EPOXY RESINS AND CURING AGENTS

Toxicology, Health, Safety and Environmental Aspects

August 2017

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1. Introduction

The manufacture, formulation and application of epoxy products involve a variety of separate substances, such as epoxy resins, hardeners, reactive diluents and solvents.

Considerable knowledge and experience has been gathered about their physical and chemical properties, hazards and risks to man and the environment.

The aim of this document is to provide the reader with reference information concerning the main aspects of human health, occupational and environmental safety of epoxy products.

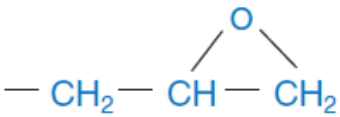
It is not intended to be fully comprehensive in answering all questions that might arise for the wide variety of products available. Rather it is intended as a useful reference guide for safe handling of products which due to their chemical nature have some toxicological properties requiring special precautions for human health and the environment.

In view of the increasing demand for information to producers, suppliers, converters and users of epoxy resin systems this document is intended to support all involved parties of the value chain to disseminate appropriate safety information for this group of chemicals.

For detailed information on specific products please consult the supplier's Safety Data Sheet or special product literature.

2. General Description and Properties of Epoxy Products

Epoxy resins are a family of synthetic resins, including products which range from viscous liquids to high melting point solids. The resin molecule contains as reactive site one or more oxirane or epoxide groups, usually in the form of the glycidyl group (below), in addition they often contain hydroxyl groups:



The most commercially important resin is the glycidyl ether of bisphenol A produced by the condensation of epichlorohydrin (ECH) and diphenylpropane (DPP), also known as bisphenol A (BPA).

Epoxy resins with different characteristics are also produced commercially by reacting ECH with other materials.

For use the resins must be cross-linked with a curing agent or hardener. The choice of curing agent is of paramount importance in designing an epoxy resin for a given application.

The major reactive groups in the resin – the epoxide or hydroxyl groups – can react with many other groups so that many types of chemical substances can be used as curing agents. These include acid anhydrides, aliphatic and aromatic amines and polyaminoamides. Some curing agents will cross-link the resin at ambient temperature while others require the application of heat.

However, the simple mixture of resin and curing agent rarely provides a material containing all the desired properties for a specific application. Other materials are therefore added in formulating the system.

The major types of additives include:

- Cure accelerators
- Diluents
- Solvents
- Flexibilisers, plasticisers, toughening agents
- Fillers and pigments
- Reinforcements, particularly fibres

PlasticsEurope's Epoxy Resins Committee (ERC) has prepared specific guidelines and position papers covering residual monomers such as ECH or BPA. Copies are available from ERC member companies or the PlasticsEurope secretariat.

3. The Terminology of Toxicology and Industrial Hygiene

Industrial hygiene and toxicology are important sciences which help to provide data for better understanding of the hazards posed by industrial products, and assessing their risks to human health. The following chapter provides an explanation of some of the most frequently used specialist terms and definitions encountered in the literature and safety documentation such as the Safety Data Sheet (SDS).

3.1. Toxicity, Hazard and Risk

Toxicity is defined as the adverse effects of a chemical on organic life, specifically the human body, but also animals and plants. It is an inherent characteristic of a substance like odour or colour or other physical and chemical properties.

Hazard is also determined by inherent characteristics of a substance like physical and chemical properties or its toxicity. A health hazard can only become a problem if there is sufficient exposure to cause a harmful or toxic effect on the organism. A typical hazard is the ability to cause irritancy or corrosion. Therefore hazard requires an exposure to result in risk.

Risk describes the probability or likelihood that a hazard will result in an adverse effect. The hazard of a chemical cannot be changed, but by controlling exposure the risk can be minimized.

3.2. Local Toxic Effects

Local toxic effect can occur if exposure to a substance causes damage directly at the point of contact. The effects of substances on eyes, skin, and mucous membranes are of significant concern in the workplace.

The potential of a chemical to cause a local effect is determined in animal tests as well as in tests using tissues or cells only, unless such an effect can already be predicted due to the physical or chemical properties of the substance (e.g., pH-value). Based on tests on laboratory animals or cells/tissues, and depending on the degree of damage and potential for reversibility, substances are classified as non-irritants, irritants, or corrosives.

Irritating Substances cause local reactions resulting from single or multiple exposures. They are characterized by the presence of redness and swelling. Depending on the degree of inflammatory response, a substance may be classified as mild, moderate, or severe irritant. Irritant reaction of the tissue is generally reversible within hours or days.

Corrosive substances will cause necrosis or irreversible tissue destruction, especially in the eyes.

Skin

Occupational skin disorders are among the most common work-related diseases. Direct skin lesions are "dose"- or "concentration"-dependent, but should not occur if proper personal protective equipment (PPE) and clothing are used.

Eyes and Mucous Membranes

The tissues of the eye and the mucous membranes around the eye are even more sensitive than the skin.

Furthermore, eye damage is more serious and can have more serious consequences for the person involved. The effect of a substance in the eye is normally tested in laboratory animals or in animal-free test systems such as tissues or cultured cells. If the substance is already a proven skin irritant the test will not usually be performed and an eye irritation potential is assumed by analogy.

3.3. Systemic Toxic Effects

Acute Toxicity

The acute toxicity of a chemical substance is identified by its ability to cause lethality after a single

Exposure, described as the ‘lethal dose 50’ or LD50. For classification purposes the degree of toxicity, based on LD50 value, will be used by Regulatory Authorities. Exposure can occur by ingestion, dermal contact or by inhalation.

The degree of toxicity of a single dose of a substance is expressed as the LD50: the lethal dose for 50 percent of treated animals. The LD50 value is the amount of substance administered – normally expressed as dosage in mg/kg bodyweight and statistically estimated from actual data – that is likely to kill 50 percent of a group of test animals. Acute toxicity by inhalation is usually expressed as the LC50 value or median lethal concentration.

