Clinical Review: Thioureas and Allergic Contact Dermatitis

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GOAL

To recognize cases of thiourea-induced allergic contact dermatitis (ACD)

OBJECTIVES

Upon completion of this activity, dermatologists and general practitioners should be able to:

1. Explain possible sources of thiourea-induced ACD.
2. Understand the lack of detection of thiourea-induced ACD with the standard T.R.U.E. Test.
3. Discuss patch tests to use in the detection of thiourea-induced ACD.

CME Test on page 374.

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Thioureas are an uncommon underrecognized cause of allergic contact dermatitis (ACD). This article presents the findings in 3 individuals with ACD to thioureas and reviews the medical literature concerning thiourea-induced ACD. Thioureas are often the allergenic sources in ACD involving high-grade rubber products made of neoprene. Standard patch test series and rubber allergen patch test series usually do not contain thiourea allergens and will fail to diagnose these causes of ACD. Thioureas—most notably diethylthiourea, dibutylthiourea, and diphenylthiourea—should be considered in individuals with potential rubber allergy who fail to react to antigens in the standard allergen patch test tray.

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Case Reports

Patient 1—A 60-year-old publishing executive was referred after more than a year of bilateral erythematous eruptions on her hands that were accompanied by burning and occasional pustules. She had a history of atopy and nickel allergy. She denied any occupational exposures other than handling newspapers and magazines and using a computer. Biopsy results demonstrated a psoriasiform dermatitis. Treatment was unsuccessful with nickel avoidance, high-potency corticosteroids, dapsone, calcipotriene, and hand psoralen plus UVA. The patient exhibited erythematous plaques over her thenar and hypothenar eminences bilaterally with a rim of hyperpigmentation and scaling (Figure 1A). Initial patch test results

