

Contact dermatitis from polyfunctional acrylic monomers*

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Five out of 26 men employed formulating radiation drying printing ink developed eczematous dermatitis. Positive patch tests were obtained with two polyfunctional acrylic monomers, pentaerythritol triacrylate and trimethylol propane triacrylate and with formulations containing these in four affected employees. Cross sensitization was observed to dipentaerythritol monohydroxy pentaacrylate in each case. A fifth employee appeared to have developed irritant dermatitis from contact with these materials.

Key words: Cross sensitization – dipentaerythritol monohydroxy pentaacrylate – occupational dermatitis – pentaerythritol triacrylate – radiation drying ink – trimethylolpropane triacrylate.

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Allergic contact sensitization to several monofunctional acrylic monomers has been previously reported (Fisher 1954, Malten 1956, Smith 1959, Pegum & Medhurst 1971, Magnusson & Mobacken 1972, Fregert 1974, Jordan 1975). Methyl methacrylate has been most frequently incriminated, although acrylonitrile, acrilimide, ethylhexyl acrylate and N-tert butyl maleamic acid have also produced human sensitization (Fisher 1954). Patch testing with methylmethacrylate has been shown to be ineffective in screening for allergic contact sensitization to the latter materials.

Recently there has been relatively widespread use of the technology of inducing free radical polymerization in order to cure inks or coatings. For this purpose either ultraviolet radiation (UV) or less frequently electron beam radiation is used (Emmett et al. 1977). The resins or varnishes for

such inks generally consist of multifunctional acrylate monomers, UV reactive polymers (often an acrylated epoxy resin) and UV absorbing photoinitiators. A variety of other materials may be present depending on the application.

Two multifunctional acrylic monomers, pentaerythritol triacrylate (PETA) and trimethyl propane triacrylate (TMPTA), were introduced into a printing ink formulation facility in November 1974 as components of a radiation drying ink (syn. ultraviolet cured ink). Five of the 26 employees potentially exposed to the formulation of radiation drying inks subsequently developed eczematous dermatitis.

Case Histories

Patient 1

A 51-year-old male lye tank operator re-

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sponsible for cleaning the containers for ink ingredients developed areas of vesicular dermatitis on the trunk, back, hands and forearms. These reactions had been originally attributed to lye burns although there was no clear history of contact with lye.

Patient 2

A 53-year-old black male employed weighing ingredients for the radiation-dried ink developed an eczematous dermatitis on the forearms, the dorsal aspects of the arms and around the ears.

Patient 3

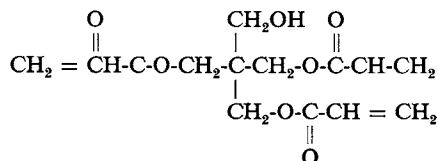
A 63-year-old white millhand developed eczematous dermatitis of the forearms, dorsal aspects of the hands and fingers and the right loin above the belt line.

Patient 4

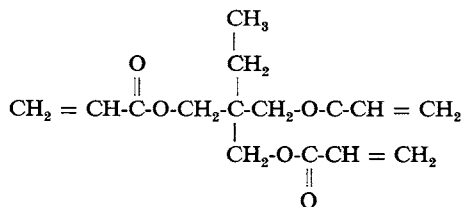
A 45-year-old maintenance operator who had been cleaning containers of ingredients for inks developed an eczematous eruption of the eyelids, wrists and dorsal aspects of the hands and fingers. There was a history of rubbing his eyes when his hands were contaminated by ink ingredients.

Patient 5

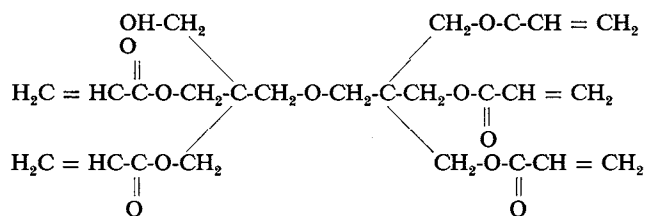
A 37-year-old production manager developed erythema and a few isolated papules on 3 to 5 occasions confined to the area of his left hand covered by his wrist watch. These symptoms had not been present prior to the introduction of the multifunctional acrylates. The dermatitis appeared related to his habit of holding his watch over an ink mill to observe the condensation of vapors on the metal watch case.



Pentaerythritol Triacrylate



Trimethylolpropane Triacrylate



Dipenta erythritol monohydroxy penta acrylate

Fig. 1. Structure of PETA, TMPTA and DEMPA.