LC50 values are usually expressed as airborne concentration of a substance in mg/m3 air or mg/l of air or in ppm in air and should specify the length of exposure in hours or minutes. An example of a dose-response relationship is illustrated in the following graph.

Substances and preparations with an acute toxicity within the ranges indicated must carry the legally prescribed warning labels and the appropriate classification. Corrosive substances will cause necrosis or irreversible tissue destruction, especially in the eyes.

The Regulation 1272/2008 (CLP)_on Classification & Labeling of Products replaces EU Directive 67/548/EEC on the Classification and Labelling of Dangerous Chemical Substances and sets the cut-off values for the classification of the acute toxicity based on data from tests conducted in rats (see table below).

Exposure Route	Category 1	Category 2	Category 3	Category 4	Category 5
Oral (mg/kg)	5	50	300	2000	5000 See detailed criteria in note e
Dermal (mg/kg)	50	200	1000	2000	
Gases (ppm) see: Note a	100	500	2500	5000	
Vapours (mg/l) see: Note a Note b Note c	0.5	2.0	10	20	
Dusts and Mists (mg/l) see: Note a Note d	0.05	0.5	1.0	5	

Sensitisation

Sensitisation is an allergic reaction to a substance that may develop upon repeated exposure, although even a single exposure can be adequate to initiate the response. The degree of the sensitising effect of substances varies widely from person to person and the potency of sensitisers varies across substances. Allergic response can manifest themselves as skin rashes or skin swelling in case of dermal sensitisation or as an asthmatic-type reaction in cases of respiratory sensitisation.

The extent of the sensitisation reaction does not depend solely on the degree of exposure. Contact with trace amounts of sensitising substances can cause an allergic reaction, if the person is already sensitised or if the substance has very high potency.

Sub-acute and sub-chronic Toxicity

In daily working practice or in use over a prolonged period of time, small quantities of substances in concentrations far below the acutely toxic range may enter the body, possibly resulting in adverse effects either by accumulation in target tissues or by prolonged stress of the liveror other organs. Specifically designed toxicity tests are performed in order to assess the hazard of this particular exposure duration.

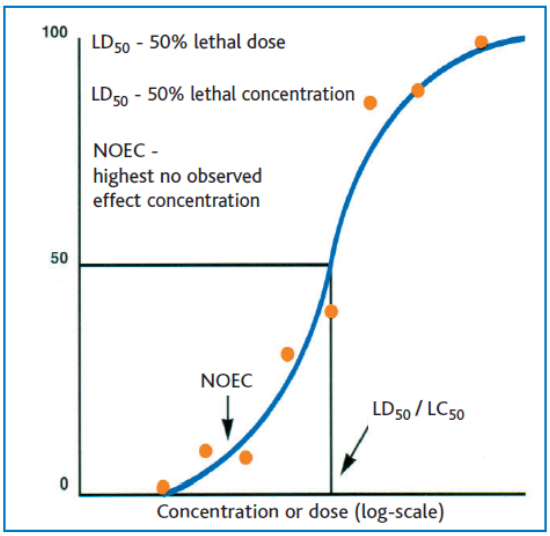
The substance is administered at various dose levels to groups of test animals over a prolonged period of time (weeks or months). Information is most relevant when administration of the dose corresponds to the likely route of potential exposure in humans.

The results provide dose-response information and the basis for determining, for sub-acute/subchronic exposure:

- What the possible safe levels might be in humans
- What the toxic levels might be in humans
- What type of effects might occur in humans

CONCENTRATIONS

A typical dose-response curve



Chronic Toxicity

Chronic toxicity is defined as the occurrence of adverse health effects which have been caused by exposure to a substance over a significant part of a lifetime. Chronic effects can arise following repeated exposure to substances by dermal, oral or inhalation routes at dose levels far below the ones causing acute toxicity.

The aim of chronic toxicity testing is to define a specific dose or exposure level that will not produce a measurable, long-term toxic effect e.g., that allows potential workplace exposure over a working lifetime with negligible risks of any health effects.
The study will also provide information on what the chronic effects are and at what doses no effects occur (NOEL).

Mutagenicity, carcinogenicity and reproductive/developmental toxicity have been the most important long-term health effects investigated. Other effects such as neurotoxicity and immunotoxicity can also be studied specifically.

Mutagenicity

Mutagenicity is the ability of a substance to cause changes (Mutations) in the genetic material of cells.

Mutations can occur in germ cells or somatic cells. Genetic changes in germ cells can have an adverse effect on fertility or may lead to malformations or even death in the embryos. Currently science assumes that mutations in somatic cells represent an initial step in one of the pathways that can potentially lead to tumor induction in mammals, which provides an additional reason to understand the mutagenic potential of a substance.

The most frequently performed "in vitro" test for mutagenicity of chemical substances involves Salmonella Bacteria, also known as the "Ames test". It is sensitive, fast and relatively inexpensive for screening purposes. Other in vitro tests use mammalian cells in culture to screen for the mutagenic potential of a substance and to obtain information possibly relevant to its carcinogenic potential. More extensive testing for mutagenicity is performed in animals (in vivo).

The outcome of a single test is not adequate or appropriate to establish the carcinogenic potential of a substance.

Carcinogenicity

Carcinogenicity is the ability of a chemical substance to cause or enhance the formation of benign or malignant tumours. The present scientific view is that many types of cancer originate from unrepaired genetic changes (mutations) in the body's cells. Such changes can have natural causes, such as excessive sunlight exposure, but can also be induced by over-exposure to synthetic chemical substances.

Chemical substances are normally classified as carcinogens when they have been demonstrated to cause an increase in the formation of tumours in lifetime animal studies (normally in more than one species) or there is reliable evidence in humans (epidemiological studies). For the interpretation of the results, and their significance for humans, additional information needs to be considered such as metabolism (which can be species-specific), mutagenicity, and the degree of exposure.

