

Factors Associated with Textile Pattern Dermatitis Caused by Contact Allergy to Dyes, Finishes, Foams, and Preservatives

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KEYWORDS

• Formaldehyde • Dermatitis • Textile allergies

Allergic contact dermatitis because of textiles is most severe in areas of perspiration and friction where garments have greatest skin contact, such as the axillary lines, medial thighs, posterior neck, and antecubital and popliteal folds. Because there are only a few textile finish resins that are widely used, sensitized patients are usually exposed from many of their garments and tend to have chronic dermatitis. There are many more textile dyes, and sensitized patients may be allergic to only a single item of clothing causing a more acute presentation. Allergic contact dermatitis because of textiles in furniture usually presents on the posterior thighs and forearms.

Essentially all textile materials used in apparel and furniture products contain dyes and finishes to impart color and a wide range of performance attributes. These textile materials can be natural or nature-based, like cotton, wool, silk, cellulosic and cellulose acetate; or synthetic like nylon, polyester, and acrylic. As a result of the chemical nature of these materials and the essentially infinite palette of colors desired by the consumer, there are a substantial number of dyestuffs available to impart the desired coloration.

A dye is an organic compound composed of a chromophore, the colored portion of the dye molecule, and an auxochrome, which slightly alters the color. The auxochrome makes the dye

soluble and is a site for bonding on to the textile material (fiber). Dyes are molecules that can either be dissolved in water or some other carrier so that they will penetrate into the fiber. Any undissolved particles of dye remain on the outside of the fiber, where they can bleed and are sensitive to surface abrasion.

Dyes are classified by chemical composition or method of application. **Table 1** lists major dye classes along with the fibers that they are used to color.¹

Hatch reported that as early as 1869 dyes were suspected to be a cause of dermatitis when Wilson suggested that a French soldier's foot lesion was because of his red aniline dyed socks.^{2,3} Since that time there has been a substantial body of research that connects dermatitis to textile dyes exposure.

Hatch presented a table of early references from 1869 to 1950 for dermatitis caused by dyes on clothing and this work continues to the present by many researchers.

Recently, Lazorov and colleagues⁴ looked at 286 consecutive dermatitis patients in Israel (190 females and 96 males) and found a significant number of patients' allergy to the following commonly used textile dyes and permanent press finishes: 12 to Disperse Blue 106, 21 to Disperse Blue 124, 9 to ethylene urea melamine

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Table 1
Major dye classes

Dye Class	Fabrics
Acid (anionic)	Wool, silk, modified rayon, modified acrylic, and polyester
Azoic or Azo	Cotton and polyester
Cationic (basic)	Acrylics, polyester, nylon, and direct prints on acetate and discharge prints on cotton
Developed (direct)	Cellulosic fibers including cotton
Direct (substantive)	Cellulosic fibers including cotton
Disperse	Most synthetic fibers including nylon and polyester
Mordant	Wool, silk, modified rayon, modified acrylic, and polyester
Reactive	Cotton and other celluloseics, wool, silk and nylon
Sulfur	Heavyweight cotton fabrics (mostly used for black color)
Vat	Cotton and cotton/polyester blends

formaldehyde, 7 to urea formaldehyde, and 7 to melamine formaldehyde.

EXPOSURE OF SKIN TO TEXTILE DYES AND FINISHES

Many clothing items are in direct contact with the skin. During contact there can be perspiration which involves moisture transport between the skin and the dyed and finished clothing items. Although modern dyes and finishes are chemically bound to the fibers in the clothing, there is always the possibility that residual dye (dye bleed) and finish are released and contact the skin. Degree of colorfastness can be a measure of dye bleed.

Textile materials are a capillary and porous material with different pore sizes, and can be saturated with both liquid and gaseous water during wear. The transportation of perspiration through this material at different temperatures is a very complex process, which can involve convection,

capillary flow, penetration, molecular diffusion, evaporation, and solidification.

The transport of perspiration through clothing from the surface of human body is shown in **Figs. 1** and **2**. This process includes mass and heat transfer, as a temperature difference during the moisture (perspiration) transfer through the clothing exists. During the heat and mass (perspiration) transfer through the clothing medium, there generally exist 2 states of water phase, gaseous and liquid, and consequently several different interfaces between perspiration and clothing.⁵

These phenomena of moisture transfer and subsequent release of dyes from the textile material can be quantified and characterized as colorfastness. Colorfastness is commonly measured according to the American Association of Textile Chemist and Colorists (AATCC) standard test method 15 “Colorfastness to Perspiration.”⁶ The principle involves a specimen of dyed textile in contact with other fibrous materials. For color transfer, the test specimen is wetted out in

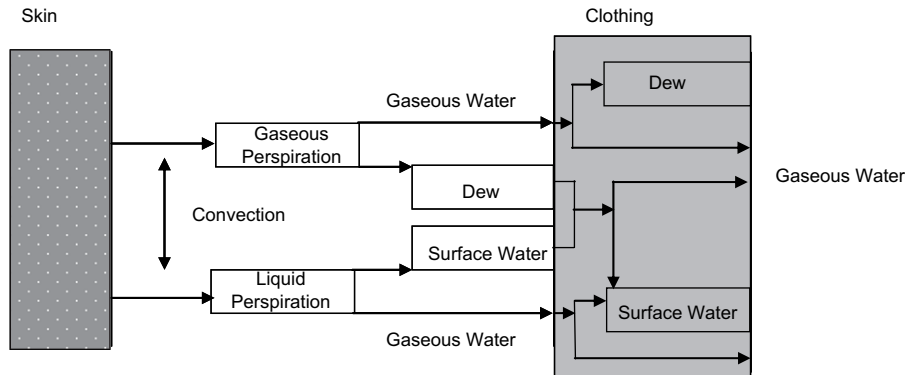


Fig. 1. Transport of perspiration through clothing.

