead to the growth of mould. Many of the process chemicals used in the manufacture of leather can act as nutrients for mould growth, for example phosphates, surfactants and fatliquoring agents. DMF has been found in sachets placed within the furniture structure or inside the shoe box, often

labelled as 'anti-mould agent'. Its function is as a biocide to kill any mould that may arise from storage and transportation from hot and humid climates. In these environments, the volatile DMF in the sachet evaporates and can impregnate the leather. However, it has also been found to severely affect some consumers when they come into contact with these products.

Skin sensitization

In 2006-7 a number of cases emerged in Europe with patients showing signs of severe contact dermatitis on their legs, buttocks and back, which was resistant to topical treatment. Through research carried out by dermatologists, it was found that the patients had all purchased leather furniture prior to developing the rash and the unusual dermatitis patterns could be related to sitting position and style of furniture purchased¹. The cases seen in countries such as the UK, Finland and France were traced back to furniture manufactured in China. Patch tests were carried out with a number of allergens associated with leather and these confirmed that the cases of dermatitis were most likely to have been caused by the presence of DMF in the furniture, resulting in a painful rash at levels as low as 1ppm². The reaction causing the dermatitis was

found to be allergic, as not all people in contact with the furniture showed signs of a rash, and patients often stated that they had no direct contact with the leather, only having sat on the furniture fully clothed³.

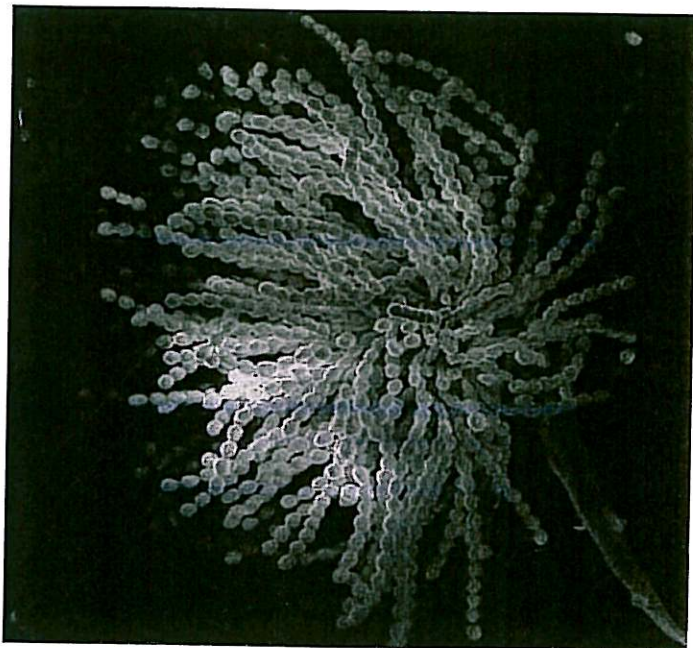
It was found that anti-mould sachets were being placed in the packaging, or being stapled to the wooden frame, or directly under the leather covering and, over time, the volatile DMF was evaporating and permeating the leather.

The release of DMF was then exacerbated by body temperature and perspiration, leading to levels adequate to cause sensitization. Anti-mould sachets are often used in conjunction with silica gel sachets, which contain an inert desiccant that removes moisture, but is relatively ineffective in the prevention of mould growth in large leather products. Although silica gel is inert and safe to use, BLC has found cases where the silica has combined with dimethyl fumarate and shown positive results when tested. In most cases, these were labelled as mould inhibitor sachets.

The law

On the basis of the research findings, France, Spain and Belgium adopted measures to regulate the use of DMF, and to ban the importation and placing on the market of products such





as footwear containing DMF. The French Decree also orders the recall of all footwear and furniture products that visibly contain DMF in the product or packaging.

The Biocide Directive – 98/9/EEC – states that a biocidal product can only be used if 'it has no unacceptable effects ... on human health'⁴. Under this directive, products containing dimethyl fumarate are already banned for use in the European Union. This means that biocidal products containing DMF for use in manufacture and production of products within the EU are not legally available for protection against mould growth. However, this legislation does not cover the importation of products such as furniture, from countries outside the EU.

