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1 SUMMARY

On April 11, 2003, a working conference on health and safety of epoxy products was held in London. Experts from the United Kingdom, Germany, The Netherlands, Denmark and Norway met, in order to exchange information on working safely with epoxies, to investigate the possibilities to address manufacturers, to express their opinion on a Dutch proposal for a ‘ranking system’ for the health effects of epoxies and to identify possibilities for further cooperation. Ton Spee from Arbouw, the Netherlands, chaired the conference.

Paul Evans from the Health and Safety Executive (UK) presented a study on the uses of epoxies in the UK, and on observed health effects and protective measures. Over the last years the use of epoxies has increased as a result of stricter hygiene regulations, and more general, their superior technical performance. Sensitisation is frequently found, particularly with low molecular weight DGEBA epoxy resin, polyamine hardeners and low molecular weight, relatively volatile reactive diluents. Reactive diluents are more and more used in epoxy resins. The exposure to epoxies in the construction industry is poorly controlled. Potential measures include protective clothing and gloves, ‘smart’ mixing equipment and using epoxy systems with reduced risk of sensitisation (e.g. higher molecular weight resins).

Ulrich Goergens from the Bau Berufsgenossenschaft (D) presented the activities in Germany on risk assessment, product substitution and ‘good practices’ with respect to safe handling. While in the German construction industry cement allergies are the most common in absolute numbers, the relative incidence is much higher for epoxy allergies. Two working groups were established, which develop guidelines for working with epoxies.

Regarding risk assessment, the problem was that the supplier does not always fully define the components present in the product. Furthermore, data from sensitisation tests are not always known, and consequently the classification of components (by R-phrases) may differ from supplier to supplier.

Product substitution (by non-epoxy) products was found to be very difficult in most cases, as a result of the superior technical properties of epoxies. However, less hazardous epoxies can be chosen in some cases. Regarding ‘good practices’, a draft of a general guideline was presented at the conference, including many ‘practical solutions’.

Other activities in Germany include a multicentre patch testing study with a new range of test-substances, and multi-component testing of glove materials.
Christian Pedersen from Aalborg BST Center (DK) presented a study on exposure to epoxy monomers during sanding of hardened epoxy at a shipyard and in a windmill blade factory. It appeared that sanding dust from cured epoxy may present a risk of allergic eczema. In many cases in sanding operations at the shipyard and the windmill blade factory the exposure to epoxy monomers was at such a level that the specific Danish regulations regarding epoxies would have to be followed. The amount of free epoxy present was determined by the accuracy of weighing and adding resin and hardener, the effectivity of the mixing process, the curing temperature and the curing time.

Olve Rømyhr from the University Hospital Trondheim (No) presented a study on contact dermatitis among industrial painters. Approximately 2/3 of the paint volume in the Norwegian oil and shipyard industry is epoxy-based. The aim of the study was to quantify the incidence of allergic eczema and occupational asthma among this group, and to characterise exposure to polyurethane and epoxy-based paints. In a questionnaire survey among industrial painters, 31% reported skin complaints and 15% airway complaints caused by work. Subsequently, clinical observation and patch testing was performed at patients with skin disease. Results of positive patch tests (23 cases) show that 70-80% of the cases of epoxy-related allergic skin disease will be recognised by the standard commercial test series. Further on, measurements of the exposure to amine hardeners was performed, during spray painting in non-ventilated test chambers. The concentrations appeared to be very low. The Norwegian association of occupational hygienists is planning to produce a guide on safe handling of epoxies, and would like to exchange experiences.

Jeroen Terwoert from IVAM (NL) presented a proposal for a ranking system for the health effects of epoxies, that was developed together with Arbouw and in close cooperation with Dutch suppliers of epoxy products. The aim of such a system is twofold:

- to inform the user about the harmfulness of epoxy’s with comparable applications,
- to stimulate suppliers to perform product development into less harmful products.

Because the current classification on the MSDS is based on a ‘hazard’ approach the new ranking system should in addition take the chance of exposure into consideration. Also, the information needed to rank the products must be easily accessible. The criteria for the ranking that have been developed consist of two major groups: toxicity data, as a measure for the hazard (to be found on the MSDS), and physical-chemical data, as a measure for the chance of exposure (partly to be found on the MSDS, partly in handbooks). Each criterion leads to the assignment of
‘malus points’ to the product. The more points, the more harmful the product is. The total amount of points leads to classification into a limited number of classes. A first test with the classification system shows that the system seems to discriminate well. The system offers sufficient room for variation by varying the amount of malus points per criterion. A problem is that it is not always easy to obtain all information from the suppliers. In this respect, a more international approach would help.

In the general discussion, experiences were exchanged on possible non-epoxy substitutes for epoxy products (which are scarce, as said), on ‘good practices’ with respect to packaging and mixing, and on ‘good working practices’. Many (simple) measures relating to good practices were discussed, many of which had been identified in more than one country already. It was agreed that a ‘common Code of Practice’ with respect to working safely with epoxies should be defined. Regarding a ‘ranking system’ for the health effects of epoxies it was agreed that this would be a welcome tool to ‘finetune’ existing classifications by R-phrases (with respect to ‘sensitisation potential’ of epoxy products), to help SME-users to choose for relatively less hazardous products, and to stimulate product development towards less hazardous products. However, it was stressed, that such ranking systems should be well-communicated and explained to users, in order to avoid confusion. Also, some participants feared that in some countries it might not be easy to get the cooperation of the suppliers.

Finally, a number of opportunities for further cooperation were identified, most of them focussed at the exchange of ‘good practices’. It was agreed that the participants would try to set up a European project, with as the main objective the definition of a common ‘Code of Practice’ with respect to working safely with epoxies.
Op 11 april 2003 heeft in Londen een internationale workshop plaatsgevonden over veiligheid en gezondheid met betrekking tot epoxy producten. Deskundigen uit Groot-Brittannië, Duitsland, Nederland, Denemarken en Noorwegen ontmoetten elkaar, om kennis en ervaring uit te wisselen met betrekking tot ‘veilig omgaan met’ epoxy’s, om de mogelijkheden om leveranciers hierop aan te spreken te inventariseren, om hun mening te geven over een Nederlands voorstel voor een classificatiesysteem voor de gezondheidsrisico’s van epoxy’s en om mogelijkheden voor verdere samenwerking te bezien. De workshop werd voorgezet door Ton Spee van Arbouw.

Paul Evans van de Health and Safety Executive (UK) presenteerde een studie naar het gebruik van epoxy’s in Groot-Brittannië, en naar bij gebruikers vastgestelde gezondheidseffecten en naar beheersmaatregelen. De laatste jaren is het gebruik van epoxy’s toegenomen als gevolg van strengere hygiënische eisen en, meer in het algemeen, hun superieure technische eigenschappen. Allergieën komen veel voor, met name allergieën voor epoxyharsen van bisphenol-A met een laag molecuulgewicht, voor polyamine verharders en voor relatief vluchtige reactieve verdunners met een laag molecuulgewicht. Reactieve verdunners worden steeds meer toegepast in epoxy’s. De maatregelen die in de bouw in het algemeen worden genomen om blootstelling aan epoxy’s tegen te gaan laten veel te wensen over. Mogelijke maatregelen zijn o.a. beschermende kleding en handschoenen, ‘slimme’ mengsystemen en het gebruik van epoxy producten met een lagere allergene potentie (b.v. epoxyharsen met een hoger molecuulgewicht).

Ulrich Goergens van de Bau Berufsgenossenschaft (D) presenteerde de activiteiten die in Duitsland worden uitgevoerd, met betrekking tot risico-evaluatie, vervanging van epoxy’s en ‘good practices’ (‘goede werkpraktijken’). In de Duitse bouw komen cement-allergieën wat betreft absolute getallen het meest voor, maar epoxy-allergieën komen naar verhouding veruit het meest voor als de aantallen betrokken medewerkers worden meegenomen. De Duitse overheid heeft twee werkgroepen ingesteld, die richtlijnen ontwikkelen voor het werken met epoxy’s. Voor de risico-evaluatie bleek het een probleem te zijn dat leveranciers niet altijd de exacte chemische namen van de bestanddelen vermelden. Bovendien zijn niet alle bestanddelen getest op sensibilisatie, zodat de classificatie van bestanddelen met behulp van R-zinnen kan verschillen van leverancier tot leverancier. Vervanging van epoxy’s door andere typen producten is meestal erg moeilijk, door de superieure technische eigenschappen van epoxy’s. Wel kunnen in bepaalde
gevallen (relatief) minder schadelijke epoxy’s worden gekozen. Wat betreft ‘good practices’, werd een concept van een algemene richtlijn gepresenteerd, waarin vele ‘praktische oplossingen’ zijn aangegeven.

Andere activiteiten in Duitsland zijn de uitvoering van allergietests (lapjesproeven) met een nieuwe, uitgebreide standaard-testreeks van verbindingen, en tests op de doorlaatbaarheid van handschoen-materialen voor epoxyproducten.

Christian Pedersen van het Aalborg BST Center (DK) presenteerde de resultaten van een studie naar de blootstelling aan epoxy-monomeren tijdens het schuren van uitgeharde epoxyproducten op een scheepswerf en in de productie van windmolenwijken. Het bleek, dat het schuurstof van uitgeharde epoxy’s inderdaad nog een risico op allergisch eczeem kan geven. In veel gevallen was de blootstelling aan epoxy-monomeren tijdens schuurwerk op de scheepswerf en in de windmolenwijken productie zo hoog, dat de specifieke Deense regelgeving voor (niet uitgeharde) epoxy’s van kracht zou zijn. Het gehalte ‘vrij epoxymonomeer in de uitgeharde producten bleek bepaald te worden door de nauwkeurigheid waarmee de hars en verharder afgewogen en gemengd werden, de temperatuur tijdens het uitharden en de tijd die was verlopen tussen het aanbrengen van het product en de meting.

Olve Rømyhr van het Universiteits Ziekenhuis in Trondheim (No) presenteerde een studie naar contacteczeem onder industriële verfspuiters. Ongeveer 2/3 van het verfvolume in de olie- en scheepsbouw-industrie in Noorwegen is namelijk op basis van epoxy’s. Het doel van de studie was het bepalen van de incidentie van allergisch eczeem een beroepspastma bij verfspuiters, en het meten van de blootstelling aan polyurethaan- en epoxy-verven. Met behulp van een enquête onder verfspuiters, rapporteerde 31% huidklachten en 15% luchtweg-klachten als gevolg van het werk. Vervolgens werden patiënten met huidaandoeningen klinisch onderzocht, en werden allergietests uitgevoerd. De resultaten van de positieve allergietests (23 gevallen) lieten zien dat 70-80% van de gevallen van epoxy-gerelateerd allergisch eczeem vastgesteld kunnen worden met de commerciële standaard-testreeks voor allergietests.

Verder werden metingen verricht van de blootstelling aan amineverharders tijdens verfspuitwerk in niet-geventileerde ruimten. De concentraties aminen in de lucht bleken zeer laag.

De Noorse vereniging van arbeidshygiënisten bereidt de uitgave van een brochure met betrekking tot ‘veilig werken met epoxy’s’ voor, en zou graag ervaringen en kennis uitwisselen met collega’s in het buitenland.

Jeroen Terwoert van IVAM (NL) presenteerde een voorstel voor een classificatiesysteem voor de gezondheidseffecten van epoxy’s, dat samen met
Arbouw is ontwikkeld, in nauwe samenwerking met de Nederlandse leveranciers van epoxy’s (ook hier in het kader van het uitbrengen van een brochure – ‘A-blad’ – over ‘veilig omgaan met’ epoxy’s’). Het doel van een dergelijk classificatiesysteem is tweeledig:
Gebruikers informeren over de schadelijkheid van epoxy producten met een vergelijkbare toepassing
Leveranciers stimuleren om minder schadelijke producten te ontwikkelen.
Omdat de bestaande classificatie op Veiligheidsinformatiebladen (VIB’s) uitsluitend is gebaseerd op de (‘intrinsieke’) ‘schadelijkheid’ van de bestanddelen, zou het nieuwe classificatiesysteem in aanvulling daarop ook de ‘kans op blootstelling’ moeten meewegen. Ook zou de informatie die voor de classificatie nodig is, eenvoudig toegankelijk moeten zijn. De criteria voor de classificatie die zijn ontwikkeld, bestaan uit twee hoofdgroepen: gegevens over de toxiciteit (giftigheid; te vinden op het VIB), en fysisch-chemische gegevens, die een maat zijn voor de kans op blootstelling (gedeeltelijk te vinden op het VIB, en gedeeltelijk in ‘handboeken’).
Tijdens de algemene discussie werden ervaringen uitgewisseld over vervanging van epoxy’s door niet-epoxy’s (hetgeen veelal moeilijk is, zoals gezegd), en over ‘good practices met betrekking tot verpakkingen, en het mengen en verwerken van epoxy’s. Vele (simpele) maatregelen om de blootstelling te beperken werden besproken. Veel daarvan werden al in meerdere landen aanbevolen. De deelnemers waren het erover eens dat een gezamenlijke ‘Code of Practice’ met betrekking tot het ‘veilig omgaan met epoxy’s’ zou moeten worden vastgesteld.
Met betrekking tot het classificatiesysteem voor de gezondheidsrisico’s van epoxy’s waren de deelnemers het erover eens dat dit een welkom instrument zou zijn om de bestaande classificeringen met behulp van R-zinnen te verfijnen (t.a.v. de ‘allergene potentie’ van de producten), de gebruikers te helpen bij de keuze voor minder schadelijke producten en de leverancier te stimuleren om minder schadelijke producten te ontwikkelen. Wel werd benadrukt dat een goede communicatie en uitleg van het classificatiesysteem nodig is, om verwarring te voorkomen. Ook werd door
sommige deelnemers gevreesd dat de leveranciers in sommige landen niet makkelijk tot samenwerking te bewegen zouden zijn.