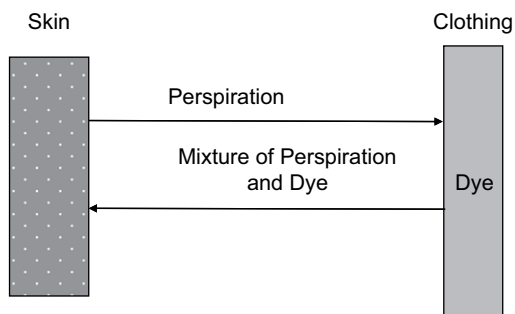


Fig. 2. Equilibrium mixing of perspiration and residual dye.

simulated acid perspiration solution, subjected to a fixed mechanical pressure and allowed to dry slowly at a slightly elevated temperature. After conditioning, the specimen is evaluated for color change and other fiber materials are evaluated for color transfer. An excellent review of the relationship between dye structure and fastness properties is provided by Giles and colleagues.⁷

DYE CLASSES OF CLINICAL INTEREST

Hatch and Maibach conducted a seminal clinical review of textile dye dermatitis.⁸ It was found that the incidence of dye dermatitis varied from 1% to 15.9% depending on the country, patient sample, and number of dyes in the patch test series. Disperse Blue 106 and Disperse Blue 124 were the strongest clothing dye sensitizers. Disperse dyes with azo and anthraquinone structures were the most common dye sensitizers.

Today, worldwide there are 2 classes of dyes that are widely recognized as having the potential to cause allergic contact dermatitis and possibly cancer. These 2 dye classes are azoic (azo) and disperse dyes. In the European Union their use is regulated by law; in the United States, at this time, there exists only voluntary regulation by those companies agreeing to regulate their use.

Azo Dyes

Azo dyes are characterized by a chromophoric azo group $-N=N-$, whose nitrogen atoms are linked respectively to sp^2 -hybridized carbon atoms. At least 1 of these carbon atoms belongs to an aromatic carbocycle (usually a benzene or naphthalene derivative) or the terocycle (eg, pyrazolone, thiazole), whereas the second carbon atom adjoining the azo group may also be part of an enolizable aliphatic derivative (eg, acetoacetic acid). The most common types of azo dyes can be summarized as follows:

aryl- $N=N$ -R, where R can be an aryl, heteroaryl, or $-CH=C(OH)$ -alkyl

As a result of the simple nature of the synthesis, usually in aqueous medium, and the almost unlimited choice of starting products, an extremely wide variety of azo dyes is obtainable. The number of combinations is further increased by the fact that a dye molecule can contain several azo groups. This diversity of inexpensively produced azo dyes permits a wide spectrum of shades and fastness properties suitable for use on a variety of textile substrates.

Depending on the number of azo groups, the azo dyes are called monoazo, disazo, trisazo, tetraakisazo dyes and so on, and those with 3 or more azo groups, polyazo dyes. The structure of an azo dye can be described by means of typical azo structural formulas such as those shown in **Figs. 3** and **4**.

Most azo dyes contain only one azo group, but some contain two (disazo), three (trisazo) or more. In theory, azo dyes can supply a complete rainbow of colors. However, commercially they tend to be used to produce more yellows, oranges and reds than any other colors.

Mechanism of Azo Dye Allergic Reaction

Hatch and Maibach reported that individuals who develop clothing dye dermatitis are rarely sensitized to the dye by repeated wearing of garments containing the dye.⁸ Rather the skin is sensitized by either repeated exposure to the same dye in another product (primary sensitizer) or to a closely related chemical compound (cross sensitizer). Thus, sensitization and the latent or incubation period in the development of allergic contact dermatitis may have occurred before the wearing of the offending garment. Hatch and Maibach conclude that for individuals who are sensitive to azo dyes, paraphenylenediamine (PPD), a compound chemically related to azo dyes, is often the sensitizer. They further conclude that most of the positive reactions were from the disperse dyes with monoazo symmetric structures. Saunders and colleagues⁹ reported a patient that developed a textile dye allergy following sensitization to PPD from a temporary tattoo. It was reported that PPD can be added to a temporary tattoo to produce a darker than normal color and this is often referred to as "black henna." Mayer, in his seminal papers, provided an explanation of

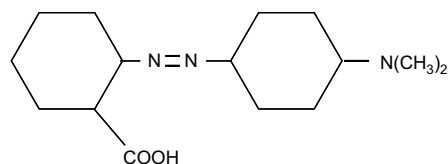


Fig. 3. Chemical structure of Methyl Red (MR).

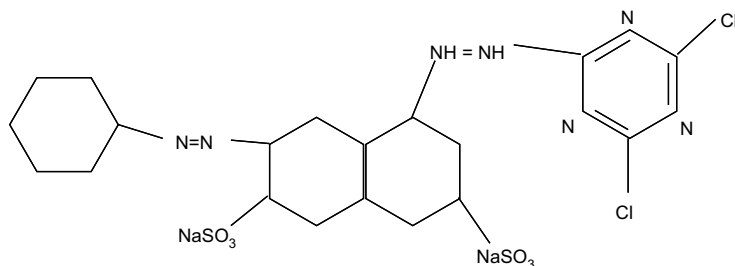


Fig. 4. Chemical structure of Procion Red Mx-5B.

cross hypersensitivity of PPD to azo dyes and the results were translated by Dobkevitch and Baer.^{10–13} The common chemical basis is the quinine structure. It was hypothesized that PPD can be oxidized at skin cells to quinonediimine. Further, some azo dyes are converted to quinonediimines by way of metabolism to PPD. The mechanism of conversion from a typical azo dye (4-aminoazobenzene) to aniline and PPD and then the conversion from PPD to quinonediimine is depicted in Fig. 5.

