

Dr. Albert conducting a test on mercaptobenzothiazole migration from footwear materials using artificial sweat.

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Allergens in footwear

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Many chemical substances are used throughout the manufacture of a shoe and, more specifically, in the production processes and/or treatments that footwear materials undergo to achieve certain qualities, such as strength, durability, flexibility, etc. Some of these substances are known to be sensitising/allergenic upon contact, and hence materials like leather, rubber, adhesives, synthetic polymers and dyes are the main sources of allergens in footwear.

Foot occlusion and prolonged, direct contact generate adverse temperature and humidity conditions in the in-shoe microclimate, together with skin physiological conditions that favour allergen migration via perspiration from shoe materials to the foot's skin. This, in turn, promotes sensitisation or allergic contact dermatitis (ACD) in individuals

who are already sensitised to a certain allergen, the clinical symptoms being skin erythema, oedema, vesication and pruritus in the contact area. The prevalence of allergic contact dermatitis caused by footwear ranges between 1.5% to 24.2% and the condition can even cause such severe discomfort that people affected are forced to stop their daily activities and also find it difficult to purchase suitable shoes.

Chrome VI is the most relevant allergen found in footwear leather, followed by formaldehyde. However, Chrome VI is not added during the leather production process, but its presence in leather tanned with Chrome III salts (80-85% of world production) is mainly due to three reasons:

1. Contamination with chromates present in chromium salts or certain pigments such as lead yellow or orange which can contain lead chromate;

2. Chrome III oxidation during neutralisation or dyeing in a basic medium;
3. Chrome III oxidation under heat, light and low humidity conditions due to the presence of free radicals released by highly unsaturated fatliquoring agents.

There are other allergens that can be found in leather and textiles, such as para-Phenylendiamine and 4-aminoazobenzene from azo-dyes and some disperse dyes such as disperse red 1, disperse blue 106/124 mix and disperse orange 3. P-tert-Buthylphenol formaldehyde (PTBF) and rosin resins are the main allergens found in polychloroprene (natural or synthetic rubber adhesives), which are commonly used in manufacturing stages such as lining and insock attaching. Synthetic and/or natural rubber materials may also contain other sensitising additives such as thiurams, mercapto chemicals, carbamates, paraphenylendiamine



Eczematous response caused the presence of cobalt in a piece of leather applied to an ACD patient's back for 48 hours.



Eczematous response on the dorsum of a voluntary patient's left foot after 14 consecutive days contact with leather containing 21.1 ppm of Chrome VI.

derivatives and thioureas. Buckles and eyelets can contain nickel and cobalt which can also be found in pigments and dyes applied to materials.

Nowadays there are severe restrictions contained in current legislation relating to sensitising substances found in footwear and its components. According to REACH regulations (Registration, Evaluation, Authorisation and Restriction of Chemicals), since May 2015, Chrome VI content in leather in direct contact with the skin is limited to less than 3 mg/kg of dry leather. However, nickel content in footwear metallic pieces that may come into prolonged contact with the skin is restricted to 0.5 g/cm²/week.

With regard to formaldehyde, there is no restriction for leather in Europe, although some countries including Norway, Finland and the Netherlands do have restrictions for textiles. In China, formaldehyde is limited in footwear, leather goods and textiles according to their final use and whether direct contact with the skin is envisaged. In Japan, the same considerations apply but only for textiles (Law 112). REACH Regulations of 2015, limit 4-aminoazobenzene to 30 mg/kg in leather and textiles. In China, this restriction is also applicable to leather, although it is stricter for textiles (20 mg/kg) in footwear intended for

children under 14 (shoe size no larger than 250 mm).

In 2008 several skin injury cases were detected in the EU related to contact allergic reactions caused by footwear coming from China that was contaminated with dimethyl fumarate found in sachets placed in shoe boxes to fight humidity during transportation and storage. After these incidents, the EU restricted dimethyl fumarate to 0.1 mg/kg. However, this substance is not commonly used in the production of footwear materials. In relation to other allergens, such as mercaptobenzothiazol, thiuram and carbamates used as accelerators for the vulcanisation of rubber intended for soles and insoles, or rosin resins and PTBF, there is no restriction on their content in footwear or standard analytical methods applicable to footwear materials that allow these substances to be controlled.

There are only standardised chemical methods to determine Chrome VI content in leather, 4-aminoazobenzene and formaldehyde content in leather and textiles, and extractable nickel and cobalt content in metallic pieces or polymeric materials. Nevertheless, some of these methods do not provide for allergen release conditions that simulate the scenario in the foot-shoe microclimate which is necessary in

order to approximate the 'real' exposure conditions during footwear use. Furthermore, these analysis methodologies should reach quantification limits below the allergic response thresholds established in dose-response clinical research studies in order to ensure to some extent that materials may not imply ACD risk in people sensitive to a certain allergen.

On the other hand, tanning methods using tetrahydroxymethyl phosphonium sulphate (THPS) and oxazolidine are being investigated as alternatives to chrome tanning. Best practices in post-tanning operations to avoid Chrome VI formation are being implemented and research conducted on Chrome VI sequestering agents such as ascorbic acid, sodium bisulphite or lactic acid. To avoid the presence of formaldehyde, possible treatments are based on its transformation by reduction, oxidation or condensation using amine compounds. Adhesives based on rosin and PTBF (para tertiary butyl phenol formaldehyde) resins could be replaced with water-based adhesives containing acrylic resins. However, there is no research work to avoid the rest of allergens in footwear, mainly due to the absence of restrictive legislation and the low awareness of footwear companies about the sensitising potential of such allergens. 