Tenslotte werden de mogelijkheden voor verdere samenwerking besproken. In het algemeen concentreerden deze zich op de uitwisseling van ‘good practices’ op diverse terreinen. Ook werd overeengekomen dat getracht zou worden om een Europees project op te zetten, met als voornaamste doel het definiëren van een gezamenlijke ‘Code of Practice’ met betrekking tot veilige werkwijzen met epoxy’s.
3  

PREFACE

On April 11, 2003 a working conference on working conditions in relation to the use of epoxy products was held, which was kindly hosted by the Health and Safety Executive in its London office. Experts from the United Kingdom, Germany, The Netherlands, Denmark and Norway met, and exchanged experiences and ideas on how to deal with health risks arising from the use of epoxy-resin based products. In order to facilitate an active and interactive exchange of ideas, the number of participants was kept small:

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<thead>
<tr>
<th>Country</th>
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<tr>
<td>Denmark</td>
<td>Christian Pedersen</td>
<td>Aalborg BST Center</td>
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<td>Germany</td>
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<td>Bau Berufsgenossenschaft</td>
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<td>Jeroen Terwoert</td>
<td>IVAM</td>
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<td>Tamara Onos</td>
<td>Arbo Advies Onos</td>
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<td></td>
<td>Ton Spee</td>
<td>Arbouw</td>
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<td>Norway</td>
<td>Olve Rømyhr</td>
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<tr>
<td>United Kingdom</td>
<td>Bob Rajan</td>
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<td>Paul Evans</td>
<td>Health and Safety Executive</td>
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In this report, summaries of the presentations are presented, and a report of the discussions is given. Finally, the opportunities for further cooperation that were identified are described.
## PROGRAMME OF THE MEETING

<table>
<thead>
<tr>
<th>Time</th>
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<tbody>
<tr>
<td>08.45 – 09.00</td>
<td>Ton Spee</td>
<td>Introduction, purpose of the working conference</td>
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<tr>
<td>09.00 – 09.30</td>
<td>Paul Evans</td>
<td>Epoxies in the Construction Industry</td>
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<tr>
<td>09.30 – 10.00</td>
<td>Ulrich Goergens</td>
<td>Activities in Germany: risk assessment, substitution, protective measures</td>
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<td>10.00 – 10.30</td>
<td>Christian Pedersen</td>
<td>Exposure to epoxy-monomers from hardened epoxy</td>
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<td>10.30 – 11.00</td>
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<td>Coffee break</td>
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<td>11.00 – 11.30</td>
<td>Olve Rømyhr</td>
<td>Contact dermatitis among Norwegian industrial painters.</td>
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<tr>
<td>11.30 – 12.00</td>
<td>Jeroen Terwoert</td>
<td>A ranking system for health effects of epoxies in the construction industry</td>
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<td>12.00 – 12.30</td>
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<td>Discussion, questions to be raised, parallels and differences in approach</td>
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<td>12.30 – 13.15</td>
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<td>Lunch</td>
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<tr>
<td>13.15 – 14.45</td>
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<td>General discussion</td>
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<td>Tea break</td>
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<tr>
<td>15.00 – 15.55</td>
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<td>Exploration of possibilities for cooperation or for other arrangements</td>
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<tr>
<td>15.55 – 16.00</td>
<td></td>
<td>Conclusions, closure</td>
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Ton Spee; Arbouw; The Netherlands

Ton Spee is the occupational hygienist of Arbouw: the ‘bipartite’ institute for the improvement of working conditions in the Dutch construction industry. Arbouw conducts and commissions research, develops instruction materials and training courses and takes care of occupational health service for the construction industry.

Ton Spee welcomes the participants and expresses his gladness that all who were invited have been able to come. The main purposes of this conference are the following:

- **Exchange of information on working safely with epoxies:**
  Which activities are carried out in each country, and what is known about current working practices, observed health effects and ‘good practices’?

- **Investigate the possibilities to address manufacturers**
  Which experiences exist with regard to addressing manufacturers in order to obtain information on products, and to cooperate on improving products and work practices?

- **Get the opinion of the participants on a Dutch proposal for a ranking system for the health effects of epoxies**
  Dutch suppliers would favour an international approach (see presentation of Jeroen Terwoert).

- **Identify possibilities for further cooperation or other arrangements**

A short introduction on epoxy products’ health risks and on potential control measures is given. Some (scarce) epidemiological data indicate that about 20% of the ‘epoxyworkers’ in the Dutch construction industry develop allergic contact dermatitis. These workers will not be able to continue working with epoxies, and will have to change jobs. A number of relatively ‘simple’ measures can significantly reduce exposure. These have been described in a ‘good practice guide’ (“A-blad”) on concrete repair. A guide on other uses of epoxies in the construction industry is being developed. Some examples of measures include:

- **Transportation:**
  - Create a ventilated cupboard in the loading space of the vehicle, or:
  - Create a partition between the loading space and the cabin.

- **Mixing the product:**
  - Cover the floor with a foil sheet, and delimit the mixing area
- Mix with a low rotation speed (< 75 rpm)
- Use mixers with a diameter of only 1/3 of the vessel’s diameter
- Fill the vessel up to max. 20 cm under the rim
- Use unit dose systems when possible
- Use hardener from a polyethylene bottle instead of a can, in order to reduce spillage (now supplied by one manufacturer in the Netherlands).

- Hygienic measures
  - Wrap stem of tools with tape in order to reduce cleaning need
  - Use acetone for cleaning instead of aromatics
  - Use plastic covers over arms and legs, in addition to gloves and overall.
  - Follow ‘good practices’ regarding protective clothing, cleaning hands with water and soap instead of industrial cleaners etc.

Although simple, these measures are not always brought into practice. Another problem is the international nature of many suppliers of resins and other components (most formulators are Dutch). An international approach is therefore favoured by most suppliers.

**Discussion**
The participants agree with the purposes of the conference, as described by Ton Spee. Paul Evans (HSE) indicates that for HSE, exchange of information is the most important purpose of this conference.
Introduction
In the use of epoxies, both inhalation and dermal exposure are very relevant. While at HSE, there is a certain separation in the activities along the three strands ‘dermal disease’, ‘respiratory disease’ and ‘cancer’, these have to be integrated when one’s dealing with epoxies. The current version of COSHH-essentials (HSE’s tool that assists SMEs in exposure assessment and the selection of control measures) does not cover very ‘nasty’ products such as epoxies (strong sensitizers), nor substances that are generated during the process, such as wood-dust. The next version of COSHH-essentials will. For now, a separate approach is necessary.

In the UK, an increase in dermatitis connected to epoxy products was seen recently. The question arose as to whether this increase was caused by more aggressive formulations, a more widespread use of epoxies or a more careless use of the products. Therefore, HSE commissioned a study on work practices using epoxies in the construction industry. Dr. Mehdi Tavakoli from TWI in Cambridge conducted the study. The aims of the study were:
- Survey work practices using epoxy reins in the construction industry;
- Determine which formulations are used;
- Establish if usage or formulations changed.

The study involved a literature review, contacting resin manufacturers and suppliers in order to get data on toxicity and usage, and contacting professional bodies and technical universities in order to identify trends.

Uses
Main uses of epoxies include:
- Coating and paints
- Impregnating and repairing concrete, brick and wooden structures
- Repair and sealing of pipework, window frames etc.
- Adhesives for ceramic tiles
- Binders and resins for fibre reinforced composites.
Over the last years the use of epoxy resins in the UK has increased for a number of reasons. New versions of UK Food Hygiene Laws prescribed that joints between the tiles in kitchens or production facilities should be impervious, easy to clean and disinfect and should not taint food. The observation of erosion of cementitious grouts in swimming pools resulted in an increased use of epoxy grouts, despite increased cost. In the growing number of leisure pools that have wave machines, and as a result of the increased use of power showers, epoxy grouts are used for the same reason. In addition, formulations have become more easy to use. Modern epoxy grouts are water washable and easy to apply and clean. Consequently, resistance from the tiling contractors reduced. Finally, epoxy grouts continue to be specified for their chemical resistance.

**Sensitisation**

The main constituents of epoxy systems are the base epoxy resins, the curing agents and the (reactive) diluents.

Regarding *base resin* sensitisation, most people who experienced contact allergy have been sensitised to the DGEBA type of epoxy resin. However, allergic contact dermatitis due to non-DGEBA epoxy resins has also been reported. It is mainly the epoxy resin oligomer of MW = 340 which is responsible for epoxy resin allergy. The sensitising capacity decreased in inverse proportion to the increase in the average molecular weight of the resin mixtures.

Regarding *curing agents* sensitisation, polyamine curing agents have been found to be contact irritants and sensitisers. Aliphatic and cycloaliphatic polyamines are low-viscosity hardeners which can melt with epoxy resins at room temperature. These curing agents may be employed in some two-part, room temperature curing epoxies used in the construction industry. Polyamides and epoxy-amine adducts that are less volatile, less reactive and less irritating have been developed to reduce skin sensitisation effects.

One-component epoxy systems contain curing agents which are inactive at storage temperature but initiate a curing process when heated. Typical latent curing agents include organic acid anhydrides. These types of curing agent may be used in one-part, powder epoxy or epoxy-polyester paints, one-part adhesive sealants or encapsulants and polymer composite laminates. Most of the publications referred to contact allergy to polyamine hardeners. A few reports on non-amine hardeners have been published.

*Reactive diluents* have also been found to cause contact allergy. Contact allergy to reactive diluents without contact allergy to epoxy resins is also possible. These materials are more volatile than DGEBA epoxy resin and may cause an airborne

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1 DGEBA: diglycidylether of bisphenol-A
dermatitis pattern. Again it was shown that low molecular weight (MW = 175-360) diluents can cause sensitisation. A higher molecular weight diluent (aliphatic polyglycidyl ether) of MW = 1700 produced no reactions. There is an increasing tendency to use reactive diluents in epoxy resins. As the demand for the development of a new generation of epoxy resins with improved properties increases, new hardeners, diluents or epoxy base resins may be introduced with unknown skin sensitisation effects.

**Controlling exposure**

The use of epoxies in the construction industry is not an example of a well-controlled exposure situation. Mixing and application of epoxy resins in the construction industry is usually done by hand on site, using simple methods. Contamination of the workers’ skin occurs easily. The development of a contact allergy may be expected. It was also concluded among various materials tested, that epoxy resin was clearly the offender, and the curing agent played an additional part in this respect. Some construction workers may become allergic to rubber chemicals in gloves and this may sometimes be confused with epoxy resin sensitisation. A number of control measures can be indicated:

- Make workers aware of the risk of epoxy sensitisation
- Wear protective clothing, particularly effective gloves. Change protection regularly for continued effectiveness.
- Use higher (> 900) MW epoxy resins/diluents
- Use one-part, instead of two-part, epoxies to reduce the risk of skin contact during hand mixing
- Use two-part or pre-mixed epoxies supplied in single or twin cartridges, or mixing of two components with an automated internal mixer or dispensing equipment.
- Avoid contact with incompletely cured epoxy resins
- Provide ventilation to avoid airborne dermatitis
- Susceptible individuals should not be selected to work with epoxies
- Use epoxy systems with reduced risk of sensitisation
- Proper instructions for workers on good housekeeping, education in hygiene, proper methods of disposal, handling procedures.

Barrier creams may be effective (see General discussion). However, their use in some applications in the construction industry is often impractical. Damaged skins, including even small wounds and abrasions, should be protected from epoxy-compound exposure because of increased skin sensitisation. Finally, all epoxy users should have access to material safety data sheets and understand the possible harmful effects if not used properly.
Regarding the use of gloves, it’s hard to make an optimal choice. Fluorinated rubber gloves are suitable, but have a high price and poor mechanical properties. Butyl or brominated butyl rubber are suitable for solvent-free formulations but not with solvents. Besides, they have a higher price compared to nitrile. PVC may be used for some solvent-free epoxy resins and epoxy curing agent systems. Nitrile rubber is suitable in many cases, with some limitations. They may be used for a short time for solvent based formulations. Nitrile rubber has a low price, excellent mechanical properties. Polychloroprene might be used with few formulations, but additional testing is required. Finally, natural rubber is not suitable for handling epoxy resin or epoxy curing agent formulations.

Discussion
Ulrich Goergens, Bau-Berufsgenossenschaft Rheinland und Westfalen

Ulrich Goergens works at the ‘service center’ occupational health, dep. hazardous substances of the Bau-Berufsgenossenschaft, which is the institute for statutory accident insurance and prevention in the construction industry.

Introduction
In Germany as well, a growing use of epoxies can be seen. One example is the use of epoxy resin in laying cobblestone road pavement. In addition, a growing number of occupational diseases that are caused by epoxies are seen. These include acute skin irritation, corrosive burns, allergic contact dermatitis (many cases) and respiratory diseases. The latter only occur when using hot-curing epoxies, and can be attributed to the use of acid anhydrides. Table 1 presents the number of officially established (compensated) occupational skin and respiratory diseases over the period 1999-2000. The construction industry showed by far the highest numbers of occupational skin diseases.

Table 1 Compensated occupational diseases 1999-2000

<table>
<thead>
<tr>
<th>Skin diseases (BK 5101)</th>
<th>238</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industry branches:</td>
<td></td>
</tr>
<tr>
<td>- Nonmetallic minerals</td>
<td>1</td>
</tr>
<tr>
<td>- Metal</td>
<td>15</td>
</tr>
<tr>
<td>- Electro technics</td>
<td>23</td>
</tr>
<tr>
<td>- Chemistry</td>
<td>18</td>
</tr>
<tr>
<td>- Wood</td>
<td>6</td>
</tr>
<tr>
<td>- Textile/ leather</td>
<td>1</td>
</tr>
<tr>
<td>Construction</td>
<td>144</td>
</tr>
<tr>
<td>Trade</td>
<td>21</td>
</tr>
<tr>
<td>Health service</td>
<td>9</td>
</tr>
</tbody>
</table>

| Respiratory diseases (BK 4301, BK 4302) | 6 |

Figure 1 shows the main causes for allergic contact dermatitis among male workers in the German construction industry. While cement allergies are the most common in absolute numbers, the relative incidence is much higher for epoxy allergies, when the numbers of workers involved are taken into account. The 231 cases of cement-
allergies arise from 100,000’s of workers, while the 59 cases of epoxy-allergies arise from only 1000’s of workers.

