Tricresyl phosphate in polyvinylchloride gloves: a new allergen

Marie-Noëlle Crépy\textsuperscript{1,2}, Eddy Langlois\textsuperscript{3}, Sandrine Mélin\textsuperscript{3}, Alexis Descatha\textsuperscript{1}, Lynda Bensefa-Colas\textsuperscript{2}, Anne-Marie Jonathan\textsuperscript{1} and Jacques Ameille\textsuperscript{1}

\textsuperscript{1}Department of Occupational Health, AP-HP, Groupe Hospitalier Raymond Poincaré, 92380 Garches, France, \textsuperscript{2}Department of Occupational Health, AP-HP, Groupe Hospitalier Cochin, 75014 Paris, France, and \textsuperscript{3}Institut national de recherche et sécurité, Analytical Organic Chemistry Laboratory, 54519 Vandœuvre-lès-Nancy, France

doi:10.1111/cod.12213

Key words: allergic contact dermatitis; gloves; occupational; polyvinylchloride; tricresyl phosphate.

Case Report

A 58-year-old hospital cleaner with a long-standing history of hand eczema was referred to our department by her occupational physician.

She had no atopy history. Her hand eczema began in 2005 after 20 years of latex glove use. At work, she used a mean of 20 thin medical latex gloves per day. Her physician reported that, on patch testing, she had important allergic reactions to thiuram mix (+++). Her eczema healed after she changed from using latex medical gloves to using medical polyvinylchloride (PVC) gloves. She remained free from hand eczema for 5 years.

In 2010, eczema reappeared, with a severe aggravation in March 2012. At work, she used a mean of 20 thin PVC gloves (LCH\textsuperscript{®}) per day. She reported intense sweating under her gloves.

At examination, she had severe erythematous and desquamative infiltrated lesions on all parts of the hands.
Fig. 1. Allergic contact dermatitis on the dorsal part of the hands in a cleaner.

Fig. 2. Allergic contact dermatitis on the palmar part of the hands in a cleaner.

Fig. 3. Patch test at the 3-day reading showing sensitivity to tricresyl phosphate.

(palmar and dorsal parts), with spreading on the wrists and forearms (Figs. 1 and 2). She used Diprosone cream® twice daily for < 1 year to treat her eczema, without improvement.

Patch tests were performed with Finn Chambers® on Scanpor® tape, with the European baseline series of the European Contact Dermatitis Research Group, a cosmetics series, a rubber series, a plastics and glues series (Chemotechnique Diagnostics, Vellinge, Sweden), and a piece of the PVC gloves. Tests results were read after 48 and 72 hr, by the same dermatologist, in accordance with the recommendations of the International Contact Dermatitis Research Group.

There were positive patch test reactions to the piece of vinyl glove (+++), tricresyl phosphate (TCP) 5% pet. (+++) (Fig. 3), thiuram mix 1% pet. (+++), and stearyl alcohol 30% pet. (+).

Analysis was performed on the PVC glove (LCH®) used by the patient at work, and on two kinds of PVC gloves usually used in French hospitals in the Paris area: Exanyl® and Flexam®. Substances of interest were TCP, triphenyl phosphite (TPPi), and triphenyl phosphate (TTPa). TPPi was identified as a possible allergen in the PVC gloves, but TTPi is known to be transformed to TTPa during the analysis, and the same transformation is suspected to occur within the plastic manufactured products (1).

A known mass of gloves, cut into small pieces, was extracted for 15 min in an ultrasonic bath with 10 ml of acetonitrile/water (65:35) for TTPa and TPPi, and in 10 ml of acetonitrile for TCP. The extracted solution was then injected into a high-performance liquid chromatography (HPLC) system equipped with an ultraviolet–visible detector. HPLC was preferred to gas chromatography (GC) for reasons of better sensitivity: the quantification limit for TCP is 1.3 μg/g of glove with HPLC, whereas it is ∼10 μg/g for GC, which can be insufficient in some cases. The column used was a reversed-phase KINETEC C18 [100 × 4.6 mm; particle size, 2.6 μm (Phenomenex, Le Pecq, France.)]. The mobile phase was acetonitrile/water (65:35), the flow rate was 1 ml/min, the injected volume was 20 μl, and the wavelengths used for detection were 264 nm for TPPi and TTPa (2) and 220 nm for TCP (3).

Figures 4 and 5 show superpositions of standard and glove extract chromatograms. TCP, TPPi and TTPa were identified and quantified by comparison with standard solutions (Aldrich ref. 268917, T84654, and 241288 respectively). The results of the analysis are shown in Table 1.
Stearyl alcohol was found in the dermocorticoid Diprosone® cream.

The patient was advised to stop using gloves (either vinylchloride or rubber gloves) and the corticosteroid Diprosone® cream. She benefited from arrangements for early retirement. Her eczema healed completely, without any recurrence after 4 months of follow-up.

Discussion

In this case study, we observed a severe eczema caused by an additive in PVC gloves, TCP. This cleaner had been wearing medical single-use gloves, first of latex and then of PVC, to clean with irritant detergents and disinfectants. Medical single-use gloves are made for anti-infection protection, and they are not indicated for chemical exposure. Detergents and disinfectants are likely to penetrate inside the gloves, alter the skin barrier, and facilitate allergen sensitization. This cleaner first became allergic to thiurams, which are vulcanizing agents for rubber, and then to plastic additives.

In spite of their widespread use, only a few cases of allergic contact dermatitis caused by PVC gloves...
have been reported. Recently, Suuronen et al. reported five cases of allergic contact dermatitis caused by TPPI in PVC medical gloves (1). The other allergens incriminated are biocides, plasticizers, stabilizers, and pigments: benzisothiazolinone (4), formaldehyde (5), mono(2-ethylhexyl) maleate (6), di-(n-octyl)-tin-bis(2-ethylhexylmaleate) and polyadipic acid-co1,2 propylene glycol (7), pigments and dyes, a reddish-copper phthalocyanine-blue complex (8), an organic pigment, and triphenyl phosphate (TPPa) concentrations in different types of gloves.

<table>
<thead>
<tr>
<th>Glove</th>
<th>TCP concentration (μg/g)</th>
<th>TPPa concentration (μg/g)</th>
<th>TPPI concentration (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCH®</td>
<td>21.4</td>
<td>54.9</td>
<td>116.0</td>
</tr>
<tr>
<td>Exanyl®</td>
<td>5.6</td>
<td>85.2</td>
<td>6.5</td>
</tr>
<tr>
<td>Flexam®</td>
<td>&lt; 0.9</td>
<td>8.0</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

TCP (CAS no. 1330-78-5) is a non-flammable, clear, faintly yellow, viscous, odourless liquid that is a mixture of mainly three isomers: tri-o-cresyl phosphate (CAS no. 78-30-8), tri-m-cresyl phosphate (CAS no. 563-04-2), and tri-p-cresyl phosphate (CAS no. 78-32-0).

It is mainly used as a plasticizer for polyvinylchloride, polystyrene, and nitrocellulose, as a fire retardant for plastic, in solvent mixtures, and as an additive to extreme-pressure lubricants and hydraulic fluid. Rare cases of allergic contact dermatitis caused by TCP in spectacle frames (13), in adhesive bandages (Band-Aid Brand Sheer Strips) (14) and in external prostheses have been reported (15).

This is the first reported case of allergic contact dermatitis caused by TCP in PVC medical gloves. Dermatologists and occupational physicians should be aware of the importance of testing all types of gloves used by the patients in cases of hand dermatitis.

References