Reproductive Toxicity

Reproductive toxicity deals with the potential influence of chemical substances on complex reproductive processes, such as male and female fertility or the development of the offspring. Based on the results of special animal experiments the possible effects on humans are assessed. Epidemiological studies can provide insights on the human relevance of animal study results.

Multi-generation studies on animals are the most common way of investigating the potential reproductive toxicity of a substance. Animal results allow some conclusions to be made on the possible effects on human reproduction and fertility.

Developmental Toxicity

Developmental toxicity describes the potential of a substance to result in toxicity targeting the developing embryo/fetus. This includes embryotoxicity, which is the potential of a substance to damage or kill the embryo. To test for developmental toxicity the following effects are studied in pregnant experimental animals:

- Embryo mortality (embryo lethal effects)
- Malformations (teratogenic effects)
- Growth retardation (developmentally toxic effects)
- Maternal toxicity (toxic effects)

3.4. Ecotoxicity and Environmental Behaviour

In addition to mammalian toxicity, the behaviour, the effects and the fate of chemical substances in and on the environment has attracted increased attention in the past several decades and has developed into a significant discipline.

During the manufacture, processing and use of chemical substances one of the main ways of potential entry into the environment is through water, but air and soil also represent significant routes. Consequently, testing for toxic effects in the environment (ecotoxicity) is generally conducted on aquatic (fish and algae, for example) and terrestrial (earthworms and plants) organisms, but also on micro-organisms of both environmental compartments.

Acute Ecotoxicity

Acute ecotoxicity is investigated by exposing aquatic or terrestrial organism (such as fish, earthworms, or plants) to a substance for a short period of time. The mortality of the organisms and the growth retardation of bacterial cultures are noted. These observations

help to determine the concentrations at which 50 per cent of the test organisms are killed, e.g., LC50 value "lethal concentration" for fish, EC50 for reduced motility of Daphnia or the EC10 when the growth of bacteria is retarded by 10 percent.

The results of these tests provide information about potential for environmental damage after accidental short-term exposure. The data can also help in risk assessment for longer term exposure, when information regarding the environmental behavior/fate is available, e.g., biodegradability.

Chronic Ecotoxicity

Prolonged or chronic ecotoxicity testing provides information on the long-term behaviour of chemical substances in the environment. These tests give information on the no-effect concentrations for animals and plants, and can help determine the lowest chronic toxic concentration in water, air and soil. In addition, the type of adverse effects on organisms can be determined. The data are most important for environmental risk assessments together with degradability and accumulation data.

Long-term fish studies also include multi-generation studies providing information on the possible reproductive effects of a substance on aquatic organisms.

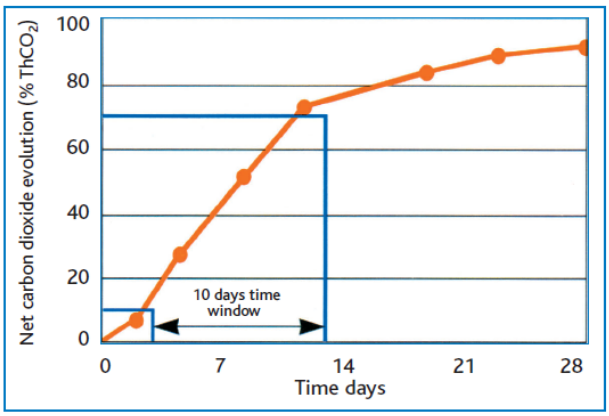
Toxicity		Degradability (note 3)	Bioaccumulation (note 4)	Classification categories	
Acute (note 1)	Chronic (note 2)			Acute	Chronic
Box 1 value ≤ 1.00		Box 5	Box 6	Category: Acute I Box 1	Category: Chronic I Boxes 1+5+6 Boxes 1+5 Boxes 1+6
Box 2 1.00 < value ≤ 10.0		lack of rapid degradability	BCF ≥ 500 or, if absent log Kow ≥ 4	Category: Acute II Box 2	Category: Chronic II Boxes 2+5+6 Boxes 2+5 Boxes 2+6 Unless Box 7
Box 3 10.0 < value ≤ 100				Category: Acute III Box 3	Category: Chronic III Boxes 3+5+6 Boxes 3+5 Boxes 3+6 Unless Box 7
Box 4 No acute toxicity (note 5)	Box 7 value > 1.00				Category: Chronic IV Boxes 4+5+6 Unless Box 7

Degradability

Apart from biodegradation, degradation by physico-chemical factors such as light, oxygen, temperature, also play an important role in the environmental fate of a chemical substance.

Biodegradation tests determine to what degree a chemical substance entering the aquatic or terrestrial environment is degradable by micro-organisms. For this purpose the substance is added to micro-organisms extracted from sludge taken from municipal waste water treatment plants. The decrease of substance concentration or the production of carbon dioxide is measured over time, and serves as an indication of the potential to be degraded biologically. Low biodegradability means that the substance remains longer in the environment. Full biodegradability means that the substance is likely to be eliminated through natural processes in a short period of time.

READY DEGRADABILITY - MODIFIED STURM TEST

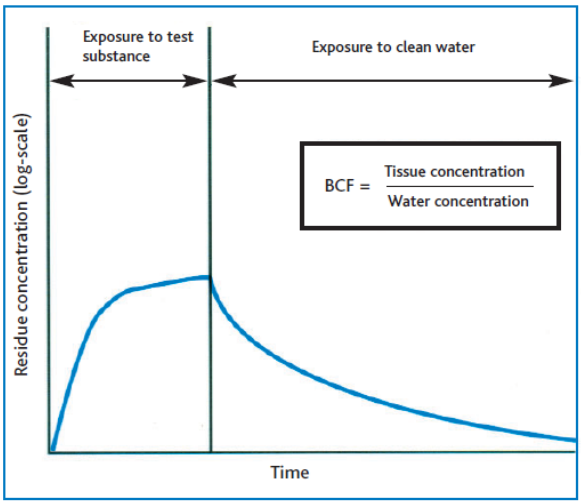


(Bio)Accumulation

Bioaccumulation or bio-concentration describes the ability of a substance to accumulate in living organisms.

