

Short Communication

Occupational epoxy dermatitis with patch test reactions to multiple hardeners including tetraethylenepentamine

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Case Report

A male spray painter, born in 1953, developed hand dermatitis and periorcular dermatitis in 1975, after 6 years of occupational exposure to paints and solvents. Patch testing was performed at a university clinic with a standard series, and a rubber chemical series, with negative results. It was concluded that the patient had occupational irritant contact dermatitis from epoxy paints. In 1983, he was referred to us for further investigation. He suspected that paints containing epoxy resins caused his dermatitis. Patch testing was performed as described previously (1). Epoxy resin gave a + reaction on D 1 and 2 (1 day occlusion (1)). By D 3, the reaction had weakened (?+), and by D 4 had disappeared. Isopropylaminodiphenylamine (IPPD) gave a ++ reaction.

In 1988, the patient had mainly spray painted ceilings with 2-component epoxy paints cured with amine hardeners, and acrylic paints. He developed dermatitis on the face, upper back and shoulders. On patch testing, diglycidyl ether of bisphenol A epoxy resin (DGEBA-ER) gave a ++ reaction. Furthermore, Cl+Me-isothiazolinone (0.01% aq. Chemotechnique Diagnostics AB, Sweden) gave a +++ reaction, whereas (meth)acrylates, other antimicrobials and 50 plastic and glue allergens (2) were negative.

The patient continued his work and was referred to us again in 1996, because his hand dermatitis had worsened (Fig. 1). He was patch tested with a series of epoxy resin compounds (Table 1, ref. (3)). Brominated DGEBA epoxy resin, which contains DGEBA-ER, and several epoxy resin hardeners gave positive reactions (Table 1). It was concluded that the patient had become sensitized to DGEBA-ER, several amine hardeners (possibly cross-reacting) and Cl+Me-isothiazolinone, which had probably been used in water-based paints as a preservative. Among the rubber additives (30 chemicals, see (4)), IPPD, but no other amines or other chemicals, gave a + reaction.

Discussion

In 2-component epoxy resin paints, polyfunctional aliphatic amines, aromatic amines, cycloaliphatic amines

and solid polyamides are mostly used as hardeners (5, 6) (Fig. 2). Polyamine hardeners were identified as sensitizers as early as the 1950s (5, 6). Polyamides are prepared by combining aliphatic amines, e.g., diethylenetriamine (DETA) or triethylenetetramine (TETA), with fatty acids. Amine-epoxy adducts are formed by reaction between epoxy resin and excess polyamine, mostly DETA, TETA or isophoronediamine (IPDA) (5, 6). The amine-epoxy adduct hardeners used in metal paints contain about 5% free amine, whereas those used in floor and concrete coatings contain as much as 20%. Free DGEBA is not found in amine-epoxy adducts (5–7). When DGEBA epoxy resins are cured by polyamine-bearing hardeners at room temperature, amounts of unreacted DGEBA and polyamine diminish rapidly within 1 to 2 days, but thereafter, the decrease is slow. After 1 week's cure 0.02–12% free DGEBA and 0.01–1% free DETA were found when 6 different epoxy resin products were experimentally cured by DETA (8). Accordingly, workers may become sensitized to both DGEBA and amine hardeners, as in our patient.

We have an over-20-year follow-up of our patient, who developed allergic contact dermatitis from DGEBA-ER and amine hardeners (5, 6). Our epoxy resin



Fig. 1. Spray painter's allergic contact dermatitis from epoxy resin and amine hardeners.

Table 1. Patch test results with an epoxy series

Epoxy compound	Source	Concentration	D2	D3	D4
1 hexamethylenetetramine	C	2.0			
2 diaminodiphenylmethane (MDA)	C	0.5			
3 triethylenetetramine (TETA)	C	0.5			
4 phenylglycidyl ether (PGE)	C	0.2			
5 diethylenetriamine (DETA)	C	1.0		?+	+
6 isophoronediamine (IPDA)	O	1.0	++	++	+++
7 cycloaliphatic epoxy resin (CA-ER)	C	0.5			
8 ethylenediamine hydrochloride (EDA)	C	1.0			
9 brominated DGEBA-epoxy resin (Br-ER)	O	1.0	++	++	++
10 bisphenol A	C	1.0			
11 BIS-GMA	C	2.0			
12 BIS-MA	C	2.0			
13 epoxy diacrylate (BIS-GA)	C	0.5			
14 epichlorohydrin	T	0.1			
15 1,4-butanediol diglycidyl ether	O	0.2			
16 tetrapropylene glycol diglycidyl ether (DER 736*)	O	0.5			
17 di- and triglycidyl ether of glycerol (LX 112*)	O	0.5			
18 vinyl cyclohexene diepoxide (ERL 4206*)	O	0.5			
19 ethyleneglycol diglycidyl ether (QUETOL 651*)	O	0.5			
20 2,4,6-tris-dimethylaminomethylphenol (Tris-DMP)	O	1.0			
21 triglycidyl isocyanurate (TGIC)	O	1.0			
22 xylylenediamine (Euredur 14*)	O	1.0			?+
23 trimethylhexamethylenediamine	O	1.0	?+	++	++
24 tetraethylenepentamine	O	1.0		?+	+
25 DEG-diluent (80% diethyleneglycol diglycidyl ether, see ref. (3))	O	0.5			
26 3-dimethylaminopropylamine (DMAPA)	O	1.0			