The azo dye is reduced to 2 amines at the azo linkage, the resulting amines depending on the structure of the original compound. The split amines then undergo further reaction (ie, oxidation) and are then converted into quinonediimines. This reduction mechanism to aromatic amines is also sometimes referred to as cleavage and azo cleavage is suspected as causing some azo dyes to be carcinogenic.

Su and colleagues¹⁴ report that the finding of multiple azo dye sensitivities may represent concomitant sensitization or cross-reactivities. Four groups of azo dyes have been described, based on their chemical structure: (1) aminoazobenzenes, (2) PPD, (3) thiazol-azoly-PPD,

and (4) benzothiazol-azoly-PPD. Cross-sensitivity between the aminoazobenzene Disperse Orange 3 and its metabolite PPD is common. Although cross-sensitivity between Disperse Orange 3 and the aminoazobenzenes Disperse Red 1 and Disperse Red 17 has been described, PPD does not generally cross react with these latter 2 aminoazobenzenes.

There is substantial worldwide concern, and in some cases standards and regulations, associated with the use of azo dyes in textiles, apparel, and home furnishings. In 1992 the European Union published a Directive (2002/61/EC) to restrict the marketing and use of certain dangerous substances and preparations (azo colorants) in textile and leather products.¹⁵ The legislation is relevant for all products made of textile and leather, or in which textile and leather is used, and which come into direct and prolonged contact with the skin and mouth. These include producers of textiles and garments, leather goods, shoes, toys, furniture, decorative articles, jewelry and accessories. The concern has not been directed at acute contact dermatitis but instead the carcinogenic nature of certain azo dyes. Many of the

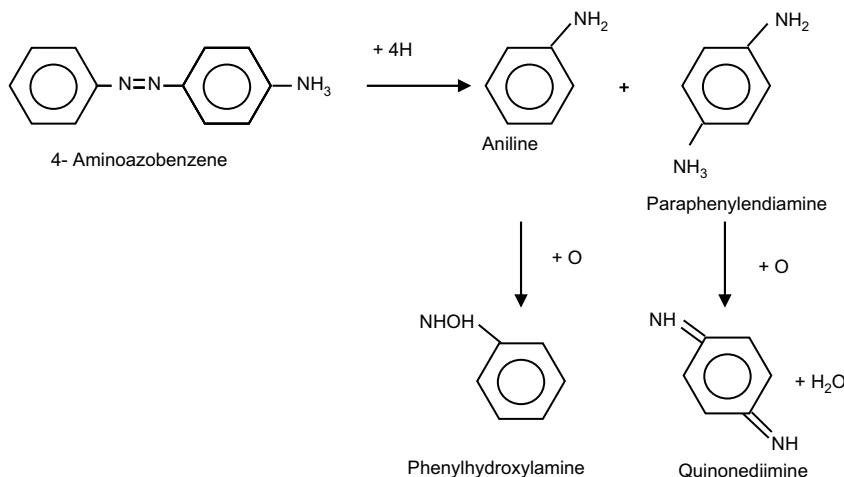


Fig. 5. Conversion of azo dye (aminoazobenzene) to quinonediimines.

same azo dyes that are now banned in the European Union for carcinogenic considerations are the same ones that have the potential for eliciting allergic responses. In the Directive it is stated “Textile and leather articles containing certain azo dyes have the capacity to release certain arylamines, which may pose cancer risks.”

The standards required in the Directive state:

1. Azo dyes which, by reductive cleavage of 1 or more azo groups, may release 1 or more of the aromatic amines listed in the appendix, in detectable concentrations, of above 30 ppm in the finished articles or in the dyed parts thereof, according to the testing method established in accordance with Article 2a of this Directive, may not be used in textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity, such as:
 - clothing, bedding, towels, hairpieces, wigs, hats, nappies and other sanitary items, sleeping bags,
 - footwear, gloves, wristwatch straps, handbags, purses/wallets, briefcases, chair covers, purses worn round the neck,
 - textile or leather toys and toys which include textile or leather garments,
 - yarn and fabrics intended for use by the final consumer.
2. Furthermore, the textile and leather articles referred to in point 1 may not be placed on the market unless they conform to the requirements set out in that point. By way of derogation, until 1 January 2005, this provision will not apply to textile articles made of recycled fibers if the amines are released by residues derived from previous dyeing of the same fibers and if the listed amines are released in concentrations of less than 70 ppm.

The list of azo dyes covered by Directive (2002/61/EC) is provided in **Table 2**.

European Standards 14,362-1:2203 (Part 1) and 14,362-2:2003 (Part 2) provide the worldwide accepted method for determining certain aromatic amines derived from azo colorants. Although they are worldwide standards, at this time they are only enforced in the European Union. Part 1 is focused on detection of the use of certain azo colorants accessible without extraction and Part 2 is focused on the detection of certain azo colorants accessible by extracting the fibers.^{16,17}

Although the Directive has authority in the European Union, the United States consumer market has no current regulations associated with azo dyes. Nonetheless, the American Apparel and Footwear Association (AAFA), the leading trade

group for the industry, has published a Restrictive Substance List (RSL) that calls for voluntary acceptance by its members.¹⁸ The AAFA RSL lists azo dyes which, by reductive cleavage of 1 or more azo groups, may release 1 or more of the following aromatic amines listed in **Table 3**.