The most common method used to predict the potential of a material to concentrate in aquatic organisms is the Octanol/Water partition coefficient, log Pow or log Kow (logarithmic ration of concentration in octanol to concentration in water at equilibrium). A substance with a log Pow t >3 may have the potential to bioaccumulate. However, such calculations do not take into account any potential role for metabolism of substances, which may influence its log Pow and thus its potential to bioaccumulate. Therefore, tests in animals or plants have to be conducted to establish a reliable bioaccumulation potential of such chemicals, known as the bioconcentration factor (BCF).

BIOCONCENTRATION FACTOR (BCF)



More recently, bioaccumulation and persistence in the environment have become major issues in the EU and the USA. PBT chemicals (persistent, bioaccumulative, and toxic) and vPvB (very persistent, very bioaccumulative) are treated by the EU as dangerous substances, which have to be eliminated from the environment as much as technically possible.

4. Toxicology, Industrial Hygiene and Ecotoxicology Aspects of Epoxy Products

4.1. Toxicology and Industrial Hygiene

Bisphenol A and bisphenol F epoxy resins

Unmodified liquid epoxy resins based on bisphenol A or bispheol F (Mn <700) have a low acute oral toxicity (LD50 >8 g/kg). They are mild to moderate primary irritants for skin, eyes and mucous membranes.

The irritant potential is increased by their sticky nature which tends to lead to prolonged skin contact. Solvents should not be used for their removal, because this further increases the risk of skin irritation due to the "de-fatting" ability of the solvents. These resins are generally mild to moderate skin sensitizers (can cause allergic reaction upon repeated use). In vitro they show a mutagenic potential which is absent in whole animal (in vivo) tests; no carcinogenic potential is associated with these epoxy systems. These epoxy systems are not toxic to reproduction. Based on extensive data available on BIsphenol A diglydicyl ether (BADGE), there is negligible risk for any in vivo mutagenic or carcinogenic potential associated with these unmodified liquid epoxy resins, BADGE has been evaluated for reproductive and developmental effects in vivo in laboratory animals, including rats and rabbits, using guideline study designs and typically in accordance with Good Laboratory Practices (GLPs) and has not shown targeted toxicity to reproduction.

Unmodified solid resin grades (Mn >700) are not readily bioavailable and their acute toxicity is very low (LD50 >30g/ kg). They present a low risk of skin irritation. Only direct contact with solutions of these resins can cause mild to moderate irritation of the skin and the eyes, principally because the solvents "de-fat" the skin. While lower molecular weight liquid epoxy resins are dermal sensitizers, data for the higher molecular weight solid resins are mixed, likely in part due to impurities. When crushed to a fine powder the materials should be treated as having potential foran irritant dust. No in vivo mutagenic or carcinogenic potential are associated with solid resin systems, and they are not expected to be toxic to reproduction.

Modified liquid resin grades, e.g., by the addition of lower molecular weight epoxy components such as reactive diluents, are mild to moderate primary skin irritants. The low molecular weight resins or reactive diluents present are moderate to strong sensitizers. Their sensitising potential tends to increase with decreasing molecular weight. Epoxy components with significant volatility could cause irritation to skin, eyes and respiratory tract. Some of these epoxy resin systems show a mutagenic potential *"in vitro".*

Reactive diluents

Certain low molecular weight modifiers with epoxide functionality - so-called reactive diluents - are added to epoxy resin formulations to decrease their viscosity. As epoxides they take part in the cross-linking reaction.

Reactive diluents and epoxy resins modified by the addition of these diluents are likely to be more severe irritants to skin, eyes, mucous membranes and more severe skin sensitizers than the unmodified resins. Very low molecular weight reactive diluents, with increased vapour pressure, present a higher risk of inhalation exposure with consequent irritating effects on the mucous membranes, eyes, and respiratory system.

Reactive diluents in general show the same toxicological profile as liquid epoxy resins but with more pronounced effects in humans. Some of the reactive diluents are mutagenic "in vitro" and in whole animals (in vivo).

Details for individual products are given in the Safety Data Sheet (SDS), however, it is essential to avoid exposure to this class of diluents, especially via the dermal route.

Aliphatic and Cycloaliphatic Amines

These products, such as isophoronediamine (IPDA) diethylenetriamine (DETA), and triethylentetramine (TETA) are strong bases of low molecular weight. They are moderately toxic by ingestion, inhalation or by skin contact and severe irritants for skin and eyes, and corrosive materials which in undiluted form can cause severe tissue damage to the skin, eyes and mucous membranes. In addition, some are skin sensitizers and a few are suspected of causing respiratory sensitisation. DETA and TETA are not in vivo mutagens or carcinogens; they chelate copper, which can lead to developmental effects at very high doses which are believed to be due to maternal toxicity. The risk of vapour exposure increases with increasing volatility of the amine and increasing heat of the curing reaction. The vapours of these amines are irritating for the eyes, skin and mucous membranes.

Aromatic Amines

Aromatic amines e.g., methylenedianiline (MDA) are less caustic, irritating, and sensitising than the aliphatic and cycloaliphatic amines or their formulations. However, within this group of substances there are some, such as MDA, which have been identified as dermal sensitisers, mutagenic (in vitro and in vivo), carcinogenic in animals, and possibly carcinogenic in humans. When ingested they can cause damage to internal organs, specifically the liver and kidney, and may decrease the ability of the blood to transport oxygen due to the formation of methaemoglobin. It is important to strictly avoid exposure to this class of high hazard hardeners via inhalation and especially the dermal route.

