

Formaldehyde-related textile allergy: an update

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Part I of this study explores whether clothing today contains formaldehyde levels likely to cause contact allergy in formaldehyde-allergic patients. Part II of this study examines whether current reactions to textiles may be due to allergy to textile resins and whether individuals with formaldehyde-related textile allergy will react to the newer low formaldehyde resins used in the textile industry. Part I: free formaldehyde was measured in 16 fabric specimens produced in the US and overseas. Additionally, since the textile industry has moved to the use of newer methods for measuring fabric formaldehyde content, the newer methodology was compared with the older methods used in the medical literature. Part II: 10 subjects with known textile contact allergy were patch tested to available Chemotechnique textile resins and 6 new low-formaldehyde resins used by the textile industry. Part I: 8 fabric specimens yielded no detectable formaldehyde and 7 specimens yielded <200 ppm free formaldehyde, using Schiff's reagent and Merck testing methods. 1 specimen showed approximately 2000 ppm formaldehyde, as measured by the Merck test, but only 24 ppm free formaldehyde when retested by the method described in Japanese Law #112. Part II: all subjects reacted strongly to formaldehyde and DMDHEU (the predominant resin currently used in textiles). 6 subjects reacted to EUMF. 2 subjects had mild reactions to the newer low-formaldehyde resins and 1 to the non-formaldehyde Fixapret NF. Our results suggest that most clothing today yields free formaldehyde levels unlikely to cause contact allergy in formaldehyde-allergic individuals. Japanese method #112 is the recommended methodology to measure free formaldehyde in future studies. DMDHEU may now represent the main cause of textile allergy and may be a better screen than EUMF for this problem. Newer resins yielding fabrics with <75 ppm free formaldehyde may cause occasional reactions, but are more likely to be tolerated by individuals with textile contact allergy. Treatment of these individuals should be directed at identification of reliable sources of garments utilizing these newer resins.

Key words: allergic contact dermatitis; textiles; clothing; formaldehyde; formaldehyde resins; glycolated dimethylol dihydroxyethylene urea resins; chemical analytical methods; prevention.
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Accepted for publication 11 February 1998.

Allergic contact dermatitis due to clothing is one of the most miserable dermatologic conditions. Affected individuals are often almost erythrodermic and experience persistent intractable pruritus which can be debilitating. Since 1926, formaldehyde-containing resins have been used in the clothing industry to make wrinkle-resistant fabrics. These resins employ methylol reactive groups to crosslink cellulose fibers in cotton, linen, and rayon (cellulose-based natural polymer) garments. Formaldehyde-related contact allergy to clothing is still a concern today, despite efforts by the textile industry in the US to move to the use of resins imparting fabrics with lower amounts of free formaldehyde (1, 2). The industry now claims that the average level contained by textiles made in the US

is approximately 100–200 ppm free formaldehyde (2).

Part I of this study was designed to explore whether reported contact allergy to textiles today is due to free formaldehyde. Additionally, since the textile industry has moved to the use of newer methods for measuring fabric formaldehyde content, we compared the newer methodology with the older methods used in the medical literature.

It has previously been reported that some individuals will experience allergic contact dermatitis from the actual formaldehyde resins used by the textile industry (2). However, since the date of that report, fabric manufacturers have increasingly moved to the use of methylated and glycolated dimethylol dihydroxyethylene urea (DMDHEU)

resins. Part II of this study will look at whether allergic contact dermatitis due to the newer resins employed by the textile industry occurs.

Materials and Methods

Part I: 16 1-g samples of cellulose-containing fabrics were selected randomly from a local clothing retailer for testing. 9 specimens were manufactured in the US and 7 samples were manufactured overseas (in Indonesia, Taiwan, Lesotho, Brunei, and Thailand).

All samples were tested using the Schiff reagent method (3) and with a commercially available Merck formaldehyde test (ordered from Wilkens-Anderson Co., Chicago, IL). The Merck test is performed by immersing a 1×1 cm piece of fabric in 5 ml of 0.1N HCl, heating the specimen in a water bath at >66°C for 10 min, allowing the solution to cool to room temperature, adding 10 ml concentrated NaOH to the supernatant, dipping a test strip into this mixture and comparing the color of the strip to a standardized color chart, giving a semi-quantitative measure of fabric formaldehyde content that can be converted to ppm.