In 2001, a workshop was held on the occupational health and safety aspects of the use of epoxies. The main conclusions were that epoxies cause growing problems in many industrial branches, that high disease incidences can be seen, that the period between start of work and occurrence of sensitisation usually is short (indicating a high allergenic potency), that high numbers of airborne contact dermatitis can be seen and that most users of epoxies are not aware of the special risks connected to the products. Therefore, the Minister of Labour appointed two working groups on epoxies:

− A working group, elaborating general guidelines (a ‘Technische Regeln für Gefahrstoffe’ on epoxies)
− A working group, elaborating branch specific guidelines regarding epoxies.

The first working group concentrated on risk assessment and possible substitutes for epoxy products, the second working group concentrated on the possible organisational, technical and personal protective measures. Ulrich Goergens takes part in both working groups.

Figure 1 Main causes for allergic contact dermatitis among male workers in the German construction industry (see overheads as well)
Risk assessment
The risk assessment included both substance specific aspects and handling aspects. Regarding the substance specific aspects one deals with the questions which chemicals are used in epoxy systems, and what is known about these substances (sensitisation potential, casuistry experiences etc.). First, an inventory was made of chemicals used in epoxy systems, using product information (Material Safety Data Sheets; MSDS’s) from manufacturers. The inventory, which was distributed at the conference, contains the following data:

- Substance name
- CAS-nr, EG-nr.
- Frequency in 1500 MSDS’s studied
- Hazard designation
- Physical data
- Legal characterisation.

A number of problems were observed. First, part of the curing agents were chemically not fully defined, but were indicated by general names such as polyamines, polyamides and aminoamides. Furthermore, these curing agents may contain various amounts of ‘free’ amines, which are not specified. The content of ‘free’ amine may be as high as 30%. In addition, only part of the chemicals have been classified by regulations (i.e. the Dangerous Substances Directive; Ed.) and in particular, data from sensitisation tests are missing for many substances. Consequently, the characterisation of many substances (by R-phrases and hazard symbols) differs from manufacturer to manufacturer. One example is the curing agent xylylenediamine, which does not have an ‘official’ European classification. In literature, several casuistry indications of a high sensitisation potential can be found for this substance. However, only a few suppliers have labelled the substance with R43 (skin sensitiser).

Product substitution
An inventory of possible substitute materials is going on, and suggestions and experiences from other countries are very welcome. At the moment, there are only very few areas for which alternative materials are known that fulfil the technical demands. Epoxy-free groutings for tiles are one of these, as long as there are no specific demands on e.g. chemical resistance. In other cases, choosing less hazardous epoxy products is advised, following some general rules:

- No aromatic amines in the hardener
- Content of residual epichlorohydrin-monomer < 20 ppm
- Low vapour pressure substitutes
- Substitutes with a low allergenic potential.
Handling aspects
Ulrich Goergens distributes the draft of the general guideline “How to handle epoxies – advice for the safe handling of epoxies in the construction industry”. The activities that are described in the guideline include transport, proportioning of the components, mixing, distribution, application (by spatula, roller, brush, spray, injection etc.) cleaning and disposal. Practical solutions, when possible illustrated by photo’s are given. An international exchange of ‘good practices’ would be very helpful. One of the problems (still) is the selection of glove materials. Many glove-test results in literature refer to solvents, while most epoxy products are solvent-free. Besides, multi-component testing should be performed. In Germany, multi-component testing of gloves with epoxy products has started, using a new ‘modified test cell’ method. The first results are expected in two months.

Other activities is Germany
In the EPOX 2002 project, which is a multicentre study of the German Contact Dermatitis Research Group (DKG), patch tests are performed with the currently-used ‘standard’ range of test-substances for epoxy products, and with a new range of test-substances, including much more different hardener-components and reactive diluents. The first results are now being processed. A problem of the old range of test-substances was that only a very limited number of components was tested. This resulted in the observation that people at work developed severe allergic contact dermatitis, while they appeared to be ‘negative’ in the standard patch-tests performed by dermatologists. The new list of test-substances was distributed at the conference.

Finally, the German suppliers association for construction chemicals agreed upon a guideline for their own members. These include, among other things, setting a good example for construction companies (in brochures, demonstrations etc.), developing optimal package sizes, implementation of improved information for users, by implementation of a classification system such as the German GISCODE, follow APME-rules regarding free epichlorohydrin content, to minimise vapour pressure and free amines content of products and to contribute technically and financially to the study on protective glove materials. The guideline was distributed at the conference.

Discussion
Ton Spee asks whether standard ‘DIN’-test methods are used in he glove-study. Unfortunately, these standard-tests do not exist yet. There is a working group that is working on it. However, it will probably take years before e.g. the new ‘modified test cell’ method will be accepted as the ‘standard’.
Introduction
This presentation dealt with the question whether exposure to monomers as a result of processing cured epoxy might be an overlooked health risk. The question arose at a shipyard, that started using epoxy filler. The company requested measurements of the exposure to sanding dust, and asked whether this dust could constitute any specific health risk. Evaluation against the current occupational exposure limit of 3 mg/m³ for ‘organic dust’ might not lead to sufficient protection when free monomer is present in the sanding dust.

The goal of the project carried out was therefore, to evaluate the amount of free and uncured epoxy (e.g. BADGE, see figure) in sanding dust. In addition, the risk of getting sensitised by exposure to epoxy-monomer in sanding dust was to be estimated.

Figure 1 – BADGE (bisphenol-A diglycidylether)

Methods
Sampling was performed during sanding operations at a shipyard (epoxy filler) and at a manufacturer of windmill blades. Curing time and curing temperature of the epoxy products were varied, in order to study the influence on the amount of free monomer in sanding dust. After sampling the sanding dust, extraction in acetonitril took place, and subsequent analysis by HPLC/DAD or GC/FID.

Criteria for evaluation of the results were found in the type of epoxy concerned (molecular weight of the resin), the type of exposure (inhalation or skin) and in the specific Danish regulations towards epoxies. This regulation, an attachment on “Working with epoxy resins and isocyanates” to the general chemical agents’ directive applies to circumstances in which:
- Epoxy resins (ER) with molecular weight < 700 is used
- Materials that contain > 1% of such epoxy resins (M < 700) are used
- Reactive diluents (RD) with 1 or more free functional epoxy-groups are used
- Materials that contain > 0,2% of such reactive diluents are used.

A general calculation rule determines whether or not the specific rules apply for specific activities:

**ER/1% + RD/0,2% > 1**

When the outcome is > 1 for the activity of sanding epoxy filler at shipyards or sanding windmill blades, the specific rules will apply. These rules include the following subjects:

**MSDS:**
- Curing time must be specified in MSDS

**Security-precautions:**
- Precautions until the materials are cured and the exposure to epoxies have stopped
- Warning signs

**Prohibitions:**
- Persons with epoxyallergy or "hyperhidrosis manuum" must not work with the materials

**Education:**
- Special training (2 days)

**First aid:**
- Sufficient first-aid equipment available
- Medical aid if worker has eczema, eye-injuries or corrosive damages to skin

**Handling etc.:**
- Skin contact must be avoided
- Wash-basin must not be hand operated
- Shower with cold and hot water available
- Cleaners, soaps, creams, disposable towels available
- Changing-rooms available
- Separate wardrobes for daily clothes and working clothes
- Proper hygiene
- Eating, drinking and smoking forbidden
- Working clothes must not be worn in lunch-room
- Waste, empty packing, used towels, discarded protectionclothes, gloves etc. must be placed in waste containers marked "contains epoxy-waste".
Results
The results of the measurements at sanding filler materials at the shipyard are presented in table 1.

Table 1 – Results – Filler (sanding dust)

<table>
<thead>
<tr>
<th>Sampling</th>
<th>Temp. °C</th>
<th>Curing time</th>
<th>BADGE w/w %</th>
<th>HDDGE w/w %</th>
<th>BADGE + HDDGE w/w %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 dec. 2001</td>
<td>?</td>
<td>24h</td>
<td>3,7</td>
<td>3,2</td>
<td>6,9</td>
</tr>
<tr>
<td>2 dec. 2001</td>
<td>?</td>
<td>48h</td>
<td>3,0</td>
<td>3,7</td>
<td>6,7</td>
</tr>
<tr>
<td>3 jan. 2002</td>
<td>?</td>
<td>48h</td>
<td>1,3</td>
<td>0,7</td>
<td>2,0</td>
</tr>
<tr>
<td>4 may 2002</td>
<td>23°C</td>
<td>24h</td>
<td>1,3</td>
<td>0,69</td>
<td>1,99</td>
</tr>
<tr>
<td>5 may 2002</td>
<td>23°C</td>
<td>48h</td>
<td>0,81</td>
<td>0,45</td>
<td>1,26</td>
</tr>
<tr>
<td>6 may 2002</td>
<td>30°C</td>
<td>24h</td>
<td>0,69</td>
<td>0,43</td>
<td>1,12</td>
</tr>
<tr>
<td>7 may 2002</td>
<td>20°C</td>
<td>168h</td>
<td>0,56</td>
<td>0,22</td>
<td>0,78</td>
</tr>
</tbody>
</table>

The results of the measurements gave rise to the following evaluation of the activity:

<table>
<thead>
<tr>
<th>Sample</th>
<th>BADGE/1% + RD/0,2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>

It is clear that the outcome of the calculation was in all cases > 1. Further results for the windmill blade producing facility have been presented in table 2. The outcome of the calculation ranges from 0,2 to 6,4 here.
Table 2 – Further results for the windmill blade factory

<table>
<thead>
<tr>
<th>Glass-number</th>
<th>ID</th>
<th>Material</th>
<th>Moulding</th>
<th>Time/ temp</th>
<th>BADGE 1</th>
<th>AGE 2</th>
<th>BDDGE 3</th>
<th>TMPTE 4</th>
<th>HDDGE 5</th>
<th>Total monomers</th>
<th>Monomers</th>
<th>BADGE</th>
<th>RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>3V 1</td>
<td>1</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td>0,17</td>
<td></td>
<td>0,1</td>
<td></td>
<td></td>
<td>0,27</td>
<td>1+5</td>
<td>0,7</td>
<td></td>
</tr>
<tr>
<td>1E 1</td>
<td>1</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1+5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15E 15</td>
<td>15</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td>0,48</td>
<td></td>
<td>1,19</td>
<td></td>
<td></td>
<td>1,67</td>
<td>1+5</td>
<td>6,4</td>
<td></td>
</tr>
<tr>
<td>17V 20</td>
<td>20</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td>1,65</td>
<td></td>
<td>0,52</td>
<td></td>
<td></td>
<td>2,17</td>
<td>1+5</td>
<td>4,3</td>
<td></td>
</tr>
<tr>
<td>20E 20</td>
<td>20</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1+5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19E 19</td>
<td>19</td>
<td>Filler</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1+5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12V 12 Rep.</td>
<td>12</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td>0,07</td>
<td>0,29</td>
<td>0,0045</td>
<td></td>
<td></td>
<td>0,365</td>
<td>1+2+4</td>
<td>1,5</td>
<td></td>
</tr>
<tr>
<td>18E 18 Rep.</td>
<td>18</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1+2+4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6V 6 Rep.</td>
<td>6</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td>0,5</td>
<td>0,81</td>
<td>0,03</td>
<td></td>
<td></td>
<td>1,34</td>
<td>1+2+4</td>
<td>4,7</td>
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</tr>
<tr>
<td>8E 8 Rep.</td>
<td>8</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1+2+4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4V 4 Rep.</td>
<td>4</td>
<td>Filler</td>
<td>11-feb-03</td>
<td>6h 76°C</td>
<td>0,45</td>
<td>0,63</td>
<td>0,02</td>
<td></td>
<td></td>
<td>1,1</td>
<td>1+2+4</td>
<td>3,7</td>
<td></td>
</tr>
<tr>
<td>10V 10 Root</td>
<td>10</td>
<td>Filler</td>
<td>07-feb-03</td>
<td>5h 50°C</td>
<td>0,02</td>
<td></td>
<td>0,04</td>
<td></td>
<td></td>
<td>0,06</td>
<td>1+3</td>
<td>0,2</td>
<td></td>
</tr>
<tr>
<td>11V 11 Root</td>
<td>11</td>
<td>Filler</td>
<td>06-feb-03</td>
<td>5h 50°C</td>
<td>0,05</td>
<td></td>
<td>0,07</td>
<td></td>
<td></td>
<td>0,12</td>
<td>1+3</td>
<td>0,4</td>
<td></td>
</tr>
<tr>
<td>16E 16 Root</td>
<td>16</td>
<td>Filler</td>
<td>07-feb-03</td>
<td>5h 50°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1+3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5V 5 Root</td>
<td>5</td>
<td>Filler</td>
<td>07-feb-03</td>
<td>5h 50°C</td>
<td>0,11</td>
<td></td>
<td>0,14</td>
<td></td>
<td></td>
<td>0,25</td>
<td>1+3</td>
<td>0,8</td>
<td></td>
</tr>
<tr>
<td>13V 13 Wing</td>
<td>13</td>
<td>Filler</td>
<td>10-dec-02</td>
<td>6h 70°C</td>
<td>0,03</td>
<td></td>
<td>0,04</td>
<td></td>
<td></td>
<td>0,07</td>
<td>1+3</td>
<td>0,2</td>
<td></td>
</tr>
<tr>
<td>7V 7 Wing</td>
<td>7</td>
<td>Filler</td>
<td>25-jan-03</td>
<td>6h 70°C</td>
<td>0,03</td>
<td></td>
<td>0,03</td>
<td></td>
<td></td>
<td>0,06</td>
<td>1+3</td>
<td>0,2</td>
<td></td>
</tr>
<tr>
<td>9E 9 Wing</td>
<td>9</td>
<td>Filler</td>
<td>25-jan-03</td>
<td>6h 70°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1+3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2V 2 Wing</td>
<td>2</td>
<td>Filler</td>
<td>05-feb-03</td>
<td>6h 70°C</td>
<td>0,04</td>
<td></td>
<td>0,05</td>
<td></td>
<td></td>
<td>0,09</td>
<td>1+3</td>
<td>0,3</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions
Sanding dust from cured epoxy may present a risk of allergic eczema. In many cases in sanding operations at the shipyard and the windmill blade factory the specific regulations regarding epoxies will have to be followed. Several parameters determine the amount of free epoxy present:
- Accuracy of weighing and adding resin and hardener
- Effectivity of the mixing process
- Curing temperature
- Curing time.