Disperse Dyes

Disperse dyes are slightly water-soluble compounds whose fixation properties to fibers depend on their particle size and uniformity and on the nature of the dye disbursing agent.¹⁹ The vast majority of chemical types of disperse dyes that are used are monoazo (essentially azo dyes), anthraquinone, and disazo that are shown in **Fig. 6**.²⁰ The widely accepted standard for determining the presence of disperse dyes in textile is German Standard DIN 54,321: Textiles - Detection of disperse dyestuffs.²¹

Disperse dyes were developed in the 1920s for dyeing nature-based cellulose acetate and cellulose triacetate fibers. Today these dyes are mostly used for dyeing polyester and polyester blends. They are also used for dyeing nylon, acrylic and modacrylic fibers.²² Dye carriers are used for fixing disperse dyes to polyester and cellulose triacetate fibers. The other types of synthetic fibers that are colored with disperse dyes do not require carriers or other auxiliaries.

Allergic Dermatitis Reactions to Disperse Dyes

Pratt and Tanaka showed the allergenic nature of Disperse Blue 106 and Disperse Blue 124.²³ They advanced the concept that these dyes can be screening agents for subjects reacting to textile dyes (**Figs. 7 and 8**). Giusti and Seidenari subsequently added Disperse Orange 3 to the list.²⁴

The International Oeko-Tex Association has determined that those disperse dyes listed in **Table 4** are allergenic.²⁵ Some are also suspected of carcinogenicity. For a textile product to obtain Oeko-Tex 100 certification these disperse dyes cannot be used. It is interesting to note that Disperse Blue 1 and Disperse Yellow 3 are recognized as both allergens and carcinogens (**Figs. 9 and 10**).

The AAFA RSL (2008) identifies the disperse dyes in **Table 5** as restricted on a voluntary basis for US manufacturers and distributors of clothing.¹⁸ The International Oeko-Tex Association also lists these as allergenic.²⁵

Basic Dyes

Hatch and Maibach reported that some basic dyes are common allergens. They are mainly used to dye wool, silk, cotton cellulose, and

Table 2
Restricted azo colorants

	CAS Number	Index Number	EC Number	Substances
1	92-67-1	612-072-00-6	202-177-1	biphenyl-4-ylamine 4-aminobiphenyl xenylamine
2	92-87-5	612-042-00-2	202-199-1	benzidine
3	95-69-2		202-441-6	4-chloro-o-toluidine
4	91-59-8	612-022-00-3	202-080-4	2-naphthylamine
5	97-56-3	611-006-00-3	202-591-2	o-aminoazotoluene 4-amino-2', 3-dimethylazobenzene, 4-o-tolylazo-o- toluidine
6	99-55-8		202-765-8	5-nitro-o-toluidine
7	106-47-8	612-137-00-9	203-401-0	4-chloroaniline
8	615-05-4		210-406-1	4-methoxy-m-phenylenediamine
9	101-77-9	612-051-00-1	202-974-4	4,4'-methylenedianiline 4,4'-diaminodiphenylmethane
10	91-94-1	61 2-068-00-4	202-109-0	3,3-dichlorobenzidine 3,3-dichlorobiphenyl-4 ~ 4-ylenedia-mine
11	119-90-4	61 2-036-00-X	204-355-4	3,3-dimethoxybenzidine o-dianisidine
12	119-93-7	612-041-00-7	204-358-0	3,3'-dimethylbenzidine 4,4-bi-o-toluidine
13	838-88-0	612-085-00-7	212-658-8	4,4-methylenedi-o-toluidine
14	120-71-8		204-419-1	6-methoxy-m-toluidine p-cresidine
15	101-14-4	612-078-00-9	202-918-9	4,4-methylene-bis-(2-chloro-aniline) 2,2-dichloro-4,4-methylene-dianiline
16	101-80-4		202-977-0	4,4-oxydianiline
17	139-65-1		205-370-9	4,4-thiodianiline
18	95-53-4	612-09 1-00-X	202-429-0	o-toluidine 2-aminotoluene
19	95-80-7	612-099-00-3	202-45 3-1	4-methyl-m-phenylenediamine
20	137-17-7		205-282-0	2,4,5-trimethylaniline
21	90-04-0	612-035-00-4	201-963-1	o-anisidine 2-methoxyaniline
22	60-09-3	61 1-008-00-4	200-453-6	4-amino azobenzene

Table 3
Azo colorants on AAFA RSL

4-Amino azobenzene	3,3'-Dimethoxybenzidine
O -Aminoazotoluene	3,3'-Dimethylbenzidine
Aminodiphenyl	3,3'-Dimethyl-4,4'-diamino-diphenylmethane
2-Amino-4-nitrotoluene	4,4'-Methylene-bis-(2-chloroaniline)
O -Anisidine, Benzidine	2-Naphthylamine
P -Chloroaniline	4,4'-Oxydianiline
4-Chloro-o -toluidine	4,4'-Thiodianiline
p -Cresidine	2,4-Toluenediamine
2,4-Diaminoanisole	o-Toluidine
4,4'-Diamino-diphenylmethane	2,4,5-Trimethylaniline
3,3'-Dichlorobenzidine	2,4-Xylidine