Initial testing yielded 1 fabric specimen with a very high level of formaldehyde by current standards. This specimen was sent to an independent commercial laboratory and retested using the method adopted by the textile industry as described in Japan as The Law For the Control of Household Goods Containing Harmful Substances: Law #112 of 1973 (4). In this method, a 2.5 g specimen of fabric in 100 ml water is placed in a 40°C water bath for 1 h shaking often, 5 ml of supernatant is added to 5 ml of acetyl acetone reagent (150 g ammonium acetate + 3 ml acetic acid + 2 ml acetyl acetone + water qsad 1000 ml) and placed in the water bath for 30 additional min. After cooling at room temperature for 30 min, the maximum absorbance between 412 and 415 nm is determined, compared to a blank containing 5 ml of the acetyl acetone reagent and 5 ml water, and then compared to samples with known formaldehyde content. The resulting curve is used to determine formaldehyde content of test samples.

Part II: 10 out of 12 total patients presenting to a busy contact dermatitis practice with positive patch test reactions to the older formaldehyde resins over the past 3 years were enrolled in this study. During this time period, approximately 1200 total contact allergy cases were seen in this clinic. These patients included 9 men and 1 woman between 24 and 77 years of age. All subjects were patch tested to standard commercial allergens from Chemotechnique Diagnostics (Malmö, Sweden), including formaldehyde (1% aq.), dimethylol dihydroxyethylene urea (DMDHEU) (Fixapret CPN) (4.5% aq.), dimethylol propylene urea (Fixapret PH) (5% aq.), tetramethylol acetylenediurea (Fixapret 140) (5% aq.), ethyleneurea melamine formaldehyde (EUMF) (Fixapret AC) (5% pet.), urea formaldehyde (Kaurit S) (10% pet.), and melamine formaldehyde (Kaurit M70) (5% pet.). In addition, all subjects were patch tested with 5% aqueous solution of newer low-formaldehyde-releasing resins, including Fixapret ECO and Fixapret NF (non-formaldehyde) (BASF Corporation, Charlotte, NC, USA), Freerez PKF and Freerez CLD (Freedom Textile Chemicals Company, Charlotte, NC), and Permafresh EFR and CPD 3078-28A (Sequa Chemicals, Inc., Chester, SC). The patches were applied to unaffected skin of the upper back using standard Finn Chambers (Hermal), removed at 2 days, read at 3 days, and graded according to standard patch testing definitions.

Results

Part I: 6 out of 9 fabrics manufactured in the US showed no detectable formaldehyde, using both the Schiff's reagent and Merck testing methods (Table 1). 2 specimens showed a mild (light purple) reaction with Schiff's reagent and approximately 100 ppm formaldehyde with the Merck test. The remaining sample (a 100% cotton woven fabric) showed approximately 2000 ppm formaldehyde as measured by the Merck test and a strong reaction when tested using the Schiff method. Since it was unlikely that a light 100% cotton shirt fabric made in the United States today would contain this high

Table 1: Summary of Merck formaldehyde testing of textile specimen specimens

Manufacturing site	No. specimens		
	No formaldehyde detected	<200 ppm formaldehyde	>200 ppm formaldehyde
US	6	2	1*
Overseas	2	5	0

* This specimen was tested to have only 24 ppm free formaldehyde using the method described in Japanese Law 112.

Table 2. Summary of reactions to textile resins

Textil resins	Type	Subjects									
		1	2	3	4	5	6	7	8	9	10
formaldehyde		++	+++	++	++	+	++	++	+++	+++	+++
DMDHEU (Fixapret CPN)	O	+	+++	+	+++	++	++	++	+++	+++	+++
EUMF (Fixapret AC)	O	+	+++	+	++				+++	+++	
urea formaldehyde (Kaurit S)	O	+	+		++					+++	+
melamine formaldehyde (Kaurit M70)	O	+	+++	+	++				+	+++	+++
dimethylol propylene urea (Fixapret PH)	O	+	+++							+++	+
tetramethylol acetylenediurea (Fixapret 140)	O		+++	+	++	++		++	+++	+++	+++
Fixapret ECO	N					+					
Freerez PKF	N					+					
Freerez CLD	N		+			+					
Permafresh EFR	N		+			+					
CPD 3078-28A	N					+					
Fixapret NF	NF					+				++	

Type O: older resin. Type N: newer resin. Type NF: non-formaldehyde.