Discussion
Paul Evans asks whether all (SME) companies in the construction industry that use epoxies comply to the rather strict rules described.
This is hard to say, although the Danish Labour Inspectorate is quite ‘tough’ at this issue.
Jeroen Terwoert asks whether (part of) the monomers could also have been formed during the sanding operation, as a result of the heat produced. Probably, practically all of the monomer was present before starting the sanding operation already. The functional ‘epoxy-group’ is very high-energetic, and it’s hard to re-create such a group, unlike for instance the isocyanate group. In the case of polyurethanes, re-creation of the isocyanate monomers is an issue. Besides, a mixing inadequacy of 2% immediately results in 2% extra free functional epoxy groups in the cured product. Mixing epoxy-resin and hardener is not easy, as the resin is much more viscous than the hardener.

Ton Spee asks whether attention has been paid to (free) amines as well. This is not the case, although these will probably be present as well.
CONTACT DERMATITIS AMONG NORWEGIAN INDUSTRIAL PAINTERS

Olve Rømyhr; University Hospital Trondheim

Olve Rømyhr is an occupational hygienist at the Department of Occupational Medicine of the University Hospital in Trondheim, dealing with both skin and airway disease, the last four years in a project on industrial painters.

Introduction
Norway has a large oil- and shipbuilding industry, and the oil installations and the ships need good corrosion protection. Thus many workers are involved with blast cleaning, painting, fire protecting and metal spraying. Their working environment includes exposure to several chemicals that may cause allergy in exposed workers. Among them epoxy paints and epoxy-based fire protection.

Table 1 – Industrial paint volume 1997-2000

<table>
<thead>
<tr>
<th>Year</th>
<th>Volume (1000 liter)</th>
<th>Epoxy (%)</th>
<th>Polyurethane (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>816</td>
<td>66</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>1998</td>
<td>1029</td>
<td>67</td>
<td>12</td>
<td>21</td>
</tr>
<tr>
<td>1999</td>
<td>666</td>
<td>66</td>
<td>9</td>
<td>25</td>
</tr>
<tr>
<td>2000</td>
<td>413</td>
<td>61</td>
<td>9</td>
<td>30</td>
</tr>
</tbody>
</table>

Approximately 2/3 of the paint volume is epoxy-based paint. 10-15 % of the volume is polyurethane-based paint. The use of polyurethane products in the industry is decreasing, due to restrictions in their use. The third group is a mix of products based on zinc silicates, polysiloxanes and others. Over a few years in the early 1990-ies a number of painters with what proved to be epoxy-induced contact allergy, were remitted to our department. This awoke our interest in the allergy risks in this group of workers. In the industry there had for many years been a concern about the health and safety aspects of industrial painting, and especially about the risks of occupational diseases caused by the isocyanates.
In cooperation with the industry we proposed a project to:

- Quantify skin and lung diseases in a cohort of industrial painters, and in particular, to register the incident figures, that is, the number of new cases per year for allergic eczema and occupational asthma.
- and secondly, to characterise the exposure during painting with polyurethane- and epoxy-based paints.

The project was run in cooperation with the Department of occupational medicine, University hospital in Bergen, and the National Institute of Technology in Oslo.

*Figure 1 – Skin or airway complaints at work*

<table>
<thead>
<tr>
<th>Without complaints</th>
<th>With complaints</th>
</tr>
</thead>
<tbody>
<tr>
<td>58%</td>
<td>42%</td>
</tr>
<tr>
<td>31%</td>
<td>Skin complaints caused by work</td>
</tr>
<tr>
<td>9%</td>
<td>Skin complaints exacerbate by work</td>
</tr>
<tr>
<td>14%</td>
<td>Had contact with doctor or health services for skin complaints</td>
</tr>
<tr>
<td>15%</td>
<td>Airway complaints caused by work</td>
</tr>
<tr>
<td>5%</td>
<td>Airway complaints exacerbate by work</td>
</tr>
<tr>
<td>8%</td>
<td>Had contact with doctor or health services for airway complaints</td>
</tr>
</tbody>
</table>

**Survey**

We started with a questionnaire survey on the prevalence of skin and airway complaints, in 98 among 1200 painters employed in six of the largest Norwegian companies in this industry. We believe that there are totally about 5000 industrial painters in this industry in Norway.
In this survey we obtained a reply from 72% of the workers. The study revealed that 42% of them had skin or airways complaints caused by work. More workers reported skin complaints (31%) than airway complaints (15%). These figures of course include both minor and major skin- and airways symptoms, and we can’t tell whether they are caused by epoxy- or isocyanate exposure, or by something else.

**Cohort study**

To register the incident cases of eczema caused by epoxy, we established a dynamic cohort from the same six firms. The registration started in September -97 and lasted for four years.

- During this period a large number of the painters quit, and other start, but at any time some 1200 industrial painters were employed in these firms.
- Mean age of the painters was 36 years.
- Most of the workers had been industrial painters for many years already when the follow up period started (mean: 10 years).

Workers were remitted to us from the occupational health services of the firms, or through a personal contact we made to all workers who quit their job during the follow-up period. The workers were examined in order to diagnose cases of allergic eczema.

The eczema cases were tested with relevant commercial patch tests series. In addition we made a special series of amines and epoxy compounds present in the paint used in the industry, but not included in any of the commercial series.

Over a 4-years period (5100 person-years) we registered 24 cases of allergic eczema. These cases were confirmed by positive patch tests. One of the cases was caused by exposure to isocyanates, and the 23 other cases were caused by exposure to epoxy products. The yearly incident figure for allergic eczemas found in this study was 4.6 per 1000 person-years.
Table 2 – Number of positive patch test results – 23 cases

<table>
<thead>
<tr>
<th>Resins/reactive dilutens</th>
<th>Hardeners</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>Ethylenediamine 1</td>
</tr>
<tr>
<td>DGEBA/F</td>
<td>Hexamethylenetetramine 1</td>
</tr>
<tr>
<td>DGEBF</td>
<td>Diaminodifenylnmethane 1</td>
</tr>
<tr>
<td>Cycloaliphatic resin</td>
<td>3-dimethylaminopropylamine 1</td>
</tr>
<tr>
<td>Phenylglycidyether</td>
<td>Trietylenetetramine 1</td>
</tr>
<tr>
<td>Cresylglycidylether</td>
<td>Diethylenetriamine 1</td>
</tr>
<tr>
<td>Epoxide 8</td>
<td>Isophoronediamine 0</td>
</tr>
<tr>
<td></td>
<td>Tetraetylenepentamine 2</td>
</tr>
<tr>
<td></td>
<td>2,4,6 tris(dimethylaminomethyl) phenol 7</td>
</tr>
<tr>
<td></td>
<td>m-xylene-a,a-diamine 8</td>
</tr>
<tr>
<td></td>
<td>2,2,4 trimethylhexamethylene-diamine 4</td>
</tr>
<tr>
<td></td>
<td>n-aminoethylpiperazine 1</td>
</tr>
</tbody>
</table>

Most of the workers (17/23) had a positive patch test to the bisphenol A-resin (DGEBA), included in the standard series (‘bold’). The other test chemicals are included in the standard epoxy-series (‘Italic’), or in the test series made for this project (‘normal’).

It is an interesting finding that several of the workers had a positive patch-test to the amines: tris-DMP (7), XAD (8) or TMHMDA(4)). These three amines are not classified as skin allergens according to the European regulations on the classification and labelling of dangerous chemicals, and they are not included in any of the commercial patch-test series. In fact in four workers (almost 20% of the tested workers), had a positive patch test to one of these amines only. Thus, their allergy would have not been recognised without the use of this special test series.

The results show that the standard test alone (which is often used in general clinical practise in Norway) will recognise 70-80 % of the cases. The results show that it may be important to patch-test not only with commercial test series, but with all suspected chemicals in the paints.

**Exposure measurement**

Skin exposure is the most relevant exposure route when exposed to epoxy. Unfortunately there are as far as I know, no good methods described to describe the
exposure, and we lack limit values for skin exposure. Due to this, in our project we
did not try to characterise the epoxy skin exposure. However, at the Institute of
working life in Sweden they have developed a method recently.

But epoxy exposure may be airborne and thus, methods to quantify airborne
exposure may be relevant. Some of the cases of eczemas may be caused by airborne
epoxy exposure. Exposure to some of the amines may cause asthma (EDA, DETA,
TETA and IPDA) and Kanerva in Finland has recently documented with objective
tests (specific provocation test) that the epoxy resin itself causes asthma as well.
Epoxy resin is seldom recognised as a cause of asthma among spray painters, but
may be underestimated.

In the project we decided to quantify relevant airborne exposure with established
methods from the literature. Herrick and co-workers published in 1988 a method to
quantify the total content of epoxy groups in spray paint operations. In cooperation
with Roger Lindahl at the Swedish Institute of working life we planned to use this
method to quantify epoxy exposure in our project, but we failed due to
methodological problems.

So, in our project we ended up to try to quantify airborne amine exposure in spray
painting operations. As far as I know, data that describe the exposure to amines in
paint operations have not been published. The measurements were done in
cooperation with Roger Lindahl at the Swedish Institute of working life.

In the study four epoxy based paints where applied under the standard conditions
inside a small chamber with no ventilation. Three litres of paint were applied on 3
square meters inside this chamber in 20 minutes. The exposure conditions were far
from representative for field situations. If at all, the condition inside the chamber
may represent conditions when paints are applied inside tanks and in other confined
spaces.

Three of the hardeners contained isophoronediamine (IPDA) (2x 10-30%, 1-5%) and
one of the hardener contained diethylenetriamine (DETA) (2,5-10%), according to
material safety data sheets. No exposure to DETA, and a maximum of IPDA-
concentration of 0,13 mg/m³ was found. Also in the case of the amines, the
evaluation of the exposure levels is difficult, because TLV’s are lacking for many of
them. DETA have a Norwegian TLV of 4 mg/m3, but there is no established TLV
for IPDA.

We did also measurements of five other amines in other epoxy-paints. The
concentrations of the other amines were low as well.
Figure 2 – Concentration of diethylenetriamine after mixing of base and hardener

We were somewhat surprised of the low levels.

In one other experiment we therefore mixed the two parts of an epoxy-paint, and analysed the concentration of diethylenediamine in the paint during the two hours after mixing (figure 2). Immediately after mixing, the concentration of DETA in the paint was 0.8 %. According to this experiment the concentration was 0.1 % 10 minutes after mixing. The fast reduction of DETA-concentrations is probably due to a fast reaction between the amine- and epoxy-groups.

Based on these studies I will not expect high concentrations of amines during epoxy spray painting.

Main conclusions
To summarise the findings in our study:

- Our incidence rate for occupational allergic eczema must be considered as minimum figures, mainly because:

1. We can’t guarantee that all new cases were identified in the study. But, due to our contact to all workers who quit their work in the period, we don’t think we have missed many cases.
2. More important is that many of workers had been industrial painters for many years when the follow up period started (mean 10 years). We know from other studies that in 40 % of the cases, epoxy-allergy develops within the first year of
exposure. So our incident figures should be expected to considerably higher in a cohort of painters without earlier exposure.

3. The companies in this study are among the biggest in the Norwegian industry, and the control of exposure may be somewhat better here than in rest of the industry. Higher incident figures should be expected in other part of the industry.

I think the figures still illustrate that there is a considerably risk of allergic eczemas in this industry

- Good exposure methods are lacking

There is a need for development of both skin exposure methods, and methods to quantify airborne exposure.

- The levels of amines are not expected to be very high, but again, it is difficult to say whether the levels are high or low when exposure limits are lacking.

**Follow-up**

The Norwegian association of occupational hygienists have 350 members. The association arrange two occupational hygiene conferences each year. Last year we arranged the IOHA conference in Bergen. Besides that, the association have an ambition to publish guides on occupational hygiene matters. So far there have been published two guides: one on the safe handling on isocyanates, and one on compressed air in airline respirators. Now the association want to make a guide on safe handling of epoxies and they have asked me to lead the work.

The aim is to produce a practical guide with a focus on risk assessment and risk management for workers and for occupational health professionals. We are a working group of four occupational hygienists and one dermatologist who will do this work on voluntary basis. We plan to publish this guide during 2003. I hope this network can help me with information and discussions.

**Discussion**

-Ulrich Goergens asks which type of epoxy coatings are used in the Norwegian industry. In Germany, mainly solvent-borne epoxy coatings are used for spray painting. The resins used in these coatings have a high molecular weight, and consequently a low sensitisation potential. That’s why in Germany relatively few cases of allergic contact dermatitis are seen in industrial painting.
In Norway solvent borne epoxy coatings are used a lot as well, but high solids, solvent free and waterborne epoxies are used as well. Ton Spee adds that the ban on products with a high solvent content for interior work has resulted in an increase in the use of reactive diluents, thus increasing the allergenic potency of the products.

-Ulrich Goergens makes the remark that amines (e.g. isophorone diamin) have been shown to cause airborne contact dermatitis among spray painters. The idea is, that sensitisations occurs after direct skin contact. Subsequently, airborne exposure provokes the contact dermatitis. Untill recently, no valid method to measure isophorone diamine (IPDA) existed. IPDA reacts with the filter material that was formerly used. A newly developed method has shown to give better results. During floor covering activities, IPDA-concentrations of 10-20 ug/m³ have been measured, which are thought to be sufficient for provoking an allergic reaction.
Jeroen Terwoert; IVAM UvA BV

Jeroen Terwoert is an occupational hygienist working at the Chemical Risks department of IVAM – Research and Consultancy on Sustainability, a private consultancy firm. At the moment, one of the projects he works at is the development of health criteria for epoxies, and of the ‘good practice guide’ (‘A-blad’) on epoxies in the construction industry.