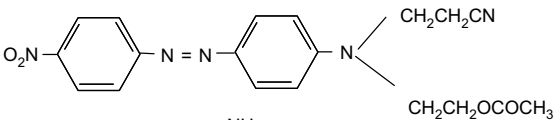
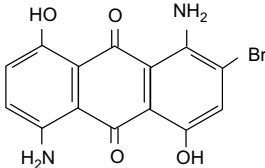
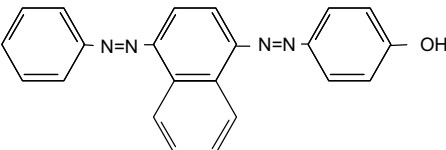
Type	Common Structure	Percent of total
Monoazo		50%
Anthraquinone		25%
Disazo		10%

Fig. 6. Major types of disperse dyes used in commercial dyeing.

polyacrylonitriles. Basic Red 46, Basic Brown 1, Basic Black 1, Brilliant Green and Turquoise have been reported to cause textile dermatitis (Fig. 11).⁸

FORMALDEHYDE AS A SKIN ALLERGEN

Formaldehyde treatment of cellulosic fibers such as cotton was first taught in an invention by the British inventors Foulds, Marsh and Wood in US Patent 1,734,516.²⁶ The inventors claimed that “one of the greatest defects of a fabric composed entirely of cotton has been the ease with which such fabric is creased or crumpled when crushed or folded under pressure in the hand.” The invention was to use a mixture of chemicals including formaldehyde to cause a chemical reaction with the cellulose that would cause cross-linking and thus render the fabric wrinkle free.

Substantial commercial interest developed as inherently wrinkle-free fabrics were commercialized and by the 1950s the family fabric caretaker (mostly women) were enlightened by the potential of wrinkle-free fabrics to reduce some of their homemaking chores. And as more and more women joined the workforce the entire family became interested in easy-care clothing. In addition to being used to produce wrinkle-free fabrics,

formaldehyde based compounds are also found in glues, adhesives in shoes, and as an auxiliary for creating flame retardant fabrics.

Prior to the 1960s formaldehyde resins for textiles were based on urea formaldehyde (dimethylol urea) and melamine and treated fabrics contained relatively high levels of free formaldehyde.²⁷ Although the earliest health concern was that which involved contact during textiles and clothing manufacturing, dermatitis often occurs from wearing permanent press apparel. In 1959, Marcussen (Denmark) reported a study from 1934–1958 in which there were 26 cases (11% of studied cases) of garment formaldehyde dermatitis.²⁸ A study in which 1%–3% of 36,000 eczematous patients from 1934–1955 showed formaldehyde sensitivity was also reported.²⁹ In 1964 Berrens and colleagues³⁰ reported that 200 ppm of free formaldehyde was less than the estimated reaction threshold for most formaldehyde-allergic individuals reported in earlier studies. In 1965, US dermatology researchers O’Quinn and Kennedy reported contact dermatitis caused by formaldehyde in clothing.³¹ Hatch published a complete review of references to clothing-based formaldehyde sensitivity.² Lazorov and colleagues⁴ found significant sensitivities to a range of formaldehyde resins used in textiles.

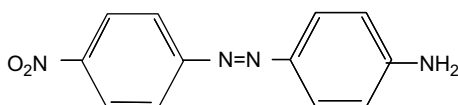


Fig. 7. Chemical structure of Disperse Orange 3.

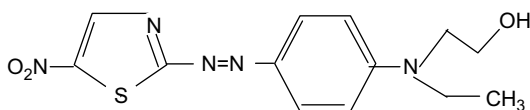


Fig. 8. Chemical structure of Disperse Blue 106.

Table 4
Oeko-Tex 100 list of textile allergens

C.I. Generic Name	C.I. Structure Number	CAS-Number	Carcinogenic
C.I. Disperse Blue 1	C.I. 64 500	2475-45-8	x
C.I. Disperse Blue 3	C.I. 61 505	2475-46-9	
C.I. Disperse Blue 7	C.I. 62 500	3179-90-6	
C.I. Disperse Blue 26	C.I. 63 305		
C.I. Disperse Blue 35		12,222-75-2	
C.I. Disperse Blue 102		12,222-97-8	
C.I. Disperse Blue 106		12,223-01-7	
C.I. Disperse Blue 124		61,951-51-7	
C.I. Disperse Brown 1		23,355-64-8	
C.I. Disperse Orange 1	C.I. 11 080	2581-69-3	
C.I. Disperse Orange 3	C.I. 11 005	730-40-5	
C.I. Disperse Orange 37	C.I. 11 132		
C.I. Disperse Orange 76	C.I. 11 132		
C.I. Disperse Red 1	C.I. 11 110	2872-52-8	
C.I. Disperse Red 11	C.I. 62 015	2872-48-2	
C.I. Disperse Red 17	C.I. 11 210	3179-89-3	
C.I. Disperse Yellow 1	C.I. 10 345	119-15-3	
C.I. Disperse Yellow 3	C.I. 11 855	2832-40-8	x
C.I. Disperse Yellow 9	C.I. 10 375	6373-73-5	
C.I. Disperse Yellow 39			
C.I. Disperse Yellow 49			

Dimethylol dihydroxy ethylene urea (DMDHEU) and modified DMDHEU are compounds which contain N-methylol and mainly N-alkoxymethyl groups and are extensively used in textile industry as durable press finishes.