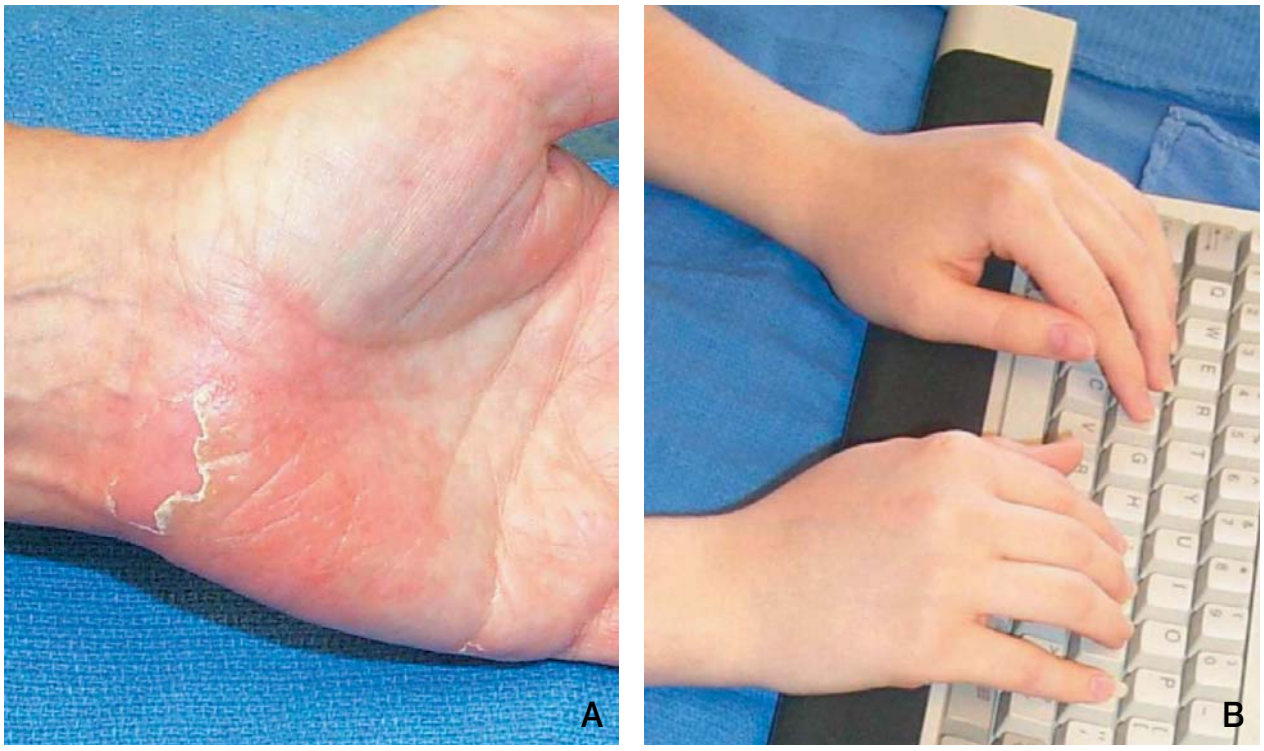

Figure 1. The left hand of patient 1 (A) and her keyboard wrist support (B).

revealed acrylate sensitivity; however, despite acrylate avoidance, her hand dermatitis persisted.

Almost one year after patch testing, the patient sustained a knee injury. Within 24 hours of wearing a foam knee brace, she developed a generalized pruritic erythematous eruption that was accentuated over the involved knee and on the palms at the sites of her previous hand dermatitis. Patch testing with an expanded set of rubber allergens revealed sensitivity to diethylthiourea. In addition to reacting to the foam from her knee brace, the patient also reacted to the wrist support she had been using at her computer keyboard at work (Figure 1B). The manufacturer of the knee brace confirmed the presence of diethylthiourea; the manufacturer of the wrist support would not disclose the presence of thioureas. Avoidance of neoprene and other products with thioureas has obviated the need for further therapy and the patient has been without dermatitis for 4 years.

Patient 2—A 49-year-old truck driver complained of a recurrent rash around his right knee ever since he was required to use a knee brace that circumscribed the leg above and below the knee. He had erythematous scaly plaques above and below the right knee that corresponded exactly with the rubber portions of the knee brace (Figure 2, A and B). He also had erythema and scaling on the dorsa of his hands. He was referred after a Thin-layer Rapid Use Epicutaneous Test® (T.R.U.E. Test) failed to identify a source of the rash. Test results to rubber allergens revealed positive reactions to thiourea and diethylthiourea. Both the rubber and foam parts of the brace tested positive. The patient's knee brace was confirmed to have neoprene rubber that contained diethylthiourea, as did the nylon adhesive used to attach the foam. After much effort, the patient succeeded in finding a brace that did not contain thioureas and thus did not cause dermatitis.

Patient 3—A 68-year-old woman with sleep apnea complained of a rash on her face and ears that had persisted for 1.5 years despite treatment with topical corticosteroids. She had symmetric erythematous patches on both superior helices of her ears and over the bony prominences of her cheeks (Figure 3A); there was no other skin involvement. Results of patch testing with the North American Contact Dermatitis Group (NACDG) standard allergens (Chemotechnique Diagnostics AB, Malmö, Sweden) performed on Finn chambers (Epitest Ltd Oy, Hyrylä, Finland) was entirely negative except for reactions to mixed dialkyl thioureas and *p*-phenylenediamine. Results of patch testing to fragrances and to the patient's personal care products was unremarkable. The patient did not react to black rubber mix or N,N-diphenyl-PPD, N-isopropyl-N-phenyl-PPD, or N-cyclohexyl-N-PPD. Thus, her reaction to *p*-phenylenediamine was not thought to be relevant. Patch testing to an expanded set of rubber allergens revealed positive

