

Contact Allergy to 2-Hydroxypropyl Methacrylate (2-HPMA) in an Ultraviolet Curable Ink

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A patient working in an ink laboratory developed dermatitis on his hands. Patch testing revealed contact allergy to the ink used and to 2-hydroxypropyl methacrylate (2-HPMA), the monomer present in the ink. Guinea pig maximisation test (GPM-test) shows that 2-HPMA is a weak sensitizer. The data suggest cross-reactivity to 2-hydroxyethyl methacrylate (2-HEMA) but not to 2-hydroxypropyl acrylate (2-HPA) or 2-hydroxyethyl acrylate (2-HEA). *Key words:* Contact allergy; Guinea pig maximization test; Hydroquinone. (Received October 21, 1983.)

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A patient working in an ink laboratory, formulating inks and varnishes for UV cure, developed a dermatitis on his hands. Patch testing revealed contact allergy to the ink he was working with and 2-hydroxypropyl methacrylate (2-HPMA), the monomer present in the composition. As 2-HPMA is a common acrylic monomer in UV-curable acrylic resins and other applications, its sensitizing capacity was investigated by means of the guinea pig maximization test (GPM test) (1, 2).

MATERIALS AND METHODS

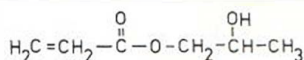
Case report

A 52 year old man has been employed for 10 years in an ink laboratory, doing research work with inks and varnishes containing acrylates for ultraviolet cure. He had never had any skin problems earlier. In December 1980 he was working with an UV lamp and in the evening noticed he had swollen and red hands. He cleared on local corticosteroids. A couple of weeks later he noticed the same dermatitis in three occasions. The ink consisted of a polyesteracrylate as a polymer and 2-HPMA as a monomer. He was tested with UV-B and UV-A and photo patch tested with the standard test series and also with the ink he has been working with in a concentration from 1% w/w diluted down to 0.01% w/w in methyl ethyl ketone (MEK). He was patch tested with polyesteracrylate (Ebecryl 810, UCB, Belgium) and 2-HPMA (BDH Chemicals Ltd, England) in a concentration of 2% w/w in petrolatum. He was also patch tested with other acrylates he might have been exposed to, such as trimethylolpropane triacrylate (TMPTA, UCB, Belgium), pentaerythritol triacrylate (PETA, Svenska Lorilleux, Sweden), OTA 480 (UCB, Belgium) all in a concentration of 0.1% w/w in pet. They are all common multifunctional acrylates in UV-curing inks. Patch testing was also performed with dimethacrylates based on bisphenol A (3), such as BIS-MA (2% w/w in pet.), BIS-EMA (2% w/w in pet.), BIS-GMA (2% w/w in pet.), BIS-PMA (5% w/w in pet.). He was also tested with two epoxy diacrylates (Epikote DRH-340 and Epoxy acrylate DOW), both in 5% w/w in pet. The epoxy diacrylates are diacrylates based on bisphenol A (3). He was also tested with a photoinitiator and an accelerator used in the ink. The chemistry of those substances were unknown to us.

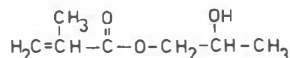
Guinea Pig Maximization Test (GPM Test)

Chemicals. The chemicals used in the GPM test were 2-hydroxypropyl methacrylate (2-HPMA) and 2-hydroxyethyl methacrylate (2-HEMA), manufactured by BDH Chemicals Ltd, England; 2-hydroxypropyl acrylate (2-HPA) and 2-hydroxyethyl acrylate (2-HEA), manufactured by Pfaltz & Bauer Inc., USA. Hydroquinone was purchased from Fluka AG, Switzerland. The chemical structure of the acrylates tested are given in Fig. 1. The purity of the acrylates, analysed by high performance liquid chromatography, was at least 95%.

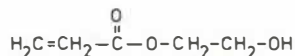
GPM-test. The methods were in accordance with the original description of the GPM test (1, 2) and under the same condition as reported in previous studies (3). Ten guinea pigs were used as experimen-



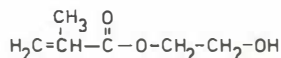
2-HYDROXYPROPYL ACRYLATE



2-HYDROXYPROPYL METHACRYLATE



2-HYDROXYETHYL ACRYLATE



2-HYDROXYETHYL METHACRYLATE

Fig. 1. Structural formula of 2-hydroxypropyl acrylate (2-HPA), 2-hydroxypropyl methacrylate (2-HPMA), 2-hydroxyethyl acrylate (2-HEA) and 2-hydroxyethyl methacrylate (2-HEMA).

tal animals and 10 animals served as controls. The sensitization procedure was repeated once with other guinea pigs than used in the first experiment.