Voncina and colleagues reported that during the finishing process the N-methylol compounds can react with hydroxyl groups of cellulose, which is the most preferable reaction. These compounds may also react with themselves or with reactive NH groups. These latter 2 reactions are not desirable, because some reaction places on cross-linking reagents are lost, and the formaldehyde can be simply released from the N-methylol compounds. Splitting of acetalic bonds is catalytically accelerated by acids and by bases as well (see Fig. 12).³²

In 1993 Espada found that since the 1970s, most manufacturers have moved to the use of

glycolated or methylated DMDHEU resins, which yielded fabrics with less than 300 ppm free formaldehyde and today fabrics treated with the latest modified DMDHEU resins predictably contain less than 75 ppm free formaldehyde.³³ There are resins available that do not employ formaldehyde, however, these resins are quite expensive and they found popularity primarily in the infant and children’s clothing market.

Scheman and colleagues³⁴ looked at contact dermatitis response to subjects exposed to glycolated DMDHEU, the predominant resin currently used in textiles as a wrinkle free or permanent press resin. It was found that reactions to DMDHEU are the cause of most reports of contact dermatitis. Reactions to low-formaldehyde resins and non-formaldehyde resins were much less common, and generally of lesser intensity, than

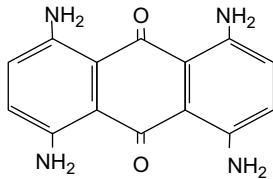


Fig. 9. Chemical structure of Disperse Blue 1.

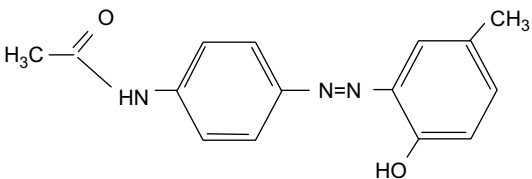


Fig. 10. Chemical structure of Disperse Yellow 3.

Table 5
AAFA Restricted Textile Dyes (Voluntary Compliance)

CAS Number

2475-45-8	Disperse Blue 1
56,524-77-7 or 56,524-76-6	Disperse Blue 35
12,223-01-7	Disperse Blue 106
61,951-51-7	Disperse Blue 124
730-40-5	Disperse Orange 3
13,301-61-6	Disperse Orange 37/76
2872-52-8	Disperse Red 1
2832-40-8	Disperse Yellow 3

reactions to the older formaldehyde resins, which release greater amounts of free formaldehyde.

Bille reported that there are a number of compounds which are capable of accepting the formaldehyde released from formaldehyde treated textiles.³⁵ For instance, urea, N-ethylurea and 1H-benzotriazole can form stable monomethyl compounds (**Fig. 13**).

Voncina showed that formaldehyde acceptors such as urea reduce the free formaldehyde value greatly and at the same time maintain dimensional stability of the treated clothing item.³²

Wu and Yang indicated that it is necessary to use a cross-linking agent to bond a flame retarding hydroxyl-functional organophosphorus oligomer (FR) to cotton so that the flame resistance of the treated cotton fabric can be durable to multiple home laundering. Both (DMDHEU) and melamine-formaldehyde (M-F) have been used as the binding

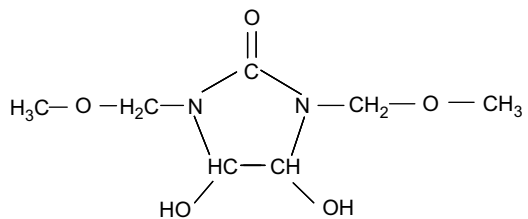
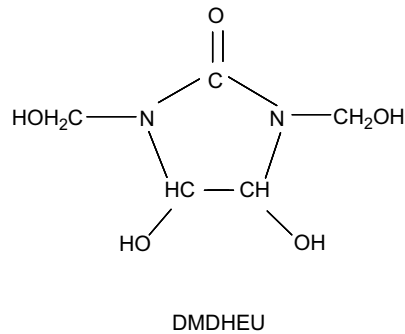


Fig. 12. Chemical structures of DMDHEU and modified DMDHEU.

agents between FR and cotton. Their data show not only that DMDHEU is much more effective for binding FR to cotton than M-F, but that the bonding between FR and cotton formed by DMDHEU is more durable to multiple home laundering than that formed by M-F.³⁶

Formaldehyde is also found in glues and adhesive used to bond materials such as in layers of shoes. In particular, para-tertiary butylphenol (PTBP) formaldehyde resin is sometimes used. Zimerson and colleagues³⁷ have reported cases of contact dermatitis among some subjects exposed to PTBP.

The current medical literature is replete with many studies showing the adverse dermatologic effects of formaldehyde. An excellent current review of this subject has been written by Fowler.²⁷ Carlson, Smith and Nedorost found that textile dermatitis is more common in retired or current machine operators compared with other occupations, suggesting primary sensitization from formaldehyde-related biocides in coolants.³⁸

As of yet, there are no formaldehyde restrictions or standards for clothing and other textile items that are distributed and sold in the United States. Nonetheless, in the recently passed Consumer Product Safety Commission Modernization Act of 2008 (H.R. 4040), there is a provision for the Consumer Product Safety Commission (CPSC) to conduct a study of the use of formaldehyde in textiles and apparel. More and more nations are adopting standards for formaldehyde in clothing and textiles. In Japan, textile fabrics are required



Fig. 11. Patient reaction to Basic Red 46 on right side. Dermatitis caused by the camisole shown (fiber content, 95% polyester, 5% spandex). (Courtesy of S. Nedorost, MD, Cleveland, OH.)