Polyaminoamides

This product group has a low acute oral toxicity (LD50 >34 g/kg) and slightly irritating effects on skin and mucous membranes compared to the aliphatic and cycloaliphatic amine hardeners. They are generally the least l materials of the hardener families, but it should be noted that some products may contain significant quantities of un-reacted amines, e.g., diethylenetetramine (DETA), which renders the substance irritating to skin, eyes and mucous membranes, and is a dermal sensitiser.

Auxiliary Materials

There are numerous auxiliary materials used in the processing and application of epoxy resin systems. Because of this wide variety only the two most common groups of products will be dealt with. For other materials please consult the SDS and the supplier’s special instructions regarding safe handling and disposal.

Solvents

In addition to the hazard of flammability, solvents and solvent blends commonly used in epoxy resin applications present special health hazards.

Contact with organic solvents will cause "de-fatting" and drying of the skin which may result in dermatitis.

Some solvents are absorbed directly through the skin and absorption may be enhanced if the skin is abraded or irritated. They also have the ability to dissolve other materials and carry them through the skin. The inhalation of solvent vapours or mists may cause respiratory irritation and depression of the central nervous system. This may result in dizziness and sleepiness, lack of co-ordination, loss of equilibrium, unconsciousness, and even death if severe over-exposure occurs. When handling solvents and degreasing agents, the observation of proper safety and industrial hygiene measures is imperative.

For specific hazards associated with particular solvents, such as reproductive toxicity and mutagenicity, the user should be fully aware of the precautions recommended by the solvent manufacturer, e.g., the SDS.

Fillers

Fillers added in powder form to resin formulations present a frequently occurring health hazard from potential overexposure to dust. The inhalation of filler dust – even so-called nuisance dust – may be detrimental to the respiratory tract. The processing of glass fibres with epoxy resins and hardeners presents a potentially serious hazard. Glass fibres irritate the skin, eyes, mucous membranes and the respiratory system. They can cause lesions of the skin which may aggravate the irritant effects of the resins and curing agents, and increase the risk of dermatitis or penetration of other materials through the skin due to the potential for abrasion.

4. 2. Environmental considerations

Ecotoxicology of Epoxy Products

Liquid epoxy resins and some reactive diluents are not readily biodegradable; although the epoxy functional groups are hydrolysed in contact with water, they have the potential to bioaccumulate and are moderately toxic to aquatic organisms. They are generally classified as dangerous for the environment according to the European Union classification criteria.

In addition, certain resin formulations contain solvents whose emission to air should be controlled. For specific details the relevant SDS should be consulted.

Uncured solid resins on the other hand are not readily bioavailable, not toxic to aquatic or terrestrial organisms, and not readily biodegradable, but they are hydrolysable, which leads to reduced residence time in air.

They present no significant hazard for the environment. They do not require any special precautions other than good industrial handling practice.

Where the use of solvent based resin systems is the only alternative, the emission of solvent vapours to the atmosphere should be kept to a minimum. In most countries solvent emissions are regulated and the legal limits must always be observed.

Waste Management

Production waste from epoxy resins and resin systems should be treated as hazardous waste in accordance with national regulations. Flame- retarded resins containing halogenated compounds should also be treated as special waste. Accidental spills of resins, curing agents, and their formulations, should be contained and absorbed by special mineral absorbents to prevent them from entering the environment. Contaminated or surplus product should not be washed down the sink, but preferably be fully reacted to form cross-linked solids which are non-hazardous and can be more easily disposed.

Finished articles made from fully cured epoxy resins are hard, infusible solids presenting no hazard to the environment. However, finished articles from flame-retarded material

containing halogenated resins should be considered hazardous waste, and disposed as required by national laws. Articles made from epoxy resins, like other thermosets, can be recycled by grinding and used as fillers in other products. Another way of disposal and recovery is combustion with energy recovery.

5. Workplace Organisation and Working Practices

Epoxy resins and curing agents are reactive compounds and should be handled sensibly and with considerable caution.

The risk to those who come into contact with epoxy products will highly depend on the process and operating procedures and will vary from job to job, task to task and workplace to workplace. However, the same general principles of control apply to all workplaces and are outlined below.

Special handling and control instructions are described in the following section or can be found in the respective SDS for individual products.

5.1. Hazard Elimination or Reduction

To insure optimum health and safety precautions for the workforce the least hazardous products or processes should be chosen, while still achieving the desired performance. Closed systems, low temperatures, appropri- ate tools and good ventilation at site of process will be of prime importance.

5.2. Epoxy Working Areas

In order to minimise hazards working areas should be designated and separated from other areas in the factory.

Rooms for eating, resting or changing clothes must be separate from the working area. Enclose and extract sources of emission which are likely to cause exposure or contamination of the workplace. General ventilation which effectively minimises the accumulation of

vapours is essential in all areas where release to the work- room air occurs.

For operations with increased risk of forming hazardous vapours, such as spraying, lay-up or casting and cur- ing of epoxy resins, local exhaust ventilation should be installed. The possible need to filter extracted air should also be included in the risk assessment.

5.3. Working Methods

Safety instructions and operating procedures for specified tasks must be written, communicated and enforced. These will include:

- Provision of hazard information and training of personnel based on previously described operating procedures and SDS, together with instructions on how to avoid exposure.
- Assessment of the risk of exposure and contact after reasonable practical steps have been taken to avoid exposure, selection and provision of suitable personal protective equipment.
- Provision of facilities for washing, storage of clothing and skin care, and promotion of their use.
- Close supervision to identify failure in the performance of process controls or in following operating instructions, the occurrence of irritation and inadequate use of personal protective equipment.
- Assessment should also be made of the need for industrial hygiene and medical surveillance, and provision of appropriate services.
- Provision of safety training of all workers involved in epoxy resin system handling.