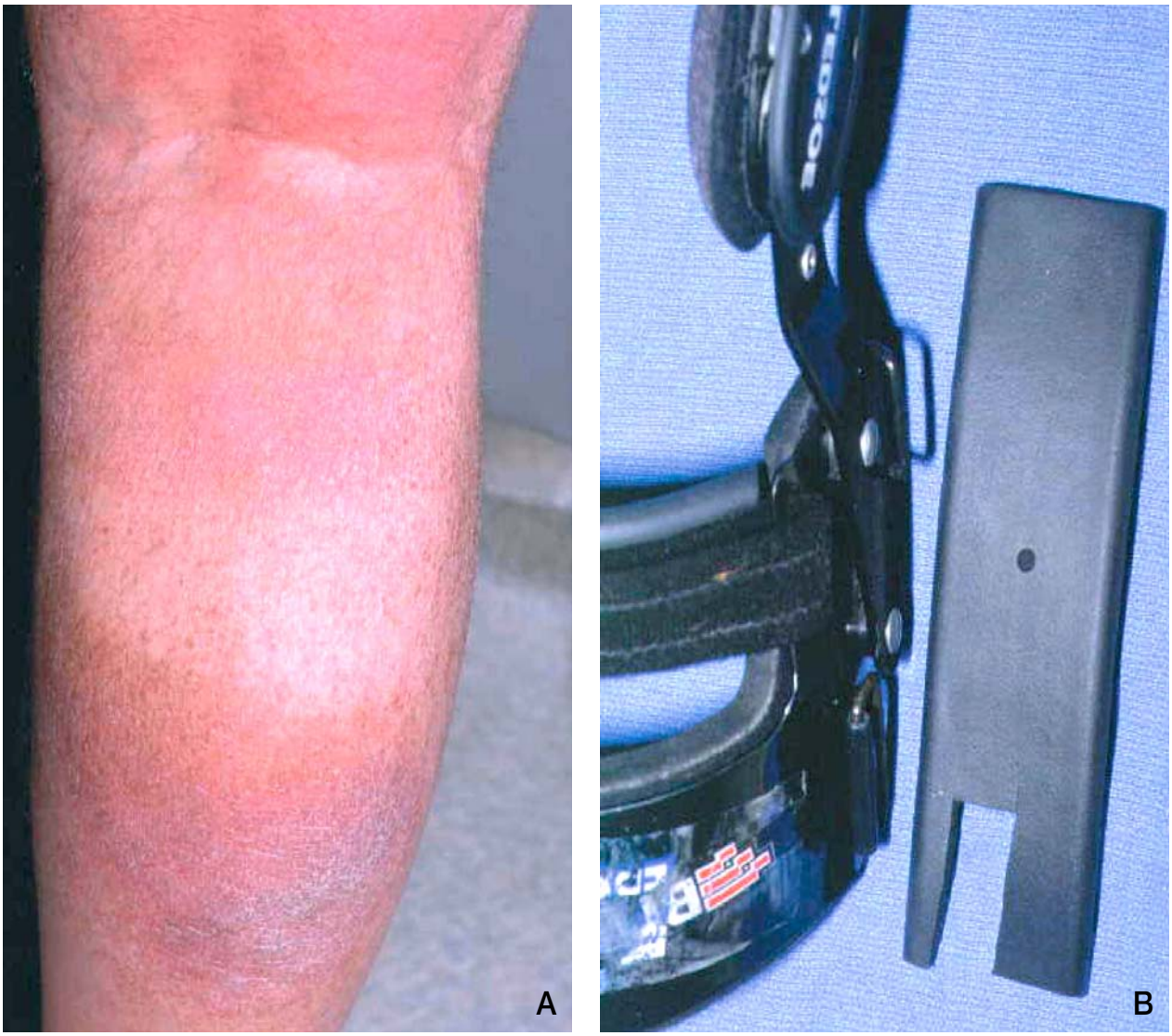

Figure 2. Posterior view of the right knee of patient 2 (A) and his knee brace (B).

reactions to diethylthiourea and dibutylthiourea. At night she wore a continuous positive airway pressure mask that attached with rubber straps around her ears and across her cheeks (Figure 3B). The mask strap also produced a strongly positive reaction. The manufacturer of the mask would not disclose information regarding the presence of thioureas in the rubber straps, but the patient's dermatitis resolved after she switched to a mask with all-cotton straps.

