

Occupational contact dermatitis caused by hydrogenated formaldehyde–benzenamine polymer (FBAP) in epoxy hardeners

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doi:10.1111/cod.12835

Key words: allergic contact dermatitis; CAS no. 135108-88-2; case report; coatings; hydrogenated formaldehyde–benzenamine polymer; occupational; painter; pipe relining worker; polymethylenecyclohexaneamine.

Amines in epoxy hardeners are known causes of occupational allergic contact dermatitis among workers who handle epoxy resin systems. We report the clinical examination and exposure of 2 patients, a spray painter and a sewage pipe relining worker, with occupational contact allergy to hydrogenated formaldehyde–benzenamine polymer (FBAP) (CAS no. 135108-88-2).

Patch Testing

We patch tested a spray painter in 2016 in accordance with ESCD recommendations (1). We read the tests on day (D) 2, D3, and D6. The tests included a modified baseline series, antimicrobials, ethanolamines, epoxy chemicals, glues and plastics, isocyanates, acrylates, coconut fatty acid derivatives, hydroperoxides of limonene and linalool, and the patient's own workplace materials including epoxy resins and hardeners.

When the reaction to one of the patient's own products was positive, without other relevant allergies, we ordered the respective ingredients and tested them separately.

After the first case, we began testing epoxy-exposed patients with a 1% FBAP-containing ingredient in pet. The pipe relining worker reacted positively to this test substance. His tests did not include acrylates, but otherwise he was tested as the first case.

Case 1

A 36-year-old car painter had worked as a welder, construction painter, floor layer, fibreglass worker and bridge worker before his current work as a spray painter starting

in May 2015, when he began using an epoxy hardener containing a FBAP derivative. He developed redness of exposed chest skin in December 2015, and eczema on the backs of his hands and forearms in January 2016. The eczema healed during a 1-week holiday but recurred at work. Later, the patient also developed eczema on his face. His job tasks were changed, and eczema healed. Later, eczema recurred on his hands and forearms even when he merely visited the workplace or drove the van that transported epoxy paints. The eczema healed repeatedly when he was on sick leave. He showed strong positive patch test reactions to his own hardener in pet.: 1%, ++; 0.32%, +; and 0.1%, ?+. Apart from a weak reaction (+) to diaminodiphenylmethane (MDA), no other allergy was discovered. Chemical analysis showed that the hardener contained no isocyanates or MDA. Further tests with the ingredients of the patient's own hardener in pet. showed a strong allergy to one of the ingredients: 2%, +++; 0.64%, ++; 0.2%, +; and 0.064%, ?+. According to safety data sheets (SDSs), this ingredient contained 20% FBAP. It also contained benzyl alcohol, triethylenetetramine (TETA), and tris-dimethylaminomethylphenol (tris-DMP), but our patient did not react to any of these. Twenty control patients had negative results with the FBAP-containing ingredient 0.64% pet.

Case 2

A 22-year-old construction worker with a history of atopic dermatitis from childhood started work in sewage pipe relining in 2014. During the first 2 years, his atopic dermatitis affected the same facial and flexural skin areas as before. In March 2016, he started in a new company with new epoxy products, and developed new symptoms on his hands in summer 2016. In November 2016, his occupational physician sent him to the Finnish Institute of Occupational Health (FIOH) because of these new skin symptoms. At the FIOH, he had positive reactions to a

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Conflicts of interest: No conflicts of interest to be declared. No exterior funding.

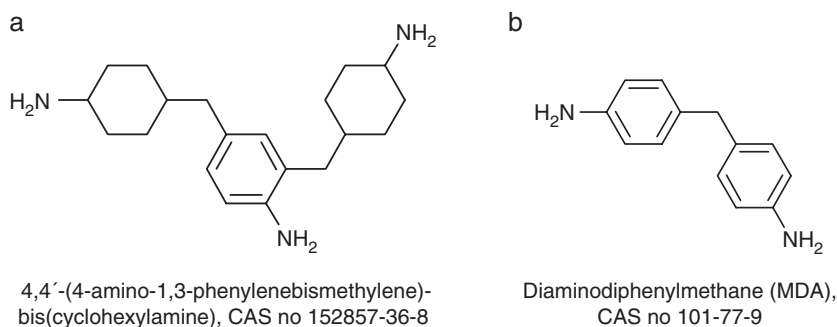


Fig. 1. (a) Structure of 4,4'-(4-amino-1,3-phenylenebismethylene)bis(cyclohexylamine), which is one of the main structures of hydrogenated formaldehyde–benzenamine polymer, and (b) structure of diaminodiphenylmethane.

1% concentration of the FBAP-containing ingredient obtained from the previous patient (+), MDA (+), and his own epoxy hardener (1% pet. +). The SDS of the hardener declared 10–20% FBAP. In the first pipe relining company, the patient had handled a diphenylmethane diisocyanate (MDI)-containing polyurethane hardener, but he was not exposed to MDI or MDA in his present work. He had negative test results with the other components of the FBAP-containing ingredient, namely TETA, tris-DMP, and benzyl alcohol.

Discussion

We describe 2 cases of occupational contact dermatitis caused by FBAP (CAS no. 135108-88-2), which is a reactive amine that is present in hardeners of epoxy resin systems. FBAP is a hydrogenated copolymer of benzenamine and formaldehyde; its molecular formula has not been univocally characterized. One internet source (2) states that FBAP consists mainly of 4,4'-(4-amino-1,3-phenylenebismethylene)bis(cyclohexylamine), meaning that its principal structure contains both a *p*-amino-substituted aromatic ring and two hydrogenated (aliphatic) cyclohexane rings (Fig. 1). According to the registration dossiers of the European Chemicals Agency, FBAP is a mixture of partly or fully hydrogenated oligomers of benzenamine and formaldehyde, some of which are identified by CAS numbers and some of which are not (3). Among these oligomers, 4,4'-(4-amino-1,3-phenylenebismethylene)bis

(cyclohexylamine) is listed with CAS no. 152857-36-8. It is possible that the patients' MDA reactions represent a cross-allergy with the *p*-amino moieties of FBAP. FBAP's final concentration in the first patient's hardener was 1–5%. On the basis of the strong reactions to the respective ingredient in low concentrations and the negative results with its other ingredients, FBAP was probably the primary allergen in the hardener. The FBAP in the epoxy hardener was probably the main reason for the patient's dermatitis on his hands and forearms. He also suffered from face dermatitis, which is quite often seen in patients who are allergic to amine hardeners or epoxy resins (4–7), the spraying of paint probably increasing contact.

According to the Finnish Chemical Product Register, several other FBAP-containing epoxy resin system products are available on the market. A patch test substance for FBAP is not commercially available, and exposure to this new allergen might be difficult to identify from the SDS unless CAS numbers are available. We recently described occupational contact allergy to another reactive amine in hardeners used for epoxy resins systems, namely derivatives of 1,3-benzenedimethanamine, *N*-(2-phenylethyl) derivatives (1,3-BDMA) (8), and others have described another novel epoxy hardener contact allergen, 2-methylpentane-1,5-diamine (9). Epoxy resin systems may contain allergens that have not been previously identified, and this should be kept in mind when occupational contact dermatitis is suspected.

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