Five % w/w 2-HPMA solved in a mixture of olive oil and acetone (10:1) was used for intradermal induction.

To achieve a uniform dispersion of 2-HPMA in petrolatum, only 25 % w/w was used for topical induction. Pretreatment with 10 % w/w sodium lauryl sulphate (SLS) in water was performed, as 25 % w/w concentration did not give any irritation.

Challenge was performed with 2-HPMA (2 % w/w in pet.), 2-HEMA (2 % w/w in pet.), 2-HPA (0.2 % w/w in pet.), 2-HEA (0.5 % w/w in pet.) and hydroquinone (0.05 % w/w in pet.).

RESULTS

Testing of the patient

The photopatch test was negative for the standard test series but positive for the ink used both at the irradiated and covered test sites with a test concentration of 1 % and 0.1 % in MEK but negative for 0.01 %. Photo tests were normal for UV-A and UV-B. The standard epicutaneous patch test was negative. Tests using the different acrylates showed positive reaction only for 2-HPMA. Patch tests with the photoinitiator and accelerator were also negative.

GPM test

One animal out of 10 reacted to 2-HPMA. The same animal also reacted to 2-HEMA with same mean response (0.15) as for 2-HPMA. None of the animals reacted to 2-HPA, 2-HEA and hydroquinone. All control animals were negative for all substances tested. The repeated sensitization procedure gave the same results.

DISCUSSION

2-HPMA is a common monofunctional acrylic monomer used in UV-curable resins. Other applications where 2-HPMA might be an important ingredient are dental fissure sealents, prosthetic appliance formulations for dentistry and orthopaedic surgery, impregnated fabric articles as orthopaedic casts and in certain shoe devices.

This investigation shows that 2-HPMA is a weak sensitizer in guinea pigs. Contact sensitization in guinea pigs from 2-HPMA has, to our knowledge, not been reported earlier. The data may suggest cross-reactivity or concomitant reactivity to 2-HEMA as the same animal reacted to both 2-HPMA and 2-HEMA in both sensitizing experiments.

The patient positive to 2-HPMA was never patch tested with 2-HEMA as he declined further testing.

There are reports on positive patch test reactions to 2-HPMA in printers exposed to NAPP® printing plates (4, 5, 6). It is unknown if the NAPP® printing plate contains 2-HPMA.

Grimalt & Romequera (7) patch tested 45 patients with shoe dermatitis, and one of those was positive to hydroxypropyl methacrylate. If 1-HPMA or 2-HPMA was used in the patch test series, is not known. It is also unknown if the shoes the patient had used contained any hydroxypropyl methacrylate.

Some reports about contact allergy to 2-HEMA have been published. Malten & Bende (8) described 5 patients which developed an allergic contact dermatitis when working with photoprepolymer printing plate making procedure. Four of them were patch tested and showed positive reaction to 2-HEMA, one of the ingredients in the photoprepolymer mixture. In order to obtain information about possible cross-reacting substances 2 of the patients were also tested with ethyl methacrylate with negative results.

Parker & Turk (9) investigated 21 different acrylate and methacrylate compounds for their ability to induce contact sensitivity in the guinea pig. It was not possible to induce contact sensitivity to 2-HEMA or any other methacrylates tested using the Polak method of immunization. However, contact reactions of varying intensities were produced to all the mono-, di- and triacrylates tested. Van der Walle et al. (10) investigated the sensitizing potential of 2-HEMA in guinea pigs with Freund's Complete Adjuvant Test (FCAT). All animals were positive on day 21 but negative on day 35. Jordan (11) described 7 patients which developed allergic contact dermatitis to an acrylic based adhesive tape. Five of the subjects were patch tested with positive results to 2-ethylhexyl acrylate, one of the ingredients in the adhesive tape. They were all negative to 2-ethylhexyl methacrylate. Two of the subjects were also positive to 1-HPA and 1-HPMA.

In our experiments tests with 2-HPA and 2-HEA were negative. 2-HEA has been shown to be a strong sensitizer in guinea pigs (12) thus, with introduction of a methyl group at the α -carbon atom, there seems to be a decrease in the sensitizing potential.

ACKNOWLEDGEMENTS

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