Thiourea-Induced Allergic Contact Dermatitis by Rubber Products

The most common allergens responsible for rubber allergic contact dermatitis (ACD) are thiurams, carbamates and diphenylguanidine (the carba mix allergens), mercaptobenzothioazole, other mercapto compounds, and phenylenediamines (in black or gray rubber).[1] Thioureas comprise a significant subgroup of rubber ACD allergens that has more recently been included in large cohorts of patch testing, such as the 1991 NACDG study, but are not included in the more widely used T.R.U.E. Test.

Thioureas are a group of chemicals that have long been used as rubber vulcanization accelerators.[2-11] Aromatic thioureas such as diphenylthiourea are now used in rubber production less commonly than alkyl thioureas such as diethylthiourea.[11] Although ACD due to thioureas is uncommon, its actual incidence remains uncertain. Studies examining sensitivity to thioureas have shown patch test reactivity ranging from 0.15% to 1.3%.[5,6,11-14] From 1992 to 1994, the NACDG study patch tested 3511 patients to mixed dialkyl thioureas (containing only diethylthiourea and dibutylthiourea); 3057 patients were tested from

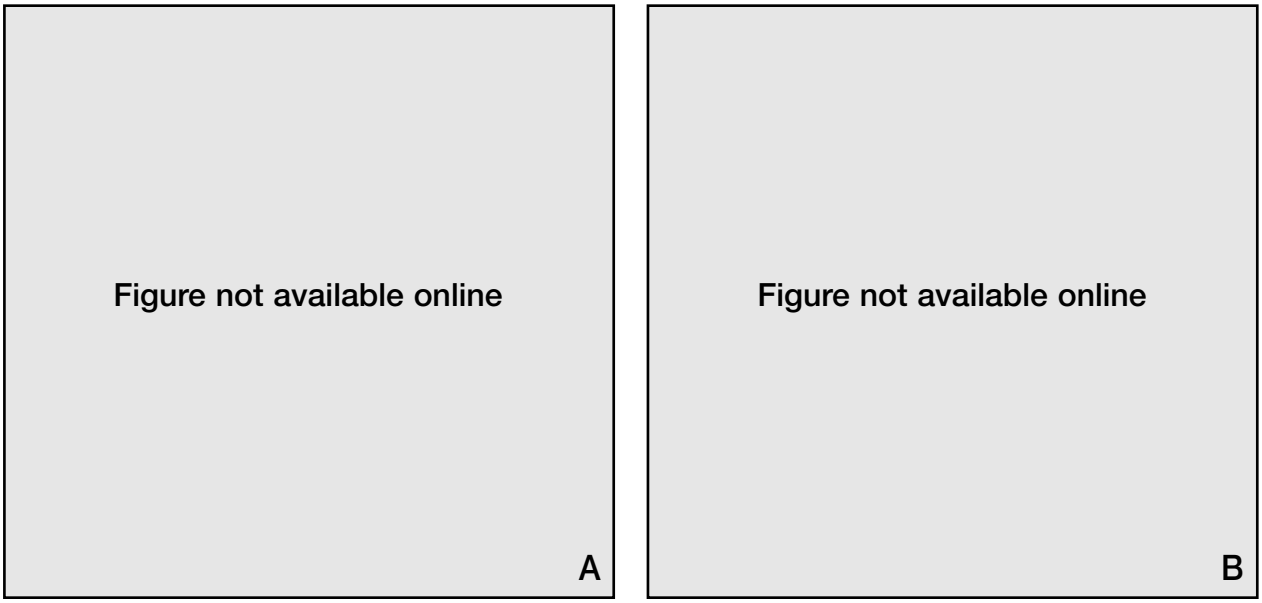

Figure 3. Patient 3 (A) and her continuous positive airway pressure mask (B).