**Introduction**

Epoxy products are widely applied in the construction industry. They have excellent adhesive characteristics on various surfaces, they are resistant to most chemicals and they do not rot. Contrary to reactive polyesters and acrylates, epoxy’s hardly shrink after application. These qualities make the use of epoxy’s extremely popular. Technically speaking however, epoxy’s also have disadvantages. Especially the discolourisation under the influence of sunlight can be disadvantageous in certain applications.

Some applications of epoxy’s are:

- rehabilitation of rotten wood, by removing deteriorated parts and replacement by epoxy mass
- repair of affected concrete, in a comparable way
- chemically resistant floor finishing
- reinforcement of cement based floor finishing to achieve a higher mechanical resistance
- anti-corrosive coating on metal
- as an adhesive in many applications, varying from anchors for concrete to restoration activities

In most cases, epoxy’s consist of two components, a resin and a hardener. The resin consists of a polycondensation product of epichlorohydrine and bisphenol. The hardener is an amine. Sometimes there is a third component, for instance in thick epoxy floor finishing layers. Generally, this third component is a filler.

Fully hardened epoxy products are inert and after hardening, little or no harm to health is to be expected. However, the individual, not fully hardened components can be harmful to health. The resin, based on bisphenol A or bisphenol F, or
mixtures of these two, is a skin allergen. Hardeners consist of amines that can affect the skin. The legal classification varies from ‘irritating’ to ‘corrosive’. Furthermore, many hardeners are skin allergens. In practice, about one out of every five epoxy workers develops a skin allergy. This can be so serious, that they have to leave the profession and a profession without exposure to epoxy’s must be chosen instead. Furthermore, residues of epichlorohydrine can remain in the resin after production. Epichlorohydrine is a carcinogen. The content of residual epichlorohydrine can be reduced to less than 3 parts per million (ppm) through optimisation of the production process. Certain amines are also carcinogens. Aromatic amines are still applied, especially with concrete injection. The allergenicity of epoxy products can be reduced by applying larger molecules. Prereacted products or prepolymer are then applied. In the hardener a higher molecular weight amine can be chosen, or a polyamino amide. However, disadvantages consist of are a higher viscosity on application and a slower hardening. Above certain molecular weights, no hardening occurs at room temperature. This does not mean a necessary disadvantage in industrial situations, when products can be heated. However, in the construction industry hardening at room temperature is indispensable. The wide range of required characteristics makes that especially of hardeners there is a large choice. The composition of the resin is less variable, this is an oligomer of bisphenol A or bisphenol F with epichlorohydrine. In general the molecular weight is below 700.

**Why introduce a ranking system for epoxy’s?**

In conclusion, the harmfulness of epoxy’s varies strongly, and depends among other things on the desired characteristics. This offers the possibility to classify epoxy’s according to their harmfulness. In general, this type of classification has two objectives:

- to inform the user about the harmfulness of epoxy’s with comparable applications,
- to stimulate investigation into less harmful products.

An ideal classification system should be based on information that is easily accessible, should not be too complex, should be controllable and, above all should be discriminating. Preferably, for each type of application, there should be products available in more than one class. The system should stimulate improvement of products, in order to create a dynamic situation.

For the reason of accessibility of information, most existing classification systems are based on the information provided on the Material Safety Data Sheet (MSDS). Our classification of epoxy products in the Product group Information System
Arbouw (PISA) is also based entirely on data from the MSDS. This has some major advantages:
- an MSDS must be set up for all epoxy products, so that the information is accessible without further procedures
- the information must be delivered according to a standard format, so that it can be found quickly and simply
- the information is composed in accordance with legal criteria, so it should be uniform for all types of products.

There are also some major disadvantages:
- only relatively large quantities, sometimes 20%, of the individual components must be specified. This disadvantage will disappear when the new Preparations Directive will come into force
- the MSDS is based on a ‘hazard’ approach. Components are classified regardless of the chance of exposure.

We have looked for an alternative classification system, that not only takes the hazard, but also the chance of exposure into consideration. But the prerequisite that information must be easily accessible, remains.

**Basis of the classification system**

Because not only the hazard but also the chance of exposure is taken into consideration, the system is based on a relatively large amount of criteria. The criteria consist of two major groups:
- toxicity data, as a measure for the hazard. These data can be found on the MSDS
- physical-chemical data, as a measure for the chance of exposure. These can partly be found on the MSDS, partly in handbooks.

Each criterion leads to the assignment of malus points to the product. The more malus points, the more harmful the product is. The total amount of malus points leads to classification into a limited number of classes. The criteria are mentioned in Table 1.

The system is inspired on, but not equal to, the system that is in use in Germany to rank the harmfulness of substances and preparations for the water ecosystem, the so-called ‘Wassergefährdungsklasse’. This system also works with malus points per substance.

During the development of the classification system, there have been five meetings with the suppliers in which an intensive exchange of information and points of view has taken place.

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2 a ‘malus point’ is the opposite of a ‘bonus point
Generally, the amount of residual epichlorohydrine is not specified on the MSDS. The concentration is below the legal limit for specification. The members of the Association of Plastic Manufacturers in Europe (APME) have agreed upon a concentration limit of 5 ppm in unmodified resins and of 20 ppm in reactive diluents.

*Table 1: criteria for attribution of malus points to epoxy products on the basis of individual components*

1. amount of residual epichlorohydrin in the resin and in the reactive diluent
2. presence of components with a T or T+ symbol (toxic or very toxic)
3. presence of components that are carcinogenic, mutagenic, reprotoxic, or sensitisers for the respiratory tract (based on R-phrases)
4. presence of hardeners with R43, R34 or R 35
5. amount of reactive diluent in the resin
6. amount of VOC (volatile organic compounds)
7. lack of product information
8. boiling point of the amines in the hardener
9. boiling point of reactive diluents
10. molecular weight of the amines in the hardener
11. molecular weight of reactive diluents
12. amount of free amine in the hardener.

In order to find the physical constants, the identity of the substance must be known. It will be impossible to find these when the information on the MSDS is limited to the specification of substance groups. The classification with the corresponding malus points is presented in Table 2.
<table>
<thead>
<tr>
<th>Criterion</th>
<th>Specification</th>
<th>Malus points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Amount of residual epichlorohydrine in resin and/or reactive diluent</td>
<td>[ECH] &gt; APME-limit</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>[ECH] unknown</td>
<td>25</td>
</tr>
<tr>
<td>2. Presence of substances with symbol T or T⁺</td>
<td>Per component with T⁺ &gt; 0,1%</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Per component with T &gt; 1%</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Per component with T⁺ &gt; 1%</td>
<td>20</td>
</tr>
<tr>
<td>3. Presence of carcinogenic, mutagenic, respiratory tract-sensitising and reprotoxic compounds</td>
<td>Per compound with one or more of the R-phrases: 39, 45, 46, 48, 49, 60, 61, 68 &gt; 0,1%, or 40, 42, 62, 63, 64 &gt; 1%</td>
<td>10</td>
</tr>
<tr>
<td>4. Presence of corrosive and/or sensitising hardener components</td>
<td>Hardener component(s) with R34, 35 of 43</td>
<td>15</td>
</tr>
<tr>
<td>5. Amount of sensitising reactive diluent in the resin</td>
<td>Per reactive diluent in the amount of: &lt; 2,5%</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2,5-10%</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>10-25%</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>&gt; 25%</td>
<td>15</td>
</tr>
<tr>
<td>6. Amount of Volatile Organic Compounds</td>
<td>&gt; 100 g/l for metal coatings</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>&gt; 60 g/l for other epoxy products</td>
<td>10</td>
</tr>
<tr>
<td>7. Lack of product information</td>
<td>Classification not possible due to lack of information</td>
<td>150*</td>
</tr>
<tr>
<td>8. Boiling point of the hardener(s)</td>
<td>Per hardener (amine) with a boiling point &lt; 250°C</td>
<td>5</td>
</tr>
<tr>
<td>9. Boiling point of the reactive diluent(s)</td>
<td>Per reactive diluent with boiling point &lt; 250°C</td>
<td>5</td>
</tr>
<tr>
<td>10. Molecular weight of the hardener(s)</td>
<td>Per hardener with molecular weight: &lt; 200</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>200-400</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>&gt; 400</td>
<td>0</td>
</tr>
<tr>
<td>11. Molecular weight of the reactive diluent(s)</td>
<td>Per reactive diluent with molecular weight: &lt; 200</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>200-300</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>&gt; 300</td>
<td>0</td>
</tr>
<tr>
<td>12. Amount of free amine in the hardener</td>
<td>Per free amine in an amount of: &lt; 2,5%</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2,5-10%</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>10-25%</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>&gt; 25%</td>
<td>15</td>
</tr>
</tbody>
</table>

* About the maximum number of malus points
Results of a test-classification

It is important that the classification system discriminates within groups of products. When for instance all putties come into a certain category and all coatings come into another, we can find out whether putties or coatings are more harmful. But within these groups of products it is impossible to discriminate.

As a test, we have performed the classification of a group of 23 epoxy coatings, 13 floorings, 5 adhesives and 3 wood repair masses. In total, 44 products from six suppliers were classified. The coatings were solvent-based, solvent free and water based. The other products generally were solvent-free. The results of the test are summarized in Figure 1.

Not all suppliers delivered the full set of data, not even after we sent them a reminder. For a number of products, the identity of the reactive diluents was unknown. For other products, information about the amount of residual epichlorohydrin was missing. Nevertheless it seems that the raw material suppliers are able to provide the data about the amount of residual epichlorohydrin. In the discussion we assume that all products meet the APME-criteria.

Ten coating products were water based. The total amount of malus points varied from 20 to 160. In three cases, 150 malus points were added due to lack of information about the reactive diluents. When those products are not taken into consideration, there are five water based coatings with 20 to 77 malus points.

Eleven coating products were solvent-free, the amount of malus points varied from 45 to 220. In two cases the identity of the reactive diluents was missing, so we also added 150 malus points. Without those two products, five products remained with malus points varying between 45 to 110 points.

Finally, two coating products were solvent based. The number of malus points amounted to 60 and 70.

The flooring products, adhesives and wood repair masses show somewhat smaller ranges of malus points, but still enable a discrimination between products.

The system appears to be well discriminating. Overall, the amount of malus points varied from 20 to 110.

Notably, some prerequisites that might exist with respect to which type of product to choose do not hold. E.g., the range of malus points is lower for water based coatings than for solvent based and solvent free coatings, but two water based coatings have more malus points than solvent based coatings. And, there are also two solvent free coatings that score lower than the water based coatings with the highest amount of malus points.
Division into classes
The discussion about division into different classes can become obscured by ‘political’ motives. It is tempting of course for a supplier to propose a limit in the classification so that his product ends up into a favourable class, or that of a competitor into an unfavourable one. For instance: a limit of 25 or 30 points can be favourable for one supplier and very unfavourable for another supplier. Therefore, we agreed with the suppliers to base the class limits on the results of the test-classification. The limit have chosen arbitrarily in such a way, that there is a small group of ‘favourable’ products, a large group of ‘average’ products and a small group of ‘unfavourable’ products. The division is of course very arbitrary, because the limits are random. However, it is impossible to draw limits on the basis of health effects, because there is such a large amount of parameters under consideration. Moreover, some parameters are only indirectly related to health effects. And for the moment, there is no allergen-free epoxy product. And one can doubt whether there will ever be one. We would say that the division is arbitrary, but pragmatic.

The results of ranking the 39 products for which sufficient data were available into four classes are presented in Table 4.
Table 4: division of products into classes

<table>
<thead>
<tr>
<th>Class</th>
<th>Points</th>
<th>Coatings</th>
<th>Floorings</th>
<th>Adhesives</th>
<th>Woodrepair</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 – 40</td>
<td>4</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>41 – 60</td>
<td>6</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>61 – 80</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>&gt; 80</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

The first class include 40 points, the next two 20 and the last at least 30, but probably much more. Water based coatings show up in the first three classes, solvent free coatings in all classes. We had only two solvent based products (in classes 2 and 3), which is insufficient to draw conclusions.

Conclusions
A first test with the classification system shows that the system seems to discriminate well. The amount of attributed malus points ranges from 20 to 110 (all product types), which is more than a factor of five difference. There is also discrimination within the various types of products, e.g. coatings, for water based coatings the difference is a factor of almost four and for solvent free coatings a factor of more than two. The degree of discrimination among the various applications of epoxy shows the following order:

coatings > floorings > adhesives > wood repair masses.

The system offers sufficient room for variation by varying the amount of malus points per property. Should we for instance want to give more weight to allergenic properties of a compound, then the number of malus points for the amount of sensitising components can be raised.
A problem is that it is not in all cases easy to obtain all information from the suppliers. This originates in part from the fact that formulators must get their information from the suppliers of raw material. This pertains for instance to the amount of free epichlorohydrin in the resin. A more international approach would therefore help tremendously. In fact, most suppliers do prefer an international approach, for the business of their raw material suppliers is in many cases international.
Discussion

-The remark is made that suppliers provide in their product information only concentration ranges of the components in the product, and not the exact concentration.
That’s true. In the proposed ranking system these ranges have been used as well (e.g. < 0,5%; < 2,5%; 2,5-10%; 10-25% etc.). The exact concentration is not needed for the ranking.

- Christian Pedersen explains about the Danish MAL-code system. The system was originally (in the beginning of the 1980’s) developed for paints only, but now includes more products. The code system consists of two numbers. The first number ranges from 00 to 5, and represents inhalatory effects from volatile components (not only organics). The number is derived from the content of each volatile substance, its occupational exposure limit and its volatility.
The second number ranges from 0 to 6, and represents all other effects, including for example carcinogenicity and sensitisation. The resulting ranking of products ranges from 00-1 (safest) to 5-6 (most hazardous).
The MAL-code system is not able to discriminate within the group of epoxy products. All products will get the number ‘5’ (sensitisation) as the second number. However, some differences will appear in the fist number.