Table 3. Comparison of methods used to determine formaldehyde content of textiles

	The Schiff reagent method	Merck test	Chromotropic acid method	Modified chromotropic acid method	Japanese Law 112
temperature used to treat fabric	>66°C	>66°C	100°C	25°C	40°C
fabric exposed to acid?	yes	yes	no	no	no
supernatant exposed to acid	yes	yes	yes	yes	no

a level of free formaldehyde, the fabric was sent to an independent commercial textile laboratory and retested. The fabric showed 24 ppm free formaldehyde when measured by the method described in Japanese Law #112.

2 of the fabrics manufactured overseas showed no detectable formaldehyde using both tests. The remaining 5 fabrics from garments manufactured overseas showed 200 ppm or less formaldehyde as measured by the Merck test. 2 of these specimens also showed a slight reaction using the Schiff's method.

Part II: All of the subjects tested reacted to formaldehyde and DMDHEU (Table 2). 6 of the 10 subjects reacted to EUMF. Only 2 of the subjects reacted to the newer low-formaldehyde resins. 1 of these subjects had + reactions to all 5 of the new low-formaldehyde resins and a + reaction to the non-formaldehyde Fixapret NF. The other subject had a + reaction to Freerez CLD and a + reaction to Permafresh EFR. The latter individual had +++ reactions to formaldehyde and 5 of the other formaldehyde-related textile resins. A 3rd subject did not react to any of the newer low-form-

aldehyde resins; however, he had a ++ reaction to the non-formaldehyde Fixapret NF.

Discussion

Allergic contact dermatitis due to formaldehyde present in textiles was commonly reported in the literature in the 1950s and 1960s (5–8). In recent years, the textile industry has attempted to lower the amount of free formaldehyde in wearing apparel and bedding fabrics, and reports of contact allergy to textiles caused by formaldehyde have become less common (4, 9, 10). The formaldehyde-based textile resins use N-methylol reactive groups to crosslink cellulose fibers in fabrics, according to the following reversible reaction (11):



This reaction employs an acid catalyst and requires heat. Although this reaction is designed to polymerize all available formaldehyde in the fabric, free formaldehyde can be present in the finished fabric for 2 reasons. First, some acid catalyst may remain

in the fabric and free formaldehyde can then be generated when the fabric is exposed to heat, as is encountered when in contact with skin under normal wearing conditions (11). In addition, some of the resin may not fully crosslink and can degrade when exposed to chlorine in laundry bleach (11).

The 2 most common methods for measuring formaldehyde in fabrics found in the medical literature have been the Schiff reagent method and the chromotropic acid technique, both of which generate formaldehyde from heated fabric samples (3, 11). Additionally, the Schiff reagent method exposes the fabric to acid. Since acid and high temperature can cause depolymerization of some or all of the cross-linked fabric resin, it has been suggested that these methods measure both free and polymerized formaldehyde and can sometimes overestimate the free formaldehyde content of fabric under normal wearing circumstances (3, 11).

Some investigators have used variations of the chromotropic acid technique, which do not expose fabric to acid and where the fabric is treated at room temperature, to obtain a more accurate estimate of fabric free formaldehyde content (12, 13). More recently, the textile industry has used newer techniques which attempt to estimate the amount of free formaldehyde released by fabric under normal wearing circumstances. The current standard method used by the textile industry is described in the Japanese Law for the Control of Household Goods Containing Harmful Substances: Law #112 of 1973 (4). This method does not expose fabric samples to acid and treats the fabrics at body temperature to approximate the conditions experienced when fabric comes in contact with skin. A comparison of techniques used to measure formaldehyde in fabrics is provided in Table 3.