6. Special Handling and Control Requirements of Epoxides

The following points cover some but not all particular health and safety aspects of epoxy products.

6.1. Storage and Transportation

Epoxy products must be stored in closed and labelled containers and the area should be designed and equipped for storing hazardous chemicals.

Resins, their formulations, curing agents and auxiliary materials should be stored in a cool place, in tight and well-designed containers away from open flames and sparks. Many epoxy products are classified as dangerous goods and are therefore subject to special transport regulations. Details for individual products are given in the appropriate SDS.

6.2. Fire and Explosion Hazard

Liquid and solid resins as supplied are not flammable, but will burn.

However, some formulated resin grades are flammable or highly flammable depending on the solvent used. Adequate precautions must be taken to avoid vapour accumulation and ignition sources. Grounding, e.g. earthing, and bonding of the containers should be practised. Storage requirements for this class of materials vary from country to country depending on the respective regulatory requirements and recommendations.

When solid resins are ground to a fine powder, dust clouds can form and result in a fire or explosion hazard, as with any other organic material of small particle size.

When solid resins are ground to a fine powder, dust clouds can form and result in a fire or explosion hazard, as with any other organic material of small particle size.

The control of the formation of dust clouds is best accomplished by installing suitable grinding equipment and extraction systems.

There must be no source of ignition, such as open flames, welding arcs or equipment which could produce electric sparks near areas where finely divided resin is handled and where the risk of dust clouds exists. Even not properly protected electric illumination of the workplace may cause sparks if not properly protected.

The generation of static electricity presents another possible hazard. The buildup of static charges sufficient to produce incendiary sparks can occur when an operator insulated from earth is emptying paper or plastic bags of resin. In order to control these hazards it is recommended that operators wear antistatic footwear and stand on a conductive and grounded surface.

6.3. Selection and Training of Personnel

It is advisable to follow a careful selection procedure for personnel working with epoxy resin systems. The following criteria should be seriously considered:

- People with chronic skin disease or a history of allergy should not be allowed to work with epoxy systems unless a doctor's permission has been obtained.
- It is most important that employees receive basic information about the materials they are working with and understand the nature of their hazards and the reasons for the recommended precautionary measures.
- It should be appreciated that dermatitis is an indication of improper handling.
- It is essential that all employees understand and diligently practise this recommended handling precautions and procedures. Compromise should not be permitted.

6.4. Personal Hygiene

The availability of certain facilities is a basic prerequisite for an effective personal hygiene programme. Workers handling epoxy resin systems should have access to:

- Separate lockers for work wear and personal clothes and effects
- A supply of clean overalls or other suitable working clothes
- Showers and washbowls with hot and cold water
- Soap, skin cleansing agents and paper towels in the work areas
- Protective cream for hands and face
- Suitable protective gloves

The use of these facilities should always be enforced. Eating, drinking and smoking in the working area should be prohibited. Employees should be instructed and understand the need for hand washing before these activities and before using the toilets. It is recommended that

fingernails are kept short and clean.

Dermatitis presents the most common health hazard when working with epoxy resin systems. Workers should be trained to avoid skin contact with all components - resins, hardeners, solvents and formulated products.

Accidental contamination of the skin should immediately be countered by cleaning with soap and water. Organic solvents should never be used to cleanse the skin because of their "de-fatting" effect. Open cuts, abraded skin or irritated skin areas should under no circumstances be exposed to epoxy resin systems.

6.5. Personal Protection

Special protection should be provided for operations where skin contact is likely to occur. Of particular concern when handling liquid epoxy resin products are hands, wrists, face and eyes. In case of vapour forma- tion the eyes and the respiratory tract are likely to be affected. To minimise exposure the following protective equipment should be provided and used:

Rubber or plastic gloves and sleeves for operations where the possibility of skin contact arises. A variety of rubber and plastic materials have been tested for this purpose. It is of prime importance to select the most adequate gloves based on tensile strength, resistance to perforation, glove thickness, breakthrough time, flexibility at room and elevated temperature, and price. (For further details refer to the literature references on page 26).

Rubber or plastic coated aprons as additional protection if necessary.

Overalls, preferably impermeable and disposable, for all workers where body exposure is likely to occur, e.g. manual application.

Goggles or full face shields for eye protection wherever there is the possibility of splashes or aerosols, e.g. handling solvents or resin solutions.

General and local exhaust systems should be installed to remove vapours, aerosols and dusts that may occur in operations such as curing or formulation.

Special skin cream for exposed parts of the body such as wrists and neck.

Respiratory protection is necessary in certain cases, such as short term spraying operations where local exhaust ventilation is inadequate to control exposure.

Soiled protective equipment can be reconditioned by washing first with acetone or methylethylketone (MEK) and then with soap and water. Heavily contaminated or damaged gloves should be removed at once and discarded properly. Equipment made from plasticized PVC must not be cleaned with strong solvents.

Once contaminated, clothing should be immediately removed from the body to avoid contact with the skin. Overalls should be thoroughly laundered at least once a week. All contaminated protective equipment must be carefully cleaned before re-use.

Most important of all is professional training of the workforce. Operators must be instructed in the use of protective equipment and understand the need for it.

7. Chemical Exposure Limits

The recognition of potential health hazards to workers from exposure to substances during the full life cycle of a product (development, manufacture, use, storage, transport and disposal of chemical) has prompted industry and legislators to set Chemical Exposure Limits.

Most of Chemical Exposure limits are established for inhalation exposure. There are two main categories of atmospheric OELs. "Health-based" OELs are set on the basis that adequate evidence is available to ensure that exposure at levels below the standard will be free from adverse health effects for nearly all workers. "Technical" OELs, while representing an exposure which is not believed to be associated with adverse health effects, cannot be considered to be entirely free from risk.