1994 to 1996; and 4098 patients were tested from 1996 to 1998. The incidences found were 1.1%, 0.7%, and 1.3%, respectively.[13,14] The actual incidences of ACD to thioureas may be higher because the patch testing in these studies did not include complete panels of thiourea allergens and therefore may underestimate the disease incidence.

Our cases represent some typical characteristics of ACD to thioureas. In all 3 patients, the diagnosis of ACD was delayed—identification of the allergen took up to 3 years. In each case, high-grade rubber products were implicated. The most common single documented source in the literature is neoprene, by far. Neoprene is popular because of its properties of cushioning and resistance to fire, oil, and ozone.[1,9] This contributes to its widespread use in products such as orthopedic braces, wet suits and other diving accessories, athletic shoes and clothing, protective goggles and gloves, weather stripping, and adhesives. Thioureas are particularly efficient accelerators for the vulcanization of neoprene. Thus, they are still preferred over other accelerators in neoprene production.[5]

Analysis of the case studies reported in the literature (Table) suggests that screening for thiourea-induced rubber ACD would fail to diagnose 25% of patients if the test was performed with mixed dialkyl thioureas, such as that used by NACDG in its studies.[13,14] This mix is composed of diethylthiourea and dibutylthiourea (available from Chemotechnique Diagnostics). These data suggest that use of an expanded set of thiourea allergens that include diethylthiourea, dibutylthiourea, diphenylthiourea, ethylbutylthiourea, and ethylenethiourea may be required to detect thiourea-based rubber contact dermatitis.

Thiourea-Induced Allergic Contact Dermatitis by Copy Paper and Chemicals

Thioureas may be found in nonrubber sources including diazo copying paper. Diazo copying involves the irradiation of the diazo-sensitized paper and the coupling of diazonium salts to produce blue, black, or brown colors in the paper. Potential allergens include *p*-diethylaminobenzene diazonium chloride and thioureas.[1] Thioureas are used in diazo-sensitized papers and blueprints as antioxidants to prevent the discoloration of unexposed areas of the paper.[10,36,41,43,44] Thiourea, without additional substituted alkyl or aryl groups, is the cause of ACD with diazo papers; however, dimethylthiourea and trimethylthiourea have also been the causative allergens, although less commonly.[10,36-39,41-44] If copy papers or blueprints are suspected sources, thiourea should be tested. Of the 14 copy paper ACD cases reviewed that have sufficient data, 11 were positive for thiourea (79%). Dimethylthiourea also should be considered for patch testing because it was positive in all 3 cases tested that were negative for thiourea. Photosensitivity of thiourea has been discussed with regard to thiourea-related ACD, particularly in diazo paper exposures. Although thiourea may cause photosensitivity, there have been as many negative reports[11,39,42,49] as positive ones.[36,41,50]

Documented chemical sources of thiourea ACD include paint and glue removers, polyvinyl chloride

Patch Test Results of Reported Allergic Contact Dermatitis Cases Due to Thiourea Allergens*