-Ton Spee explains that the proposed system more closely resembles the German water hazard class system (Wasser Gefaerdungs Klasse). At least the basic principle of attributing ‘penalty point’ to products on the basis of the components present is the same.
What we have tried to do, is to enable discrimination between more potent and less potent sensitising epoxy products. The system seems to be complicated, but for the user of the products is very simple (just one number). In The Netherlands, good experiences have been gained with a ranking system of this type in the concrete mould release agents market. Users of the products requested products from classes 1 or 2 from their suppliers, and their use has increased significantly. This has pressed a number of suppliers to develop safer alternatives as well.

-Paul Evans asks if ‘viscosity’ as a criterion has been considered. Viscosity may be one of the parameters determining the potential for skin exposure.
In the extensive discussions with the Dutch suppliers, viscosity has been mentioned indeed. In the final selection of criteria it was dropped. Easy availability of data was one of the reasons to include or not include specific criteria.

-Ulrich Goergens tells that epoxy resins with a molecular weight > 1000 used to be non-classified with R43, but recently this was changed. The R43 is now attributed to resins with M > 1000 as well. Would that change the results.
It will not. Epoxy resins used in the construction industry generally have molecular weight < 700 (except for solvent-borne metal coatings). Therefore, the molecular weight of the resin has not been chose as one of the criteria.

- Christian Pedersen makes the remark that products of class 1 will still be sensitising, just like the products from class 4. One should be careful with communicating the ranking system. Using class 1 products does not mean that one can do without protective clothing.

We are fully aware of this aspect. Communication is very important. Epoxy products will always be sensitising. However, discriminating between more potent and less potent sensitisers may reduce risks after all.

-Ton Spee says that it would be very interesting to compare the results of the German patch tests with epoxy components with the outcomes of the ranking. We might get some indications as to whether the ranking system discriminates in the ‘right’ way. See ‘general discussion’.

-Bob Rajan makes the remark that individual variations in sensitivity plays a role as well.

That’s true. However, a ranking system enables showing relative differences. When products are used under the same circumstances, products of class 1 are safer than products of class 4.
11 GENERAL DISCUSSION

The participants agree that the focus in the discussion should be on the construction industry. The most hazardous epoxy products with respect to sensitisation are used in the construction industry. Besides, they are handled manually here. Bob Rajan states that we should discuss which issues should be described in the brochures, information materials etc. We should develop a common opinion on ‘good practices’. All agree.

The following themes for the discussion were defined:

1. Replacement of epoxies by other materials
2. Good practices w.r.t. packaging and mixing
3. Good work practices
4. ‘Benchmarking’ system (ranking) for suppliers and users
5. Quality of basic (toxicity) data.

Ton Spee introduces each theme.

1. Replacement of epoxies by other materials
Replacing epoxy products is very difficult in most cases, because of their outstanding properties such as chemical resistance, excellent adhesion, abrasion resistance etc. Besides, regulations such as those regarding food safety or drinking water safety hinder the introduction of alternatives. In contrast, in some cases even epoxies with aromatic amine hardeners (carcinogenic) are prescribed. Very many technical data have to be collected before an alternative is accepted. Some alternatives are:
- Epoxy-free grouting for tiles
- Cement-based concrete repair products, except when:
  ○ Chemical resistance is needed
  ○ Very fast curing is needed.
- Prevention, in the case of wood-repair products (good maintenance of the coating)
- Silicon-epoxies: a new development in metal coatings. Possibly non-sensitising or less sensitising. More information has to be gathered on these products.
- (Replacement of aromatic amines for injection?). Still epoxies, but less hazardous.

According to Dutch suppliers, aromatic amines are needed for injection systems. In Germany however, it’s said that this is not the case. However, for very highly chemical resistant floors suppliers state that they are needed.
-In the UK and Germany, the use of epoxies is increasing even in the Do-It-Yourself market.
-Christian Pedersen states that in the production of windmill blades a very wide range of hardeners is used. A ranking system for the health effects may be useful here to make a selection.
-Waterborne epoxies may contain sensitising biocides as preservatives. However, the concentrations of biocides are usually very low compared to those of potent sensitisers as the epoxy resin, reactive diluents and hardeners.

2. Good practices w.r.t. packaging and mixing
A first inventory of good practices revealed the following:
- Create a special, demarcated place for mixing.
  Mixing should ideally take place as close to the workplace as possible, in order to reduce manual transportation of epoxy product.
- Use unit dose systems as much as possible.
  Usually, these exist only for applications in which small quantities of product are used (e.g. putties, fillers, wood repair). Products such as flooring materials come in drums. Unit dose systems would be too expensive.
- Use hardeners in polyethylene bottles instead of cans
  Generally, hardeners are relatively low viscous. Supplying the hardener in PE-bottles reduces spillage, and thus the risk of skin contact. In the Netherlands, only one supplier provides this system, but it's the largest supplier.
- Accurate weighing of the two components
- Use of automated dosage systems where possible
Unfortunately, these are hard to realise for very viscous/ solid products such as epoxy resins.
- Diameter of the mixer in proportion to the vessel (maximum 1/3)
- Variable rotation speed (in order to prevent the vessel from rotating)
- Mixing at low speed (max 75 rpm)
- Closed mixer (quantities up to 25 kg; picture in German draft brochure p.7)
- Clean mixers with sand instead of solvent
- Enable sufficient space above the epoxy mass (20 cm at minimum)
- Put a sheet of foil under the vessel/container, and in case of uneven surfaces, a piece of wood (18 mm) as well. This will prevent spillages.
-Ulrich Goergens tells that some suppliers in Germany have a system in which the hardener and resin components come in one can, separated by a sheet. The sheet can be pierced with a knife, and the product can be mixed in-can.
-In the German draft-brochure (p. 6), pictures of a ‘vessel-tilter’ and dosage systems for large drums are shown.
Ideally, the suppliers, in the technical product documentation, should prescribe work practices like these (e.g. in Technical Data Sheets; users read these more often than MSDS’s).

3. Good work practices
The following points were discussed:
- Using a caddy for transportation of drums or buckets with mixed epoxy product. After mixing, manual transportation of the product to the workplace results in many splashes. On page 8 of the German draft brochure, a transportation caddy is shown that significantly reduces spillage. It can also be used for e.g. pouring-out flooring materials.
- Work in sections when applying epoxy-primer and flooring materials ‘wet-in-wet’.
This will reduce exposure of knees and legs (and hands as well) to uncured epoxy primer.
- Use long-stemmed rollers for the application of coatings.
In addition, rollers with protection shields against spatters are available, at least in Germany (see picture on p. 8 of the German draft brochure).
- Cover the stem of the equipment with tape.
This reduces the need to clean equipment with solvents afterwards. The tape can easily be removed.
- Use a special ‘finishing machine’ for levelling and compacting epoxy floors, instead of manual finishing (‘powerfloat’).
This is only feasible for larger surfaces (> 1000 m²).
- Wear liquid-tight overalls (e.g. tyvek), and/or plastic sleeves for the arms and legs.
In many cases, e.g. tilers, workers consider completely liquid-tight overalls as being too warm. In Germany (also elsewhere?), a classification for protective clothing exists: class 1 only protects against dust, class 6 is liquid tight.
- With respect to gloves it has been stated that ‘frequent changing’ is more important than the glove material.
Nitrile rubber or Neoprene are (relatively) good materials for the moment. One should beware of cracks that form when epoxy product hardens on the glove. As mentioned earlier, results from new multi-component glove tests in Germany will come available around June 2003.
- Shoes should not be made out of leather. Leather is not liquid-tight.
- Face-shields are advised for mixing under uncontrolled circumstances.
- With respect to transportation to the workplace and back (by car):
  - Create a ventilated cupboard in the loading space of the vehicle, and/or:
- Create a partition between the loading space and the cabin
- So-called ‘barrier creams’ should not be promoted. They are not effective.
- The Dutch good practice guide (‘A-blad’) on concrete repair with epoxies from Arbouw recommends the following with regard to washing facilities for workers (see also the Danish regulations in Christian Pedersen’s presentation):
  - Taps that can be operated by foot-paddles
  - Eye-shower present
  - Skin care cream available
  - Disposable (paper) towels.
- In Germany, a new skin cleaning product has come on the market, consisting of polyethylene glycol, because water does not remove epoxy in most cases. No experiences with the product are known yet.

4. Ranking system for the health risks epoxy products
- Questions to be asked were: how to deal with ‘risk communication’ to workers in relation to (various) ranking systems, how to address the suppliers and how to apply a ranking system internationally.
- Most participants think that the system is promising. ‘Finetuning’ of existing classifications according to EU-rules (or the MAL-code system) and including ‘sensitisation potency factors’ is a good thing about the system.
- Olve Rømyhr would like to include the system in the Norwegian guide on good practices.
- However, Paul Evans, Bob Rajan and Ulrich Goergens fear that it might be hard to get the cooperation of the suppliers in the UK and Germany. They are not very open, generally. A voluntarily approach has worker in The Netherlands, but it is feared that UK and German suppliers would object further classifications in addition to the Dangerous Preparations Directive.
- Ton Spee tells that experiences in The Netherlands have shown that suppliers that initially objected classifications can turn around immediately (and become very cooperative) as soon as the customer asks for a product that has a certain ranking.
- Christian Pedersen tells about similar experiences in Denmark, with a ranking system for cleaning products in the printing industry. Customers demanded products that were ‘on the list’. Products like this may have a higher ‘added value’.
- Jeroen Terwoert states that a number of suppliers would like to create a ‘responsible’ image, which could distinguish themselves from competitors in the market. This has been a reason to take part in the Dutch ranking system for concrete mould release agents.
It is remarked that many Western-European suppliers would like to distinguish themselves from (cheaper) suppliers from Eastern Europe.
Ulrich Goergens tells about the German Gisbau classification system, which is more or less similar to the Dutch ‘PISA’ (Product Information System Arbouw). About 90% of the suppliers take part in Gisbau. In this respect, ranking systems may have a good chance in Germany. Forcing suppliers to develop safer products would be a major goal of ranking products. Christian Pedersen warns against confusion when various ranking systems exist next to each other. E.g., in the Danish MAL-code system a ‘class 1’ product is safe, while a ‘class 1’ product in the epoxy ranking system is still a product that requires skin protection. Indeed, one should be careful in communicating the meaning of ranking system to workers. Much attention is paid to this aspect in The Netherlands.

Bob Rajan fears that it might be very difficult to get the information needed when very many formulators are active on the market.

Ton Spee suggests that it would be very interesting to see whether the German patch test results and the results of the Dutch test classification with the proposed ranking system could be linked together. However, a true ‘validation’ will be hard, because people that are patch-tested generally use many different products at the same time. Besides, current positive patch test results frequently originate from ‘old’ products that the patient has used in the past. Finally, many ‘cross-sensitisations’ occur. Nevertheless, we’ll try and see what comes out of it.

5. Quality of basic toxicity data

One important question is: how to deal with unclassified components. When a component does not have a specific R-phrase (e.g. R43 for sensitisation), this may mean two things:

- The component has been tested, but appeared not to be sensitising
- The component has not been tested at all.

The participants agree to have a look at the inventory of components in epoxy products that Ulrich Goergens distributed, and to try and complement the data, if available.
All agree that it is desirable to develop a “common code of Practice” on epoxies. Subsequently, this common Code of Practice may be further specified to national circumstances and promoted in national brochures etc.

Part of the Code of Practice may be:
- Examples of replacement of epoxy materials by other materials
- Substitution of epoxies by (relatively) ‘safer’ epoxies
  Possibly with the help of a ranking system:
- Good working practices (including pictures)
- Recommended glove materials, protective clothing etc.

Jeroen Terwoert points at a recent ‘Call for Proposals’ from the European Agency for Health and Safety at Work (Bilbao), which calls for projects aimed at SME’s, with a focus on developing or promoting ‘good practices’. Our activities seem to be just what the Agency is looking for!

The participants agree to carry-out the following activities:

1. Distribute information on the Agency’s Call for Proposals: Jeroen Terwoert
2. See whether a European project on epoxies is possible: All
3. Prepare a first draft for a European project proposal: Jeroen Terwoert
4. Exchange information on replacements for epoxy products: All
5. Exchange pictures on good (and bad) working practices: All
6. Exchange data on advised glove materials: Ulrich Görgens/ All
7. ‘Validate’ ranking system with data on sensitisation frequencies: Jeroen Terwoert
   (contact Johannes Geier from IVDK in Germany)
8. Try and add missing data (toxicity/ physical-chemical data) in German inventory of epoxy-components: All
9. Meet again later and discuss the experiences: All
ANNEX: SHEETS OF THE PRESENTATIONS
Working Conference epoxies in the construction industry

11 April 2003
HSE’s Office, London

Agenda

- 08.45 – 09.00 Ton Spee Introduction, purpose
- 09.00 – 09.30 Paul Evans Epoxies in the Construction Industry
- 09.30 – 10.00 Ulrich Goergens Activities in Germany: risk assessment, substitution, protective measures
- 10.00 – 10.30 Christian Pedersen Exposure to epoxy-monomers from hardened epoxy
- 10.30 – 11.00 coffee break
- 11.00 – 11.30 Olve Rømhyr Contact dermatitis among Norwegian industrial painters.
- 11.30 – 12.00 Jeroen Terwoert A ranking system for health effects of epoxies in the construction industry
- 12.00 – 12.30 discussion, questions to be raised, parallels and differences in approach
- 12.30 – 13.15 lunch
- 13.15 – 14.45 general discussion
- 14.45 – 15.00 tea break
- 15.00 – 15.55 exploration of possibilities for cooperation or for other arrangements
- 15.55 – 16.00 conclusions, closure.
Purposes of the conference

• Exchange of information: safe working with epoxies
• Possibilities to address manufacturers
• Your opinion about the ranking system for epoxies
• Possibilities for further cooperation or other arrangements

Photo:
Occupational & Environmental Dermatology Unit and NECOD, Groningen University Hospital, NL
Measures:

- Transport
  - Ventilated cupboard in loading space or
  - Partition between loading space and cabin
- Mixing
  - Foil sheet and 18 mm sheet material
  - Low rotation speed
  - Mixer one third of diameter of vessel
  - Fill the vessel up to max 20 cm under the rim
  - Preferably unit dose systems
  - Preferably hardener from a polyethylene bottle
Measures (cont’d)

• Hygienic measures
  – E.g. wrap stem of tools with tape
  – Use acetone for cleaning instead of aromatics
  – Use plastic covers over arms and legs
  – Protective clothing, water, soap, etc.
A study of the Use of Epoxy Resins in the Construction Industry

Dr Mehdi Tavakoli, TWI, Cambridge

Aims:

• Survey work practices using epoxy resins in the construction industry
• Determine which formulations are used
• Establish if usage or formulation changed

Objectives:

• Review literature
• Contact resin manufacturers/suppliers – toxicity
• Contact resin manufacturers/suppliers – usage
• Contact academia/professional bodies/TUs – trends
• Report
Uses of Epoxy Resins

- Coating and paints
- Impregnating and repairing concrete, brick and wooden structures
- Repair and sealing of pipework, window frames etc
- Adhesives for ceramic tiles
- Binders and resins for fibre reinforced composites

Increased usage

- Changes in UK Food Hygiene Laws - joints between the tiles impervious, easy to clean and disinfect and should not taint food.
- Erosion of cementitious grouts in swimming pools - use of epoxy grouts, despite increased cost.
- Large no. leisure pools - wave machine - epoxy grouts for abrasion resistance
Increased usage cont.