As a result of the severe cases of dermatitis caused by the presence of DMF in seating, the Commission of the European Communities proposed a ban in all products placed on the mar-

ket. The restriction on use of DMF in products is governed by the Commission Decision 2009/251/EEC, and states that from May 1, 2009, all member states must ensure that any product containing DMF is withdrawn from the market. It also states that as of May 1, 2009, all products must comply with the limit of less than 0.1mg/kg of DMF per product or part of product. This was deemed to be sufficiently below the 1mg/kg level known to cause dermatitis in patch testing and, therefore, an adequate limit to address the associated risks.

Currently, there is no internationally recognised standard for the detection of DMF in sachets or leather. BLC has developed a method for detection of dimethyl fumarate and other fungicides with a reliable detection limit of less than 0.1mg/kg.

Dimethyl formamide

Within the footwear industry there has been some confusion

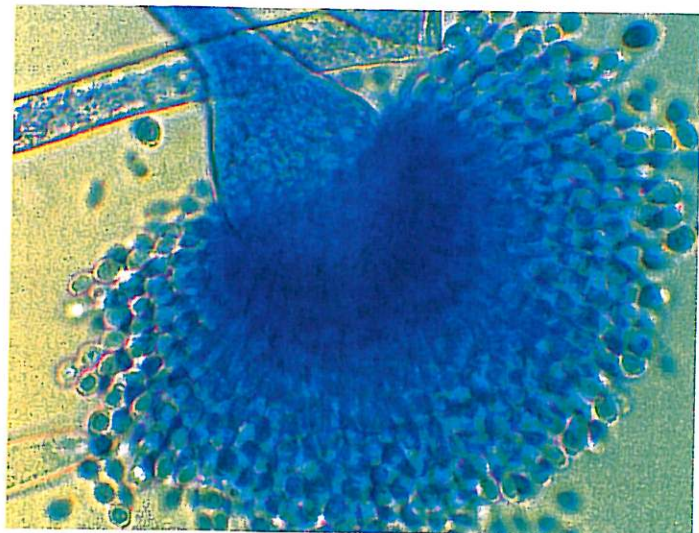
as a result of another unrelated chemical having the abbreviation DMF, dimethyl formamide. Dimethyl formamide is a volatile organic compound with the chemical structure C_3H_7NO . The most common use of DMF is as a solvent in chemical reactions, primarily in the production of plastics and polyurethane. It also has uses in the manufacture of adhesives, solvent dyes, synthetic leather and surface coatings. Exposure to DMF has been shown in studies by the US Environmental Protection Agency to cause dermatitis. However, this relates to acute exposure to DMF in its chemical form, and not to products and articles. The release of DMF into the environment is controlled in Europe under the Hazardous Waste Directive and there are currently no plans to restrict the use of DMF in the production of consumer articles.

Conclusion

Although DMF is already banned for use within the European Union, the publicity

surrounding the cases of allergic dermatitis caused by DMF-containing anti-mould sachets in furniture manufactured in China, has caused the European Commission to ban all products containing the fungicide.

The ban and recall of products containing DMF is to be policed by individual EU member states, but it is important for importers, manufacturers and retailers to be aware of the risks and to address any issues raised. Problems, such as dermal irritation, caused by elevated levels of fungicides, can lead to brand damage and can potentially lead to high costs through proceedings with customers. BLC offers a validated analytical method for the detection and quantification of DMF which can be conducted within five days or less. BLC advises that due diligence testing of products or parts of products, such as materials prone to mould growth, packaging and silica gel sachets, be carried out. If a failure occurs BLC can offer specialist technical support.



References

1. J D L Williams *et al*, p 234, *An outbreak of furniture dermatitis in the UK*, British Journal of dermatology 2008, **159**
2. T Rantanen, p 218, *The cause of the Chinese sofa/chair dermatitis epidemic is likely to be contact allergy to dimethyl fumarate, a novel potent contact sensitizer*. British Journal of dermatology 2008, **159**.
3. Williams, *Op. cit*, p 235.
4. Article 5(1)(b)(iii) of Directive 98/9/EEC, Official Journal of the European Union, L 123, 24.4.1998, p 8.

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