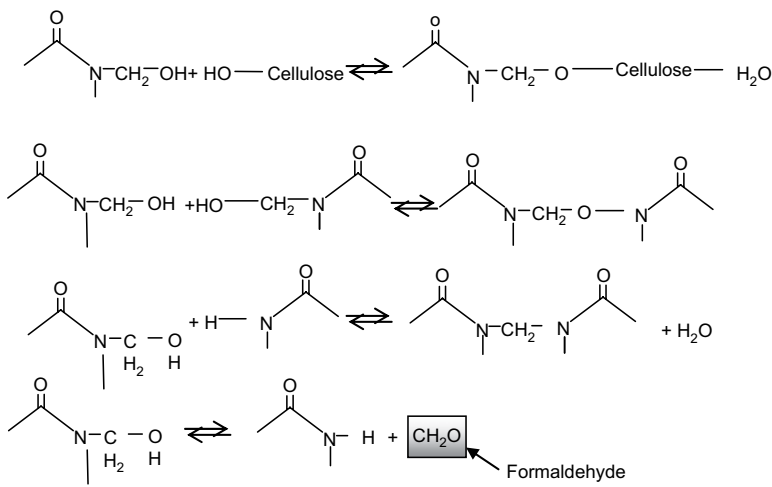


Fig. 13. Equilibrium reactions of N-methylol compounds of hydroxyl groups of cellulose, with themselves, with reactive NH groups and the formaldehyde release.

Table 6 Status of International Formaldehyde Regulations		
Country	Regulations/Requirements	Objection Limit/Limit
Germany	Gefahrstoffverordnung, (Hazardous Substances Ordinance), Annex III, No. 9, 26.10.1993	Textiles that normally come into contact with the skin and release more than 1500 mg/kg formaldehyde must bear the label "Contains formaldehyde. Washing this garment is recommended before first time use to avoid irritation of the skin."
France	Official Gazette of the French Republic, Notification 97/0141/F	The regulations apply to products that are intended to come into contact with human skin, including textiles, leather, shoes, etc. Textiles for babies: 20 mg/kg, textiles for direct skin contact: 100 mg/kg, textiles not in direct skin contact: 400 mg/kg
Netherlands	The Dutch (Commodities Act), Regulations on Formaldehyde in Textiles (July 2000)	Textiles in direct skin contact must be labeled "Wash before first use" if they contain more than 120 mg/kg formaldehyde and the product must not contain more than 120 mg/kg formaldehyde after wash.
Austria	Formaldehydverordnung, BGBl Nr. 194/1900	Textiles that contains 1500 mg/kg or above must be labeled.
Finland	Decree on Maximum Amounts of Formaldehyde in Certain Textiles Products (Decree 210/1988)	Textiles for babies under 2-years-old: 30 mg/kg Textiles in direct skin contact: 100 mg/kg Textiles not in direct skin contact: 300 mg/kg
Norway	Regulations Governing the Use of a Number of Chemicals in Textiles (April 1999)	Textiles for babies under 2 years: 30 mg/kg Textiles in direct skin contact: 100 mg/kg Textiles not in direct skin contact: 300 mg/kg
China	Limits of Formaldehyde Content in Textiles GB18401-2001	Textiles for infants and babies: ≤ 20 mg/kg, Textiles in direct skin contact: ≤ 75 mg/kg, Textiles not in direct skin contact: ≤ 300 mg/kg
Japan	Japanese Law 112	Textiles for infants: not detectable, textiles in direct skin contact: 75 ppm

by law to contain less than 75 mg/kg free formaldehyde, as measured by the method described in Japan Law 112/ISO EN 14,184.³⁹ No free formaldehyde is tolerated for infant clothing. The Hong Kong Standards and Testing Center produced in **Table 6** shows the status of formaldehyde regulations in countries that are currently addressing this situation.⁴⁰

The International Oeko-Tex Association which represents a group of 14 worldwide textile research institutes has developed the Oeko-Tex 100 standards. These standards, which are voluntary, place limitations on free formaldehyde in clothing and textiles.²⁵ For formaldehyde, the Oeko-Tex 100 standard requires no detectable formaldehyde for infant clothing (0-36 months), more than 36 months with direct skin contact (75 ppm) and more than 36 months with no direct skin contact (300 ppm).

While currently there are no US standards or regulations associated with formaldehyde in clothing and textiles, the AAFA published a 2008 RSL and requested that its members abide voluntarily to the standards listed.¹⁸ For formaldehyde, the RSL suggests no detectable formaldehyde for infant clothing (0-36 months), more than 36 months with direct skin contact (75 ppm) and more than 36 months with no direct skin contact (300 ppm).

Brookstein, Barndt and Pierantozzi reported on a recent study of the presence of formaldehyde in some children's clothing.⁴¹ Testing for free formaldehyde was conducted using a MORAPEX Extractor/Formaldimeter system. It was shown that the average free formaldehyde measured in accordance with ISO EN 14,184 ranges from essentially less than 20 ppm to 136 ppm for young men's khaki pants and from less than 20 ppm to 126 ppm for young men's dress shirts. Three of the pants and 1 of the shirts had average free formaldehyde in excess of the 75 ppm value suggested by the AAFA RSL, Oeko-Tex 100 and some countries with a 75 ppm allowable limit. Nonetheless, the data also indicate that it is possible to have a durable press finish with relatively low amounts of free formaldehyde.