• Formulations more user friendly - modern epoxy grouts water washable/wipable, easy to apply/clean. Less resistance from the tiling contractors.
• Increased use of power showers - tough waterproof grout.
• Epoxy grouts continue to be specified for their chemical resistance.

Epoxy Resins

Main constituents of epoxy systems:

Base epoxy resins
Curing agents
Diluents
**Base Resin Sensitisation**

Most people who experienced contact allergy have been sensitised to the DGEBA type of epoxy resin. However, ACD due to non-DGEBA epoxy resins has also been reported. It is mainly the epoxy resin oligomer of MW = 340 which is responsible for epoxy resin allergy. The sensitising capacity decreased in inverse proportion to the increase in the average MW of the resin mixtures.

**Curing Agent Sensitisation**

Polyamine curing agents have been found to be contact irritants and sensitisers.

Aliphatic and cycloaliphatic polyamines are low-viscosity hardeners which can melt with epoxy resins at room temperature. These curing agents may be employed in some two-part, room temperature curing epoxies used in the construction industry.

Polyamides and epoxy-amine adducts that are less volatile, less reactive and less irritating have been developed to reduce skin sensitisation effects.
Curing Agent Sensitisation

One-component epoxy systems contain curing agents which are inactive at storage temperature but initiate a curing process when heated. Typical latent curing agents include organic acid anhydrides. These types of curing agent may be used in one-part, powder epoxy or epoxy-polyester paints, one-part adhesive sealants or encapsulants and polymer composite laminates. Most of the publications referred to contact allergy to polyamine hardeners. A few reports on non-amine hardeners have been published.

Diluent Sensitisation

Reactive diluents have also been found to cause contact allergy. Contact allergy to reactive diluents without contact allergy to epoxy resins is also possible. These materials are more volatile than DGEBA epoxy resin and may cause an airborne dermatitis pattern. Again it was shown that low molecular weight (MW=175-360) diluents can cause sensitisation. A higher molecular weight diluent (aliphatic polyglycidyl ether) of MW = 1700 produced no reactions.

Increasing tendency to use reactive diluents in epoxy resins.
Findings - Usage

The use of epoxy resins has increased in recent years and they are expected to be used more in the future. This is based on the growing acceptance of epoxy systems in a variety of different industrial applications as adhesives, coatings, fillers and epoxy grouts, etc. There are several main factors which have contributed to the increased use of epoxy resin grouts in ceramic tiling over the last ten years.

As the demand for the development of a new generation of epoxy resins with improved properties increases, new hardeners, diluents or epoxy base resins may be introduced with unknown skin sensitisation effects.

Findings - Exposure

Mixing and application of epoxy resins in the construction industry is usually done by hand on site, using simple methods. Contamination of the workers’ skin occurs easily. The development of a contact allergy may be expected. It was also concluded among various materials tested, that epoxy resin was clearly the offender, and the curing agent played an additional part in this respect. Some construction workers may become allergic to rubber chemicals in gloves and this may sometimes be confused with epoxy resin sensitisation.
Controlling exposure

- Make workers aware of the risk of epoxy sensitisation
- Wear protective clothing, particularly effective gloves. Change protection regularly for continued effectiveness.
- Use higher (>900) MW epoxy resins/diluents
- Use one-part, instead of two-part, epoxies to reduce the risk of skin contact during hand mixing
- Use two-part or pre-mixed epoxies supplied in single or twin cartridges, or mixing of two components with an automated internal mixer or dispensing equipment.

Controlling exposure contd.

- Avoid contact with incompletely cured epoxy resins
- Provide ventilation to avoid airborne dermatitis
- Susceptible individuals should not be selected to work with epoxies
- Use epoxy systems with reduced risk of sensitisation
- Proper instructions for workers on good housekeeping, education in hygiene, proper methods of disposal, handling procedures.
Controlling exposure contd.

- Barrier creams may be effective. Use in some applications in the construction industry often impractical
- All epoxy users should have access to material safety data sheets and understand the possible harmful effects if not used properly
- Damaged skins, including even small wounds and abrasions, should be protected from epoxy-compound exposure because of increased skin sensitisation.

Use of gloves

- Fluorinated suitable - high price, poor mechanical properties
- Butyl/brominated butyl for solvent-free formulations but not with solvent - higher price cf nitrile
- PVC for some solvent-free epoxy resins and epoxy curing agent systems
- Nitrile suitable, some limitations. Use for short time for solvent based formulations - low price, excellent mechanical properties
- Polychloroprene use with few formulations, additional testing required
- Natural rubber not suitable for handling epoxy resin or epoxy curing agent formulations
Epoxy Resins

An assessment of skin sensitisation by the use of epoxy resin in the construction industry

Research Report 079
http://www.hse.gov.uk/research/rrhtm/index.htm
Activities on epoxies in Germany:
- risk assessment
- substitution
- protective measures

Dr. Ulrich Goergens, Bau-Berufsgenossenschaft Rheinland u. Westfalen
(statutory accident insurance and prevention in the construction industry)

Problems in Germany

- growing use of epoxies

- growing number of occupational diseases caused by epoxies
  - acute skin irritation
  - corrosive burns
  - allergic contact dermatitis
  - respiratory diseases (hot-curing epoxies only)
Compensated occupational diseases 1999/2000

<table>
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<tr>
<th>Skin diseases</th>
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<td>(BK 5101)</td>
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<td>Health Service</td>
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</table>

Respiratory diseases (BK 4301, BK 4302) 6

Production of rotor blades for wind power stations
Causes for allergic contact dermatitis among male workers in German construction industry

- Thiurame
- Mercapto-Mix
- Preservatives
- Epoxies
- others

\[ n_{ges} = 364 \]

- Cement: 231
- Epoxies: 59
- Thiurame: 34
- Mercapto-Mix: 18
- Preservatives: 11
- Others: 11

2001 Workshop „Using epoxies - occupational health and safety aspects“

Outcome of the workshop:
- Growing problems in many industrial branches
- High disease incidences
- Short period of sensitisation
- High numbers of airborne dermatitis
- User of epoxies are not aware of the special risks
2002 Appointment of two working groups by the Minister of Labour

A) elaborating a general guideline (TRGS)

Topics:
- risk assessment
- substitutes

B) elaborating of branch specific guidelines

Topics:
- organisational, technical and personal protective measures
Sheet 9

General guideline (TRGS)

Risk assessment

- Substance specific aspects
  - what chemicals are used in epoxy systems?
  - what is known about this substances?
    - (sensitisation potential, casuistry experience etc.)

- Handling aspects

Sheet 10

List of chemicals used in epoxy systems

List contains:

- substance name
- CAS, EG-Nr.
- number of nominations in 1500 MSDS
- hazard designation
- physical data
- legal characterisation
Chemicals used in epoxy systems

Problems:

- Part of the curing agents are chemically not defined substances (polyamines, polyamides, aminoamides)
- These products contain various amounts of free amines
- Only part of the chemicals are classified by regulations
- Missing data from sensitisation tests for many substances
- Characterisation differs from manufacturer to manufacturer

Example xylylendiamine (MXDA; CAS: 1477-55-0)

- No classification by European regulations
- Several casuistry indications of high sensitisation potential in the literature
- Labeling of the products with R 43 only by a few suppliers
What kind of activities are carried out using epoxies?

- transport
- proportioning of the components
- mixing
- distribution
- application (by spatula, roller, brush, spray, injection etc.)
- cleaning
- disposal

What are the main hazards?

- Skin contact caused by splashing or spillage through
  - direct contact with the materials
  - contaminated/soaked clothing, gloves, shoes
  - contamination of the tools’ handles
  - contamination of door handles

- Errors of measurement or mistaking one component for the other
Sheet 15

Proportioning of the components

Sheet 16

Mixing
Corrosive burns by soaked trousers

Substitutes:
- cmr-compounds
  - no cancerogenic aromatic amines as curing agents
  - no epichlorohydrine > 20 ppm
- Epoxy-free products
- Substitution of critical components by less hazardous substances
  - low vapour pressure, low sensitisation potential
What is the appropriate material for gloves when using epoxies?

- Solvent containing epoxies:
  glove material depends on the solvent

- Solvent free epoxies:
  ?? ?? ??
Glove materials

Single compound testing does not lead to reliable results

Standard test method is not valid for substances of high molecular weight or substances of low volatility

Modified test cell

After a period of time, the absorber plate is removed and extracted with solvent. Substances which have passed the glove material are detected by hplc.
Improvement of epoxy diseases diagnosis

Problem:

- Standard test set for epicutane testing contains only very few epoxy compounds
- In many cases strong relationship between the use of epoxies and skin reactions but no reaction in epicutane testing

Commercial available test substances

<table>
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<tr>
<th>Nr.</th>
<th>Resins</th>
<th>Testconc.</th>
<th>Supplier</th>
<th>Artikel-Nr.</th>
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<td>Epoxidharz</td>
<td>1 % Vas.</td>
<td>Hermal</td>
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<td>Cycloaliphatisches Epoxidharz</td>
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<td>Chemotechnique</td>
<td>E-020</td>
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<td>9</td>
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<tr>
<td>10</td>
<td>Phenylglycidylether</td>
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<td>11</td>
<td>Butylglycidylether</td>
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### New test kit which contains all relevant substances

#### additional substances:

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<td>Bisphenol F-Epoxidharz</td>
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<td>2</td>
<td>m-Xyliendiamin</td>
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<tr>
<td>3</td>
<td>Trimethylhexan-1,6-diamin (Isomerengemisch)</td>
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<tr>
<td>4</td>
<td>N-Aminoethylpiperazin</td>
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<td>Dipropylentriamin</td>
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<td>Aminoethylethanokamin</td>
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<td>4,4’-Methylenbis(cyclohexylylamin)</td>
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<td>10</td>
<td>1,4-Butandiol-diglycidylether</td>
<td>0,25% Vas.</td>
</tr>
<tr>
<td>11</td>
<td>1,6-Hexandiol-diglycidylether</td>
<td>0,25% Vas.</td>
</tr>
<tr>
<td>12</td>
<td>C12/C14 Alkyglycidylether</td>
<td>0,25% Vas.</td>
</tr>
<tr>
<td>13</td>
<td>Versaticsaureglycidylester</td>
<td>0,25% Vas.</td>
</tr>
<tr>
<td>14</td>
<td>Trimethylolpropandiglycidylether</td>
<td>0,25% Vas.</td>
</tr>
<tr>
<td>15</td>
<td>p-tet.-Butylphenylglycidylether</td>
<td>0,25% Vas.</td>
</tr>
<tr>
<td>16</td>
<td>1,2-Diaminocyclohexan (Isomerengemisch)</td>
<td>0,25% Vas.</td>
</tr>
</tbody>
</table>
Epoxy-monomers in cured epoxy
An overlooked health risk?

Background

• Measurements of dust-concentrations at shipyard
• Evaluation against TLV’s (organic dust = 3 mg/m³)
• Does the dust present any further risks beside inhalation?
Sheet 3

Scope

• To evaluate the amount of free and uncured epoxy in sanding dust
• To estimate the risk of getting sensibilized by epoxy in sanding dust.