Source: C=Chemotechnique, T=Trolab, O=own.

* The commercial name of the chemical which was used for the preparation of the patch test substance (5).

compound series (Table 1) contains many amine hardeners (9), because no single amine hardener can be used to screen for them all (9, 10). Our patient had patch test reactions to IPDA (10–13), DETA (3, 10), TETA (3, 10, 14), trimethylhexamethylenediamine (8) and tetraethylenepentamine (TEPA). He also showed a weak reaction to xylylenediamine (XDA), which has caused ACD on

rare occasions (10, 15, 16). According to the manufacturer, Euredur 14 (Table 1) contains 30% XDA (5). Accordingly, our patient had patch test reactions to aliphatic polyamines (DETA, TETA), to a cycloaliphatic polyamine (IPDA) and to an aromatic amine (XDA). We have not come across previous reports of allergic contact dermatitis from TEPA, but we have reported allergic

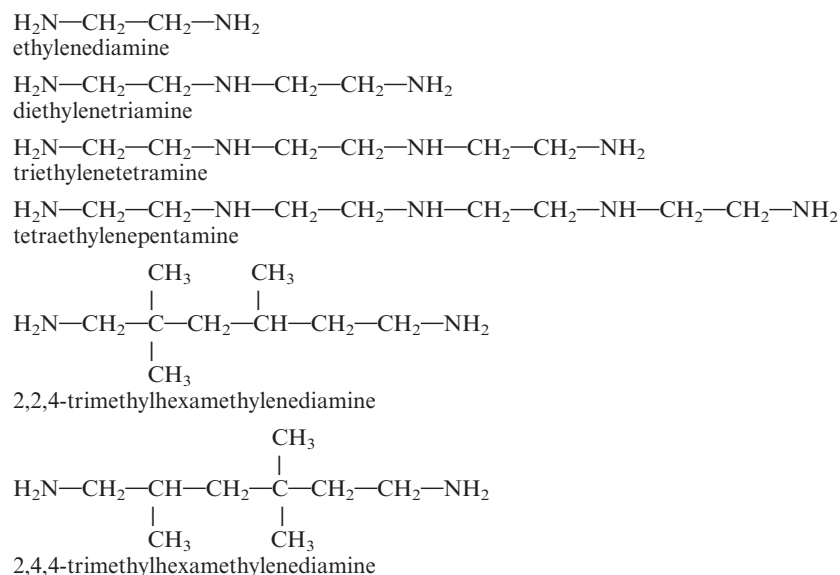


Fig. 2. Chemical structures of aliphatic polyamines used as epoxy resin hardeners.

Table 2. Occupational allergic contact dermatitis diagnosed at the Finnish Institute of Occupational Health 1995–1996 ($n=27$)

Causative chemical	No. of cases
DGEBA epoxy resin	21
epoxy reactive diluents	6
polyamine hardeners	3
triglycidyl isocyanurate	3
2,3-epoxypropyltrimethylammonium chloride (EPTMAC)	3
non-DGEBA epoxy resin	1

DGEBA=diglycidyl ether of bisphenol A.

contact dermatitis from an unidentified polyethylene-polyamide (PEPA) based hardener other than ethylenediamine, DETA, TETA, IPDA or diaminodiphenylmethane (DDM) (3), and there may be unrecognized amine hardeners present in epoxy resin systems. We previously reported a spray painter sensitized to tris-DMP in epoxy paints (9). She was negative on patch testing to the other allergens in the epoxy resin series, including the other amine hardeners and DGEBA-ER. In our clinic, allergic contact dermatitis from hardeners is much less common than from epoxy resins (Table 2).

Our patient also reacted to brominated DGEBA-ER. This probably reflects allergy to DGEBA-ER, because brominated DGEBA-ER contains both brominated epoxy resin and 10–30% DGEBA-ER (15). Though it is also possible to become sensitized to brominated DGEBA-ER, i.e., without sensitivity to DGEBA-ER (17), brominated ERs are used to make products fire-resistant and had probably not been used in our patient's paints.

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