In Japan, textile fabrics are required by law to contain less than 75 ppm free formaldehyde, as measured by the method described in Law #112 (4, 14). The threshold at which individuals allergic to formaldehyde will react to fabrics has been estimated at around 500 ppm free formaldehyde, using a modification of the chromotropic acid technique not employing acid or high temperature (13). However, some individuals may react to patch testing with formaldehyde at concentrations as low as 30 pp (15). Although there is no regulation of free formaldehyde content in fabrics manufactured in the US, OSHA regulation 29 CFR 1910-1048 regulates the exposure limit for workers in the domestic textile industry to 1 part formaldehyde per million parts of air as an 8-h time-weighted average (16). Because of this regulation, the textile industry in the US has moved to resins imparting fabrics with lower amounts of free formaldehyde and now

claims that the average level contained by textiles made in the United States is approximately 100–200 ppm free formaldehyde (2).

The earliest formaldehyde resins were based on urea formaldehyde (dimethylol urea) and melamine and treated fabrics contained high levels of free formaldehyde (2, 11). In the 1960s, a large % of textile manufacturers moved to the use of dimethylol dihydroxyethylene urea (DMDHEU), which yielded fabrics with approximately 500 ppm free formaldehyde (2, 9). Since the 1970, most manufacturers have moved to the use of glycolated or methylated DMDHEU resins, which yielded fabrics with less than 300 ppm free formaldehyde (9). Fabrics treated with the latest modified DMDHEU resins predictably contain less than 75 ppm free formaldehyde (9). In addition, there are now resins available that do not employ formaldehyde, however, these resins are quite expensive and have found popularity primarily in the infant and children's clothing market (9).

All except for 1 of the specimens tested in this study demonstrated formaldehyde content of less than 200 ppm formaldehyde, as measured by the Merck test. This is well below the estimated reaction threshold for most formaldehyde-allergic individuals reported in earlier studies (13). 1 specimen showed high formaldehyde content when measured by the Merck method, however, this specimen showed only 24 ppm free formaldehyde when measured by the method described in Japanese Law #112. This discrepancy highlights that testing methods using acid and high temperatures measure both free and polymerized formaldehyde and may sometimes grossly overestimate the true free formaldehyde content of fabric (3). The Schiff reagent and Merck methods may still be useful as easy office methods to identify fabrics with high formaldehyde content to avoid. However, it must be realized that some fabrics identified in this manner will yield inaccurately high estimates of free formaldehyde (3). Our results also indicate that fabrics being produced overseas appear also to be using resins yielding <200 ppm free formaldehyde.

In Part II of this study, all of our subjects reacted to formaldehyde, indicating that they will probably experience adverse reactions to fabrics containing high levels of free formaldehyde. However, Part I of the study indicated that most fabrics do not contain enough free formaldehyde for this to occur (3). All of our subjects also reacted to DMDHEU. It seems likely that reactions to DMDHEU are the cause of most current reports of textile allergy, since this is the predominant resin being used by the clothing industry today. Only 6 of our subjects reacted to EUMF. Previously,

EUMF was the suggested screening agent for textile resin allergy. The increased use of DMDHEU by the textile industry suggests that this agent may now be a better screening substance for textile resin allergy.

Our results also suggest that reactions to the newer low-formaldehyde resins and non-formaldehyde resins are much less common, and generally of lesser intensity, than reactions to the older formaldehyde resins, which release greater amounts of free formaldehyde. Only 2 of the 10 subjects in this study had reactions to the newer low-formaldehyde resins. 1 additional subject had a reaction to the non-formaldehyde Fixapret NF resin. All 3 of the subjects who reacted to the newer textile resins had multiple stronger reactions to older textile resins.

Conclusions

Despite the low levels of free formaldehyde present in most clothing today, there may still be some garments sold in the US. which yield high enough free formaldehyde levels to cause allergic contact dermatitis. However, our results demonstrate these garments are probably uncommon and probably do not explain current reports of clothing-related contact allergy. We recommend that future studies measuring free formaldehyde in textiles use the method described in Japanese Law #112.

Contact allergy to DMDHEU is probably the main cause of current reports of textile reactions. Reactions to the newer low-formaldehyde and non-formaldehyde textile resins are less common and less severe when they do occur. Efforts should be directed towards finding reliable sources of clothing using only the newer textile resins. Patients with formaldehyde-related textile allergy who wear only clothing made with these newer resins should experience either elimination or significant reduction of their allergic symptoms.

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