Table 1. Results of patch testing 48 h

	Patient				
	1	2	3	4	5
PETA 0.2 % pet.	+++	++	++	++	-
TMPTA 0.2 % pet.	++	++	++	+	-
DEMPA 0.2 % pet.	++	++	++	+	-
Ink varnish formulation 1: 0.5 % pet.	+++	++	++	++	-
Ink varnish formulation 2: 0.4 % pet.	++	++	++	+	-
Ink varnish formulation 3: 1 % pet.	++	++	++	+	-
Ink varnish formulation 4: 0.5 % pet.	++	++	++	+	-
Epoxy resin 1 % pet.	-	-	-	-	-
Epoxytated acrylic resin No. 1: 1 % pet.	-	-	-	-	-
Epoxytated acrylic resin No. 2: 1 % pet.	-	-	-	-	-
Butylated benzoguanamine 1 % pet.	-	-	-	-	-
Benzophenone 5 % pet.	-	-	-	-	-
Michler's ketone as is	-	-	-	-	-
Methyl methacrylate 1 % pet.	NT	NT	NT	-	NT

Materials and Methods

Patch testing was performed using dilutions which were non-irritating to the skin of five control subjects. All materials used as components of the ultraviolet ink within the plant were tested individually. Four ink varnish formulations were patch-tested at dilutions such that their polyfunctional acrylate concentration was 0.2 % in each case. The other components of these varnishes were epoxy resin, butylated benzoguanamine, benzophenone and Michler's ketone. Ink varnish formulations 1, 3 and 4 contained PETA whereas ink varnish formulation 2 contained TMPTA. In addition patch testing was performed with dipentaerythritol monohydroxy pentaacrylate (DEMPA), a material to which the workers had not been exposed. The structures of PETA, TMPTA and DEMPA are shown in Fig. 1.

Results

The results of patch testing the five employees are shown on Table 1. Positive reactions were seen in patients 1 to 4 with

the three polyfunctional acrylate monomers PETA, TMPTA, DEMPA and representative varnish formulations containing PETA and TMPTA. No reactions were seen to the other components of these varnish formulations, viz. epoxy resin, benzophenone, butylated benzoguanamine and Michler's ketone or to other materials used in the total ink formulations.

The fifth patient did not have significant reactions at 48 hr or 72 hr and appeared to have had an irritant dermatitis, the polyfunctional acrylates being markedly irritant unless considerably diluted.

Five other employees with skin complaints (varicose eczema, asteatotic eczema, epidermal cyst, transient undiagnosed dermatitis) showed no significant reactions on patch testing with any of the ink components, varnish formulations or DEMPA.

Discussion

The four sensitized subjects all reacted to each of PETA, TMPTA, and DEMPA. As all subjects had had potential exposure to PETA and TMPTA, we could not determine whether the multiple reactivity was a result

of cross sensitization or concomitant sensitization. However, the reaction to DEMPA, to which the workers had not been exposed, was interpreted as due to cross sensitization.

It should be noted that none of these commercial acrylic monomers consist of pure compounds. For example, according to the manufacturer, PETA has an average of 3.3 acrylate groups per molecule. This provides some indication of the degree to which the related pentaerythritol tetraacrylate and possibly other materials are present as contaminants. No effort was made to study the many potential contaminants present in what were obviously mixtures.

No cross sensitivity was observed with methylmethacrylate in the one subject so tested, giving further evidence of the non-effectiveness of methylmethacrylate as an all-purpose acrylate screening agent (Jordan 1975).

No reaction was seen in any of the sensitized employees to either of two different commercially available acrylated epoxy resins used as UV reactive prepolymers in the ink formulations, indicating that cross sensitization to these materials does not necessarily occur.

In another group of workers engaged in ultraviolet cured ink manufacture studied by the author, phototoxicity was observed from a mixture of amyl esters of dimethylaminobenzoic acid used as a photoinitiator (Emmett et al. 1977). The phototoxicity was associated with a pronounced smarting reaction. In the plant which was the subject of this current study, the amyl esters of dimethylaminobenzoic acid were not used and no indication of photosensitivity was observed.

The polyfunctional acrylic monomers should be regarded as relatively potent allergic sensitizers and care should be taken accordingly to minimize their contact with the skin in the course of their industrial use. Measures which appeared effective in pre-

venting the occurrence of further dermatitis in this plant included employee education, the use of impervious protective gloves, the expeditious removal of contaminating material from the skin using mild soap and water, daily showering, frequent washing of potentially contaminated skin areas, prompt removal of contaminated clothing, separation of clean and contaminated clothing, frequent changes of uniform, protective shielding against splashing from mills and rollers, and an effective vapor exhaust and ventilation system.

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