Sheet 4

Sampling

Wing (windblade-construction)
Production process - 2

Sanding of filler on shipyard

Sampling of sanding-dust on shipyard
Curing

- Curing time
- Curing temperature

Analysis

- Sampling of sanding-dust
- Extraction in acetonitrile
- HPLC/DAD (BADGE)
- GC/FID (HDDGE)
Criteria for evaluation

• Type of epoxy (molecular weight)
• Exposure (inhalation, skin …)
• Regulation
  – Danish directive on working with chemical agents (Attachment: “Working with epoxy resins and isocyanates”)

DK Regulation 1

The directive applies to:
• Epoxy resins - ER - MW<700
• Materials with >1% of ER - MW<700
• Reactive epoxy diluents - RD - 1 epoxygroup
• Materials with >0,2% of RD

\[
\frac{ER}{1\%} + \frac{RD}{0,2\%} > 1
\]
DK Regulation 2

MSDS
– Curing time in MSDS

Security-precautions
– Precautions until the materials are cured and the exposure to epoxies have stopped
– Warning signs

Prohibitions
– Persons with epoxy allergy or "hyperhidrosis manuum" must not work with the materials

Education
– Special training (2 days)

First aid
– Sufficient first-aid equipment
– Medical aid if worker has ekzema, eye-injuries or corrosive damages to skin

Handling etc.
– Skin contact must be avoided
– Wash-basin – not hand operated
– Shower with cold and hot water
– Cleaners, soaps, creams, disposable towels
– Changing-rooms
– Separate wardrobes for daily clothes and working clothes
– Proper hygiene
– Eating, drinking and smoking forbidden
– Working clothes must not be worn in lunch-room
– Waste, empty packing, used towels, discarded protection clothes, gloves etc. must be placed in waste containers marked "contains epoxy-waste"

Epoxy-meeting 10.4.03

Sheet 12

Results: Filler

<table>
<thead>
<tr>
<th>Sampling</th>
<th>Temp. °C</th>
<th>Curing time</th>
<th>BADGE w/w%</th>
<th>HDDGE w/w%</th>
<th>BADGE + HDDGE w/w%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 dec. 2001</td>
<td>?</td>
<td>24 h</td>
<td>3,7</td>
<td>3,2</td>
<td>6,9</td>
</tr>
<tr>
<td>2 dec. 2001</td>
<td>?</td>
<td>48 h</td>
<td>3,0</td>
<td>3,7</td>
<td>6,7</td>
</tr>
<tr>
<td>3 jan. 2002</td>
<td>?</td>
<td>48 h</td>
<td>1,3</td>
<td>0,7</td>
<td>2,0</td>
</tr>
<tr>
<td>4 maj 2002</td>
<td>23°C</td>
<td>24 h</td>
<td>1,3</td>
<td>0,69</td>
<td>1,99</td>
</tr>
<tr>
<td>5 maj 2002</td>
<td>23°C</td>
<td>48 h</td>
<td>0,81</td>
<td>0,45</td>
<td>1,26</td>
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<tr>
<td>6 maj 2002</td>
<td>30°C</td>
<td>24 h</td>
<td>0,69</td>
<td>0,43</td>
<td>1,12</td>
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<td>7 maj 2002</td>
<td>20°C</td>
<td>168 h</td>
<td>0,56</td>
<td>0,22</td>
<td>0,78</td>
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</table>

Epoxy-meeting 10.4.03
### Evaluation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$BADGE_1$</th>
<th>$RD_1$</th>
<th>$BADGE_2$</th>
<th>$RD_2$</th>
<th>Total</th>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
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<td>2</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td></td>
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<td>7</td>
<td>2</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Epoxy-meeting 10.4.03

### Results: Filler, moulding and reparation epoxy

<table>
<thead>
<tr>
<th>Glass- number</th>
<th>ID</th>
<th>Material</th>
<th>Moulding</th>
<th>Time/ temp</th>
<th>BADGE</th>
<th>AGED</th>
<th>Moulding Time/ temp</th>
<th>Total</th>
<th>Monomer</th>
<th>BADGE</th>
<th>$RD_1$</th>
<th>$RD_2$</th>
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</thead>
<tbody>
<tr>
<td>3V</td>
<td>1</td>
<td>Filler</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,17</td>
<td>0,1</td>
<td>0,27</td>
<td>1+5</td>
<td>0,7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1F</td>
<td>1</td>
<td>Filler</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,17</td>
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<td>0,27</td>
<td>1+5</td>
<td>0,7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15E</td>
<td>15</td>
<td>Filler</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,17</td>
<td>0,1</td>
<td>0,27</td>
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<td>0,7</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>14V</td>
<td>15</td>
<td>Filler</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>1,19</td>
<td>0,2</td>
<td>0,27</td>
<td>1+5</td>
<td>0,7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17V</td>
<td>20</td>
<td>Filler</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>1,65</td>
<td>0,52</td>
<td>2,17</td>
<td>1+5</td>
<td>4,3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20E</td>
<td>20</td>
<td>Filler</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,17</td>
<td>0,1</td>
<td>0,27</td>
<td>1+5</td>
<td>0,7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16E</td>
<td>19</td>
<td>Filler</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,17</td>
<td>0,1</td>
<td>0,27</td>
<td>1+5</td>
<td>0,7</td>
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</tr>
<tr>
<td>12V</td>
<td>12</td>
<td>Rep.</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,07</td>
<td>0,29</td>
<td>0,365</td>
<td>1+2+4</td>
<td>1,5</td>
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<tr>
<td>18E</td>
<td>18</td>
<td>Rep.</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,17</td>
<td>0,1</td>
<td>0,27</td>
<td>1+2+4</td>
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<td></td>
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</tr>
<tr>
<td>6V</td>
<td>6</td>
<td>Rep.</td>
<td>11-fb-03</td>
<td>6h 76°C</td>
<td>0,6</td>
<td>0,81</td>
<td>1,34</td>
<td>1+2+4</td>
<td>4,7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10V</td>
<td>10</td>
<td>Root</td>
<td>07-fb-03</td>
<td>5h 50°C</td>
<td>0,02</td>
<td>0,04</td>
<td>0,06</td>
<td>1+3</td>
<td>0,2</td>
<td></td>
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<tr>
<td>11V</td>
<td>11</td>
<td>Root</td>
<td>08-fb-03</td>
<td>5h 50°C</td>
<td>0,05</td>
<td>0,07</td>
<td>0,12</td>
<td>1+3</td>
<td>0,4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16V</td>
<td>16</td>
<td>Root</td>
<td>07-fb-03</td>
<td>5h 50°C</td>
<td>0,11</td>
<td>0,14</td>
<td>0,25</td>
<td>1+3</td>
<td>0,8</td>
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<td></td>
</tr>
<tr>
<td>13V</td>
<td>13</td>
<td>Wing</td>
<td>10-fb-03</td>
<td>6h 70°C</td>
<td>0,03</td>
<td>0,04</td>
<td>0,07</td>
<td>1+3</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7V</td>
<td>7</td>
<td>Wing</td>
<td>05-fb-03</td>
<td>6h 70°C</td>
<td>0,03</td>
<td>0,03</td>
<td>0,06</td>
<td>1+3</td>
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</tr>
<tr>
<td>9E</td>
<td>9</td>
<td>Wing</td>
<td>25-jan-03</td>
<td>6h 70°C</td>
<td>0,03</td>
<td>0,03</td>
<td>0,06</td>
<td>1+3</td>
<td>0,2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2V</td>
<td>2</td>
<td>Wing</td>
<td>05-fb-03</td>
<td>6h 70°C</td>
<td>0,04</td>
<td>0,05</td>
<td>0,09</td>
<td>1+3</td>
<td>0,3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Epoxy-meeting 10.4.03
Conclusions

• Sanding-dust from cured epoxy may present a risk of allergic eczema
• Several parameters determine the amount of free epoxy:
  – Outweighing of resin and hardener
  – Mixing process
  – Curing temperature
  – Curing time
Contact dermatitis among Norwegian industrial painters

Olve Rømyhr
Occupational hygienist
Department of Occupational Medicine
University hospital in Trondheim
Norway
Paint volume 1997-2000

<table>
<thead>
<tr>
<th>Year</th>
<th>Volume (1000 liter)</th>
<th>Epoxy (%)</th>
<th>Polyurethane (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>816</td>
<td>66</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>1998</td>
<td>1029</td>
<td>67</td>
<td>12</td>
<td>21</td>
</tr>
<tr>
<td>1999</td>
<td>666</td>
<td>66</td>
<td>9</td>
<td>25</td>
</tr>
<tr>
<td>2000</td>
<td>413</td>
<td>61</td>
<td>9</td>
<td>30</td>
</tr>
</tbody>
</table>

Skin- or airways complaints in work

- 31 % Skin complaints caused by work
- 9 % Skin complaints exacerbate by work
- 14 % Had contact with doctor or health services for skin complaints
- 15 % Airway complaints caused by work
- 5 % Airway complaints exacerbate by work
- 8 % Had contact with doctor or health services for airway complaints
Cohort

- Six firms
- ~1200 industrial painters
- Age: 36 years
- Mean workpractise as industrial painters: 10 years

Incidence (1997-2001)

- Occupational asthma:
  6 workers
  ⇒ 1.1 cases pr 1000 personyears
- Allergic exzemas caused by epoxies:
  23 workers
  ⇒ 4.6 cases pr 1000 personyears
Number of positive patch test results
23 cases

<table>
<thead>
<tr>
<th>Resins/reactive dilutens</th>
<th>Hardeners:</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>Ethylenediamine 1</td>
</tr>
<tr>
<td>DGEBA/F</td>
<td>Hexamethylenetetramine 1</td>
</tr>
<tr>
<td>DGEBF</td>
<td>Diaminodifenylmethane 1</td>
</tr>
<tr>
<td>Cycloaliphatic resin</td>
<td>3-dimethylaminopropylamine 1</td>
</tr>
<tr>
<td>Phenylglycidylether</td>
<td>Trietylenetetramine 1</td>
</tr>
<tr>
<td>Cresylglycidylether</td>
<td>Diethylenetriamine 1</td>
</tr>
<tr>
<td>Epoxide 8</td>
<td>Isophoronediamine 0</td>
</tr>
<tr>
<td></td>
<td>Tetraetylenepentamine 2</td>
</tr>
<tr>
<td></td>
<td>2,4,6 tris(dimethylaminomethyl)phenol 7</td>
</tr>
<tr>
<td></td>
<td>m-xylene-α, α-diamine 8</td>
</tr>
<tr>
<td></td>
<td>2,2,4 trimethylhexamethylenediamine 4</td>
</tr>
<tr>
<td></td>
<td>n-monoethylpiperazine 1</td>
</tr>
</tbody>
</table>

Epoxy paints – measurement of exposure

Skin exposure:
No good methods published

Air monitoring:
Epoxy-groups (R.F. Herrick; 1988)
Amines (not published):
  - Diethylenetriamine (DETA): not detected
  - Isophoronediamine (IPDA): max 0,13 mg/m³
Concentration of diethylenetriamine after mixing of base and hardner

![Concentration Graph]

Main conclusions

- Our incidence rates should be regarded as minimum figures.
- Good exposure methods are lacking
- Low amine concentrations could be expected

E-mail: olve.romyhr@stolav.no
"Guide to safe handling of epoxies"

• Norwegian association of occupational hygienists.

• A practical guide to risk assessment and risk management for workers and occupational health professionals
A ranking system for the health risks of epoxy products
Jeroen Terwoert - IVAM
Ton Spee - Arbouw

Contents

• Health hazards of epoxy products
• Purpose of a ranking system
• Proposed ranking system
• Test-classification
• Division into classes
• Conclusions
Some applications

- Wood repair and concrete repair
- Floor finishing (coatings/ ‘casted floors’)  
- Reinforcement of cement-based floor finishing
- Anti-corrosive coatings on metal
- Adhesives

Health hazards

- Skin allergen (resin, diluents, hardener)
- Irritative/ corrosive (hardener)
- Carcinogen (epichlorohydrin in resin)
- Neurotoxic (solvents)
Purpose of a ranking system

• Inform users about harmfulness of epoxy’s with comparable applications: *a simple ‘decision making tool’*

• Stimulate product development into less harmful products (suppliers)

An ‘ideal’ ranking system

• Easily accessible data

• Not too complex

• Controllable

• Discriminating
Advantages of using current MSDS’s for classification

• MSDS for all epoxy products available
• Standard format
• Uniform information

Disadvantages of MSDS’s

• ‘Hazard’ approach
• ‘Soft’ concentration limits for declaration of components
Basis of the ranking system

- **Toxicity data**
  - ‘Hazard’ of the product

- **Physical-chemical data**
  - (Potential) exposure

---

Criteria

1. Concentration of residual epichlorohydrin (resin)
2. Presence of (very) toxic components: T/ T+ symbol
3. Presence of carcinogens, mutagens, reprotoxics or respiratory sensitizers (R-phrases)
4. Presence of corrosive or sensitizing amine-hardeners
5. Amount of reactive diluent in the resin
6. Amount of Volatile Organic Compounds (VOC)
7. Boiling point of the amines in the hardener
8. Boiling point of the reactive diluents
9. Molecular weight of the amines in the hardener
10. Molecular weight of the reactive diluents
11. Concentration free amines in the hardener
12. Lack of product information: extra malus points
Test-classification

• 44 products:
  – 23 coatings (2 SB, 11 SF, 10 WB)
  – 13 flooring materials
  – 5 adhesives
  – 3 wood repair products

• Collection of additional data problematic for some suppliers (ECH, diluents)

Results test-classification

![Graph showing test results](image)
Division into classes

<table>
<thead>
<tr>
<th>Class</th>
<th>Points Range</th>
<th># Products</th>
<th>Coating</th>
<th>Flooring</th>
<th>Adhes.</th>
<th>Woodr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-40</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>-</td>
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<td>3</td>
<td>61-80</td>
<td>13</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>&gt; 80</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

Conclusions

• The system discriminates well
  Range of malus points: 20 – 110 (all products)

• Degree of discrimination:
  coatings > floorings > adhesives > wood repair products

• Opportunities for variability

• Not all suppliers can easily obtain all necessary data

• Many suppliers favour international approach
**Replacement**

- Difficult in many cases
  - (chemical resistance)
  - Other regulations (food safety, drinking water)
  - Data collection
- Examples:
  - Epoxy-free grouting
  - Silicon-epoxies (?)
  - Epoxy containing concrete repair only:
    - When chemical resistance is needed
    - When fast curing is needed
- Prevention
  - Mixed isocyanate/acrylate paints

**Packaging/mixing**

- Unit dose systems as far as possible
- Hardener in polyethylene bottles
- Weighing of components
- Automated dose systems
- Mixer in proportion to vessel
- Variable rotation speed (low speed, max 75 rpm)
- Closed mixer (from 25 kg) cleaning with sand
- Sufficient space above epoxy mass (20 cm)
- Work practices prescribed by manufacturers
Work practices

- Caddy for bucket with epoxy
- Sheet of foil under container
- Sheet of wood (18 mm) in case of uneven surface
- Working in sections when applying primer
- Cover the stem of the equipment with tape
- Avoid contact: finishing floor with ??
- Gloves: Nitrilrubber? (beware of cracks)
  - Frequent changing more important than material
- Long-stemmed rollers, roller with protection shield
- Liquid-tight overalls (e.g. tyvek), cuffs for arms and legs

Ranking

- For whom?
- Risk communication
- Internationally applicable?
Quality of data

- Obtainable?
- Unclassified components?
- Which data?

Working together?

- Exchange of data on prevalences – connection to ‘type of product’? (‘class’)
- Exchange of pictures about good and bad working practices (copyright!)
- Exchange of data about protection etc.
- Common code of practice? (EU Agency)
actions

• Gather information about replacement
• Circulate information about EU agency call for proposals
• See whether a project on epoxies is possible
• Circulate information
• Exchange of physico-chemical data