FURNITURE DERMATITIS

Isocyanates

Isocyanates can be combined with other polymers to enhance adhesion performance of textile fibers. Isocyanates are often used with polyurethanes and epoxides to make textile treatments. In some instances, isocyanates can be used alone to bond textiles or to bond textiles to other materials such as thermoplastic polyurethane foams

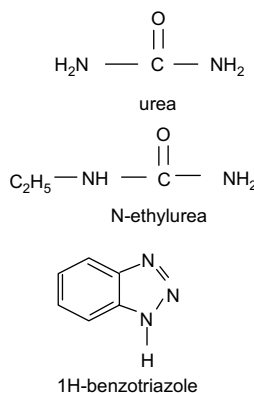


Fig. 14. Chemical structures of formaldehyde acceptors.

which are found in upholstered furniture. Isocyanates are also a constituent in the process to produce thermoplastic polyurethane foam. All isocyanates are characterized by the chemical formula shown in **Figs. 14** and **15**.

One of the key reactive materials required to produce polyurethane foams are diisocyanates. Diisocyanate (OCN-R-NCO) is reacted with a diol (HO-R-OH). The first step of this reaction results in the chemical linking of the 2 molecules leaving a reactive alcohol (OH) on one side and a reactive isocyanate (NCO) on the other side. These compounds are characterized by an (NCO) group, which are highly reactive alcohols. The most widely used isocyanates employed in polyurethane production are toluene 2,4 diisocyanate (TDI) and polymeric isocyanate (PMDI). TDI reacts with polyols to form polyurethanes. TDI is produced by chemically adding nitrogen groups on toluene, reacting these with hydrogen to produce a diamine, and separating the undesired isomers. PMDI is derived by a phosgenation reaction of aniline-formaldehyde polyamines (**Figs. 16** and **17**).

Bello and colleagues⁴² published an excellent review of skin exposure to isocyanates and they indicated that unreacted isocyanates can cause skin problems.

Researchers have shown that based on patch testing, a few cases of allergic contact dermatitis have been reported with the use of consumer products made from isocyanates and

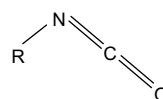


Fig. 15. Isocyanate chemical structure.

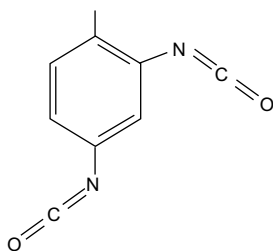


Fig. 16. Chemical structure of toluene 2,4 diisocyanate (TDI).

polyurethanes.^{43–45} Items that elicited dermatitis included watch bands and eyeglass frames.

Thermoplastic polyurethane foams are regularly used to provide cushioning in furniture items such as sofas. On occasion the isocyanate compounds that were reacted with polyol to form the foam did not fully react. Accordingly, it is speculated that residual isocyanate vapor can permeate the foam's fabric covering or when a person is sitting on the sofa, perspiration can permeate through the fabric, mix with the unreacted isocyanate and then come in contact the person's skin.

In 2006 a series of previously unreported cases of dermatitis appeared in Finland. Rantanen reported that by 2007 "tens of cases from all over the country" were reported in the Internet discussion forum of the Finnish Dermatologic Society. After an extensive investigation it was found that the cases were as a result of exposure to dimethylfumarate (DMF) (Figs. 18 and 19).⁴⁶

It was reported by British newspaper accounts that sachets of DMF were put in thousands of Chinese manufactured furniture items to prevent mold when in storage or when being transported.⁴⁷ Rantanen reported that the patients showed strong positive patch test reactions to upholstery fabric samples and to DMF, down to a level of 1 ppm. in the most severe case. It was concluded that the cause of the Chinese sofa chair dermatitis epidemic was likely to be contact allergy to DMF, a novel potent contact sensitizer.

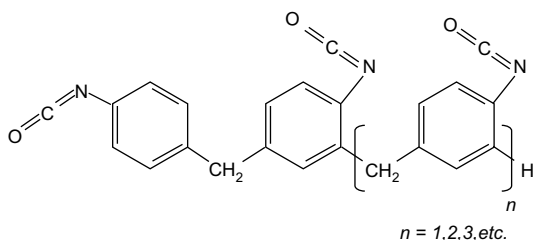


Fig. 17. Chemical structure of polymeric isocyanate (PMDI).



Fig. 18. Patient with allergic contact dermatitis from exposure to dimethylfumarate. (Courtesy of T. Rantanen, MD, Lahti, Finland.)

Although furniture fabrics themselves might not be allergenic, there could be release of allergenic agents from the foam cushioning.

SUMMARY

From as early as 1869, textile dyes and subsequently finishes have been reported to cause various manifestations of contact dermatitis, from mild to severe and debilitating. The European Union, through Directive (2002/61/EC) to restrict the marketing and use of certain dangerous substances and preparations (azo colorants) in textile and leather products, has taken the worldwide lead in restricting some dyes because of their carcinogenic nature. Some of the dyes listed in the directive are also responsible for contact dermatitis. The International Oeko-Tex Association, which is a worldwide voluntary standard and the corresponding voluntarily accepted AAFA RSL provides guidance on the use of dyes and formaldehyde. Many countries have now adopted regulations regarding the use of formaldehyde in textile and apparel products. The U S Congress

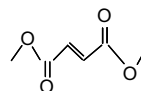


Fig. 19. Chemical structure dimethylfumarate (DMF).

has recently passed HR 4040 which modernizes the CPSC. In that Act there is a section calling for a study of the use of formaldehyde in textile and apparel products. Finally, given the recent discovery of the new route to contact dermatitis from the Finnish sofas, it is important to continue to be vigilant for new and unexpected sources of allergens from textile, apparel, and furniture items.

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