Ref	Source of Allergic Contact Dermatitis	Positive Patch Test	Negative Patch Test	Other Thiourea Allergens	Standard Tray Positive Reactions
Present cases	CPAP mask straps	DBTU, DETU	DPTU		*p*-phenylenediamine
	Wrist support/ knee brace	DETU	DBTU, DPTU		Nickel, acrylates
	Knee brace	DETU	DBTU, DPTU		None
2	Rubber manufacturing	ETU	DBTU, DPTU, DETU		Nickel, cobalt
8	Rubber manufacturing	DETU			
15	Neoprene weather strips in car assembly plant (11 cases)	DETU	ETU		
3	Wet suit	DETU			None
16	Wet suit footgear	DBTU	DPTU, DETU		None
17	Wet suit	DETU	DBTU, DPTU		Colophony
18	Neoprene wet suit, diving gloves, leg warmers, spectacle band	EBTU	DBTU, DPTU, DETU, DMTU		None
19	Neoprene wet suit	DPTU	TU, DBTU, DETU, ETU		Colophony
20	Wet suit	DBTU, DETU	DPTU		None
21	Slimming suit (neoprene)	DPTU	DBTU, DETU		Carba mix, methylchloroiso-thiozolinone, methyliso-thiazolinone
22	Swim goggles	DBTU, DETU	DPTU		None
23	Swim goggles	DETU, EBTU			
4	Athletic shoe insole of neoprene (8 cases)	EBTU			None

(continued)

Ref	Source of Allergic Contact Dermatitis	Positive Patch Test	Negative Patch Test	Other Thiourea Allergens	Standard Tray Positive Reactions
12	Athletic shoes				
	Tongue/lining	ETU	DBTU, DPU, DETU		Nickel, quinolone
	Insole/lining	DPTU, ETU	DBTU, DETU		Colophony
	Insole/foam	DBTU, DPTU, ETU	DETU		Mercapto mix
24	Athletic shoe neoprene insole (10 cases)	TU (1/7), DBTU (4/7), DETU (7/7), DMTU (3/7), ETU (0/3), EBTU (10/10)			None
25	Safety shoes	DETU	DBTU, DPTU		None
5	Neoprene gloves	DPTU	DBTU, DETU, ETU		
	Gloves	DPTU	DBTU, DETU, ETU		
	Gloves/fungicide?	DPTU	DBTU, DETU, ETU		
	Dentistry work	ETU	DBTU, DPTU, DETU		
	Knee brace	DETU	DBTU, DPTU, ETU		
	Rubber gloves	DBTU	DPTU, DETU		Dichromate, mercapto/thiuram/carba mix, *p*-phenylenediamine
	Rubber gloves	DBTU, DPTU, DETU			Caine mix, *p*-phenylenediamine
26	Neoprene gloves	DPTU	DBTU, DETU, ETU		Benzocaine, mercury
27	Neoprene knee brace	DPTU	DBTU, DETU, ETU		None
28	Rubber knee brace	DETU	DBTU, DPTU		None
29	Knee brace	DETU	DBTU, DPTU, ETU		Caine mix
	Ankle brace	DETU	DBTU, DPTU, ETU		None

(continued)

Ref	Source of Allergic Contact Dermatitis	Positive Patch Test	Negative Patch Test	Other Thiourea Allergens	Standard Tray Positive Reactions
7	Knee heat retainer	DPTU	DBTU, ETU		None
	Knee heat retainer	DPTU, ETU	DBTU		Carba mix and benzocaine
	Knee heat retainer	DPTU, ETU	DBTU		None
	Knee heat retainer	DPTU, ETU	DBTU		None
	Knee heat retainer	DPTU, ETU	DBTU		None
	Elbow heat retainer	DPTU, ETU	DBTU		Colophony
	Elbow heat retainer	DBTU, DPTU, ETU			Carba mix
30	Neoprene elbow brace	DPTU			Cyclohexyl-thiophthalimide, tetramethylthiuram disulfide
31	Elbow brace	DETU			Balsam of Peru, paraben
	Knee brace	DPTU, DETU			Colophony
	Protective glasses	DPTU, DETU			None
32	Ankle brace	DETU	DBTU, DPTU		Diphenylguanidine
33	Neoprene foam sleeve of limb prosthesis	DETU	DBTU, DPTU		None
34	Neoprene straps of CPAP mask			Mixed dialkyl thioureas	None
35	Neoprene straps of CPAP mask	DETU	DBTU, DPTU		None
10	Diazo paper	DETU, DMTU, EBTU	TU, DBTU, DPTU	Trimethyl thiourea	None
	Diazo paper	DMTU	TU, DBTU, DPTU, DETU, EBTU		None
	Diazo paper	DMTU	TU, DBTU, DPTU, DETU, EBTU		None
	Diazo paper	TU	DBTU, DPTU, DETU, DMTU		None