In addition to these two main categories, most OEL systems distinguish between longer-term – usually 8 hours – "time-weighted average" (TWA) limits and "short-term" exposure limits (5 - 30 minutes, but usually 10 or 15 min) TLV-STEL (ACGIH, 1991).

The longest established health based OELs are the threshold limit values published by the American Conference of Governmental Hygienists (ACGIH). The corresponding definitions of European OELs are essentially similar, MAK (Germany), MAC (Netherlands), OES (United Kingdom), NDS (Poland). Most other European countries also have health based OELs which are originally derived from the ACGIH TLVs. In the EU harmonisation is envisaged by the use of ILVs (Indicative Limit Vales).

In general, technical OELs are set where no threshold can be defined for adverse health effects in all or some of the persons exposed, for instance TRK (Germany) or MEL (United Kingdom).

This is the case with some mutagenic and carcinogenic substances and respiratory sensitizers where the induction of disease is a stochastic response which might occur at any level of exposure, but where the probability of disease becoming manifest increases with increasing exposure level.

Compliance with OELs is mostly determined by workplace air monitoring. For some substances, especially showing systemic health effects after dermal absorption, biological monitoring is performed. In relation to chemical exposure, biological monitoring is the measurement of the concentration of a chemical substance or its metabolite in a human biological media: e.g. blood, urine, saliva, exhaled air.

Atmospheric OELs are based upon mg/m3 or ppm. BEIs are based upon percent of hemoglobin for blood sample, milligrams or micrometers per gram of creatinine for urine sample or in ppm of exhaled air.

The biological monitoring should be considered complementary to workplace air monitoring.

Because of the uncertainties surrounding their effectiveness in protecting health there is normally a requirement to reduce exposure below the standard as far as practical. Where substances being handled in connection with epoxy resin systems have been assigned official or voluntary OELs care should be taken that these levels are not exceeded.

Where no OELs have been set by legislators internal exposure limits (IEL) can be set by the producer or user of a hazardous substance.

For substances registered under REACH Regulation in EU, when chemical safety assessment is required, Derived no Effect Levels (DNELs) are determined. DNELs should be understood as the levels of exposure above which humans should not be exposed. They are determined for different routs of exposure (e.g. oral, dermal, inhalation), different duration of exposure and different human population. DNELs are calculated on the base of toxicological studies results for the substance, with following factors taken into account: the uncertainty arising, from the variability in the experimental data, the nature and severity of the effect, sensitivity of the human (sub-population).

Most of DNELs cannot be determined by measurement, however they are used to establish set of conditions: both risk management measures and operational conditions which ensure the substance is used in a safe way and exposure for considered population is controlled.

8. First Aid

When accidental exposures occur the following procedures must always be followed:

Ingestion
In the unlikely case of accidental swallowing, drink lots of water in small quantities. Do not try to induce vomiting or apply house remedies. Get medical attention immediately.

Eyes
Following accidental contamination the eye should be immediately and continuously washed under running fresh water for at least 10 minutes. The installation of eye showers for this purpose is strongly recommended. In any case of contamination the person should be referred to a doctor for examination of potential eye damage and follow up treatment.

Skin
Contaminated clothing must be removed immediately to avoid contamination of yet unex- posed skin. In case of skin contact first remove most of the resin with a clean cloth without rubbing, then wash all affected areas thoroughly with soap and water. Never use solvents. Cured resins are not hazardous and will peel off after a short time.

Parts of the skin showing signs of a burn should be carefully washed with cold water and covered with a dry dressing. The affected person should consult a doctor. If employees develop skin irritation despite the above treatment, they should be removed from all work involving epoxy products and systems. Continuous medical attention is advised until complete remission is confirmed. Resumption of duties should not be permitted without a doctor's permission.

Employees who do not respond to medical treatment or who have recurring dermatitis should be transferred to other work and avoid any further contact with epoxy resin systems and formulations.

If skin or respiratory irritation occurs despite precautions, sensitisation may have developed. The employee should be removed from all further exposure to epoxy products and analogous compounds and not allowed to resume usual duties without medical permission. It may be necessary to transfer the person to another job.

Inhalation

In case of accidental inhalation remove the individual to fresh air and keep at rest until any symptoms of respiratory distress have disappeared. If rapid recovery does not occur or where there is a danger of unconsciousness, call an ambulance and obtain medical attention.

These general recommendations apply to most epoxy resin systems. However, there are specialised systems and applications which may require additional considerations. In these cases it is recommended that technical information and special instructions are requested from the supplier.

9. Glossary of Terms and Values

Terms, values and abbreviations used within the document are briefly described as:

Allergy

Immune response built up against a particular substance by repeated exposure, causing allergic reactions upon exposure to minute amounts of the substance.

ACGIH – American Conference of Governmental Industrial Hygienists

An organisation of professional personnel in Governmental Agencies or educational institutions engaged in occupational safety and health programmes.

Bio-concentration

The buildup and accumulation of a chemical in plants, animals and man to levels higher than found in the immediate environment.

BOD – Biochemical Oxygen Demand

A test that measures the dissolved oxygen by microbial life and oxidising the organic matter present in organic waste discharges.

Ceiling Value

The maximum allowable human exposure limit for an airborne substance which is not to be exceeded at any time. See also PEL and TLV.

Dermatitis

Inflammation of the skin, also called skin irritation. Symptoms are rash, itching, blisters, swelling and crustiness.

Epidemiology

Science concerned with the study of a disease in a general or specific population. Determination of incidence and distribution of a particular disease which may provide information about its cause.

IEL – Internal Exposure Limit

Internal occupational standard set by the manufacturer in the absence of an official governmental standard.

In vitro

"in-glass" or "in-silico" experiments with cells, tissues or parts of cells from organisms, conducted outside of the organism.

In vivo

Experiments in life animals.

Irritant

A chemical which is not corrosive that causes a reversible inflammatory effect on living tissue by chemical action at the site of contact.

