

From the Department of Dermatology, University of Lund, Lund, Sweden
(Head: G. Hagerman, M.D.).

ALLERGENS IN EPOXY RESINS

By

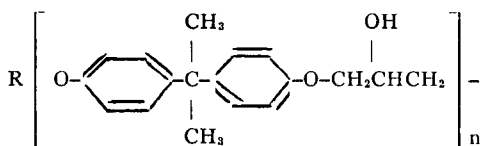
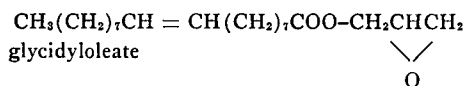
SIGFRID FREGERT & HANS RORSMAN

It is known that epoxy resins and hardeners (curing agents) for such resins are capable of causing allergic eczematous contact dermatitis (1, 2, 8). They are marketed under such trade marks as Araldit (Ciba), Cleroxide (Pure Chemicals Limited), Epikote (Shell), Lekutherm (Bayer), Ferroclere (Pure Chemicals Limited), Unox Epoxides (Union Carbide Chemicals Company).

Such contact dermatitis has, however, been described exclusively among resin workers because only uncured epoxy resins can cause allergic contact dermatitis (7). Recently, however, we observed such contact allergy due to exposure to uncured epoxy resins among persons not employed in the resin industry (6). These resins are used as plasticizers and stabilizers in polyvinylchloride (PVC) plastics, ethyl cellulose, polyvinyl acetate plastics, neoprene etc. Of 1,690 persons not employed in the resin industry and tested for contact allergy at the Department of Dermatology, Lund, 1.6 per cent proved hypersensitivity to epoxy resin. The articles responsible for this contact allergy were, among other things, plastic gloves, artificial pearl necklace, watertight adhesive tape, plastic drawers for babies, and plastic foliums.

In attempt to find out which ingredients of the epoxy resins were responsible for the allergic reactions we studied the allergenicity of two types of epoxy resins, namely glycidyl ethers (of Bisphenol A) and epoxidized oils (Table 1). In all of the cases examined the allergy was found to be due to epoxy resins of glycidyl ether type and never to epoxidized oil.

TABLE 1
Ester- and Ether Types of Epoxy Resins.



glycidylether of bisphenol A

In the literature it has been discussed whether bisphenol A might be responsible for allergy to epoxy resins. Only in exceptional cases has this proved to be so (5, 7). On the other hand, allergy to bisphenol A is not uncommon among patients hypersensitive to the so-called stilbestrol group (3,4).

We also studied the allergenicity of so-called *reactive diluents* commonly added to epoxy resins to decrease their viscosity (9, 11). As indicated by their name, they are capable of reacting in association with the hardening process. Patients with contact allergy to epoxy resins were tested with the commonest reactive diluents, namely *phenyl glycidyl ether*, *butyl-* and *allyl glycidyl ether*¹ (Table 2). Of 20 patients, 14 were found to react to phenyl glycidyl ether, 3 to butyl- and 2 to allylglycidyl ether. Four patients who reacted to phenyl glycidyl ether were also tested and found to react positively to the closely related *cresyl glycidyl ether*.²

In order to assess the concentration in which phenyl glycidyl ether might be used as a patch test without producing a primary toxic reaction, 10 patients not allergic to epoxy resins were studied. Of these, 2 became sensitized by the test (1.0 per cent phenyl glycidyl ether in acetone). In this concentration

¹ Supplied by Shell International Chemical Company Limited (AB Svenska Shell, Stockholm, Sweden).

² Ciba Produkter AB, Norrköping, Sweden.

the phenyl glycidyl ether produced no primary toxic reaction. Phenyl glycidyl ether thus appears to be a very strong sensitizing substance. Testing with epoxy resins also induced hypersensitivity in 2 of 1,690 persons tested.

TABLE 2
Test Reactions to Reactive Diluents (0.25% in acetone).

Compound	Number of tested patients	Number of positive reactions
$ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5 \end{array} $ phenylglycidylether	20	14
$ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2 \end{array} $ allylglycidylether	20	3
$ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{CH}_2-\text{CH}_3 \end{array} $ n-butylglycidylether	20	2

The investigation emphasizes the occurrence of contact allergy to reactive diluents in epoxy resin sensitive subjects (10). This allergy is of practical importance for several reasons.

Firstly, allergy to epoxy resins is fairly common and often due to contact with articles not widely known to contain epoxy resin as an ingredient. Epoxy resins should therefore be included in routine test series.

Secondly, the investigation showed that articles made of epoxy resins with reactive diluents contain strongly sensitizing substances such as phenyl glycidyl ether and cresyl glycidyl ether. It would be an advantage if these reactive diluents could be replaced by less allergenic substances.

Thirdly, it would appear that epoxidized oil is not aller-

genic, or at least less so than epoxy resins of glycidyl ether type, and should when technically possible therefore be given preference as plasticizers of artificial resins.

REFERENCES

1. *Birmingham, D. J.*: Clinical observations on the cutaneous effects associated with curing epoxy resins. *AMA Arch. Industr. Health*, **19**, 365, 1959.
2. *Calnan, C. D.*: Studies in contact dermatitis. IV. Epoxy resins. *Trans. St. John's Hosp. Derm. Soc. (London)* **40**, 12, 1958.
3. *Fregert, S. & Rorsman, H.*: Hypersensitivity to diethylstilbestrol. *Acta Dermat.-venereol. (Stockholm)* **40**, 206, 1960.
4. *Fregert, S. & Rorsman, H.*: Hypersensitivity to diethylstilbestrol with cross-sensitization to benzestrol. *Acta Dermat.-venereol. (Stockholm)* **42**, 290, 1962.
5. *Fregert, S. & Rorsman, H.*: Hypersensitivity to epoxy resins with reference to the role played by bisphenol A. *J. Invest. Dermat.* **39**, 471, 1962.
6. *Fregert, S. & Rorsman, H.*: Hypersensitivity to epoxy resins used as plasticizers and stabilizers in polyvinyl chloride (PVC) resins. *Acta Dermat.-venereol. (Stockholm)* **43**, 10, 1963.
7. *Gaul, E.*: Sensitizing structure in epoxy resin. *J. Invest. Derm.* **29**, 311, 1957.
8. *Grandjean, E.*: The danger of dermatosis due to cold-setting ethoxyline resins (Epoxide resins). *Brit. J. Industr. Med.* **14**, 1, 1957.
9. *Jahn, H.*: Darstellung und Eigenschaften aliphatischer und aromatischer Glycidäther. *Plaste und Kautschuk* **6**, 583, 1959.
10. *Malten, K. E.*: Beroepsekseem bij het Verwerken van Kunststoffen in het Biezonder van onverzadigde polyester Harsen en aethoxyline Harsen. *Stenfort Kroese N. V., Leiden*, 1956.
11. *Skeist, I.*: Epoxy resins. Reinhold Publ. Co., New York, 1958.

This document is a scanned copy of a printed document. No warranty is given about the accuracy of the copy. Users should refer to the original published version of the material.