(continued)

Ref	Source of Allergic Contact Dermatitis	Positive Patch Test	Negative Patch Test	Other Thiourea Allergens	Standard Tray Positive Reactions
36	Diazo copy paper	TU			None
	Diazo copy paper	TU			Formaldehyde
37	Diazo copy paper	TU			None
38	Diazo copy paper	TU	DBTU, DPTU, DMTU, ETU		None
39	Diazo copy paper	TU, DMTU			Hydroxylammonium chloride and sulfate
40	Diazo copy paper	TU			None
41	Photocopy paper	TU			
	Photocopy paper	TU			
42	Photocopy paper	TU			None
43	Plan printing paper	TU			None
44	Diazo-sensitized paper	DMTU			None
45	Phonecard thermocoating	DBTU			Phenylmercaptoborate, mercaptoamide chloride, amalgam
11	Adhesive tape polyvinylchloride backing (28 cases)	DPTU			
46	Adhesive tape	DPTU			
	Adhesive tape	DPTU			
	Adhesive tape	DPTU			
47	Paint remover	DBTU	DPTU, DETU, ETU		None
	Paint remover	DBTU	DPTU, DETU, ETU		Nickel
48	Paint and glue remover	DBTU			None
49	Silver polish	TU			None
50	Acidic detergent	DETU	DBTU		None

*Ref indicates reference; CPAP, continuous positive airway pressure; DBTU, dibutylthiourea; DETU, diethylthiourea; DPTU, diphenylthiourea; ETU, ethylenethiourea; EBTU, ethylbutylthiourea; DMTU, dimethylthiourea; TU, thiourea.

adhesive tape backing, silver polish, acidic detergent, and a protective thermocoating for phone cards (Table). Thioureas are sometimes used as antioxidants in silver polish, adhesive tape backing, and acidic detergents.[11,49,50] Diabutylthiourea and diphenylthiourea allergenicity occurs more commonly in these reports of chemical ACD than diethylthiourea or thiourea. Persulfate bleach accelerator is an isothiouronium salt that has been implicated in cases of ACD to motion picture film developer.[51,52] References have been made to fungicides causing thiourea-related ACD.[53] Although dithiocarbamates in fungicides may be metabolized to ethylenethiourea,[2] there have been no reports of fungicide ACD in humans who have been documented as positive to both thiourea and the fungicide in question through patch testing. In the study that introduced this idea, the association between fungicides and ethylenethiourea was weak.[53]

In these cases of chemical ACD, the decision regarding which allergens to include in patch testing must be based on the setting in which the ACD occurs. Of the 37 thiourea-induced chemical ACD cases reviewed, 31 patients patch tested positive to diphenylthiourea, 4 to dibutylthiourea, 1 to diethylthiourea, and 1 to thiourea. This data may be skewed by the large number of cases in one study of adhesive tape ACD, which is often due to rubber compounds or rosins in the adhesive tape. Exposure to paints and paint strippers indicates a different set of allergens or irritants; almost all cases would be detected if those patients affected were patch tested with mixed dialkyl thioureas and diphenylthiourea.

Conclusion

Thiourea-induced ACD may present as an allergy to high-grade rubber products, particularly neoprene. The T.R.U.E. Test allergen set does not currently include thiourea allergens and will not detect thiourea-induced ACD. Patch testing with mixed dialkyl thioureas will only identify about 75% of patients with allergy to thiourea-containing rubber products. Thiourea-induced ACD also may involve other products, most notably diazo papers, and thiourea is more likely to be the causative allergen. Thioureas should be considered as a source of ACD when patients present with ACD to rubber products of any kind, especially when they contain neoprene.

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