Irritation

A condition of irritability, soreness, roughness or inflammation of a body part.

LC50 – Lethal Concentration

The calculated or directly measured concentration of a material in air or water that is expected to kill 50 % of a group of test animals with a single exposure (normally 1-6 hours, aquatic organisms: 48 – 96 hours).

LD50 – Lethal Dose

The calculated or directly measured dose of a material that is expected to kill 50 % of a group of test animals with a single administration within a period of 14 days post treatment.

MAC – Value Maximale Aanvaarde Concentratie

Occupational standard of The Netherlands. Maximum permissible time weighted average concentration (mg/m3) at the workplace for a 40-hour working week.

MAK – Maximale Arbeitsplatz-Konzentration

German occupational standard Maximum permissible concentration in air at the workplace in the breathing zone for 8 hours per day and 5 days per week.

MEL – Value Maximum Exposure Limit

UK occupational standard. Maximum concentration of an airborne substance, averaged over a reference period, to which employees may be exposed by inhalation under any circumstances.

Mutagen

A substance or agent capable of chemically altering the genetic material in a living cell.

Necrosis

Tissue destruction or death of tissue. Corrosive materials may cause localised tissue damage at the site of contact which will lead to scarring.

NOEL – No Observed Effect Level

The dose of a substance used in a test which produces no substance-related adverse effects.

Sensitizer

A chemical that causes the development of an allergic reaction in exposed people or animals after repeated exposure. (See allergy).

Somatic Cells

Body cells except germ cells.

STEL – Short Term Exposure Limit

Defined as a 15-minute TWA exposure which should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV-TWA.

Subchronic

A health effect resulting from the repeated daily exposure of experimental animals to a chemical for part of their lifespan. Subchronic in rodents means 28 – 180 days.

Synergy

The combined action of chemicals so that their joint effect is greater than the sum of their individual effects.

Systemic Toxicity

Adverse health effects caused by a substance that affects the body in a general rather than local manner.

Target Organ Effect

The effect of a substance on an organ which is more sensitive than the remainder of the body.

TLV – TWA –: Threshold Limit Value – Time Weighted Average

Occupational guideline developed by the ACGIH in the USA. Concentrations in air for a normal 8-hour work- day and a 40-hour workweek, to which workers may be repeatedly exposed day after day without adverse effects.

TLV-C – Threshold Limit Value Ceiling

Occupational guideline developed by the ACGIH in the USA. The concentration that should not be exceeded during any time of the working exposure.

TLV-STEL – Threshold Limit Value –Short-Term Exposure Limit

Occupational guideline developed by the ACGIH in the USA. The concentration to which workers can be exposed continuously for a short period of time without suffering from (1) irritation, (2) chronic or irreversible tissue damage, or (3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency, provided that the daily TLV-TWA is not exceeded.

TRK – Technische Richt-Konzentration

German occupational guidance value. Established for dangerous chemical substances (especially carcinogens, mutagens and substances that strongly bioaccumulate) for which at present no MAK value can be defined.

TWA – Time Weighted Average

See also TLV. Average concentration over an 8-hour period.

10. Literature References

The following references are recommended for further reading:

1. T.H. Gardiner, J.M. Waechter, Jr., MA. Wiedow and W.T. Solomon. Glycidyloxy Compounds Used in Epoxy Resin Systems: A Toxicological Review Sponsored by The Society of the Plastics Industry, Inc. Epoxy Resin Systems Task Group. Vol. 15, No. 2, April 1992 Part 2 of 2 Parts.

2. Safe Handling of Advanced Composite Materials, Suppliers of Advanced composite Materials Association (SACMA), 1991, 1600 Wilson Blvd., Arlington, VA 22209, USA.

3. A Guide to the Prevention of Dermatitis, Suppliers of Advanced composite Materials Association (SACMA), 1991, 1600 Wilson Blvd., Arlington, VA 22209, USA.

4. Testing of Worker Protection. ECETOC Technical Report No. 59, May 1994. European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC). Ave. E. Van Nieuwenhuyse 4, bte 6, B-1160 Brussels, Belgium,

5. Epoxidharze in der Bauwirtschaft, Handlungsanleitung. Arbeitsgemeinschaft der Bauberufsgenossenschaften und Tiefbaugenossenschaft. Oktober 1994.

6. Guidelines for Safe Manufacture of Resins with Particular Reference to Fire and Explosion. Prepared be the European Resin Manufacturer's Association, published by the Oil & Colour Chemist's Association, October 1995.

7. Epoxidharz-Systeme sicher handhaben. Leitfaden zum sicheren Umgang mit Epoxidharz-Systemen in der Bauindustrie und verwandten Anwendungsbereichen. PlasticsEurope , Epoxy Resins Committee.
Ave. E. van Nieuwenhuyse 4/3, B-1160 Brussels, Belgium.

8. J. Pors & R. Oppl (Eurofins),, Schutzwirkung von acht Chemikalienschutzhandschuhen gegenüber von EP-Beschichtungen, Version C. Arbeitskreis CSH für Epoxidharzprodukte, Arbeitsgemeinschaft der Bau-Berufsgenossenschaften, Hungener Strasse 6, D-60389 Frankfurt/M. Oktober 2003.

9. D.H. Brower. Selection of Suitable glove (materials) for epoxy resin systems. TNO Chemistry (Zeist, NL), for PlasticsEurope , Ave. E. Van Nieuwenhuyse 4/3, B-1160 Brussels, Belgium

This guide has been developed by the members of the Epoxy Resins Committee (ERC) of PlasticsEurope, the Association of the Plastics Manufactures in Europe. The Association has more than 100 member companies, producing over 90% of polymers across the EU28 member states plus Norway, Switzerland and Turkey.

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The user should always refer to the Safety Data Sheet of the supplier of the material for specific and updated information.

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