EPOXY RESINS AND CURING AGENTS

Toxicology, Health, Safety and Environmental Aspects

May 2006

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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 and hazards to man and the environment.

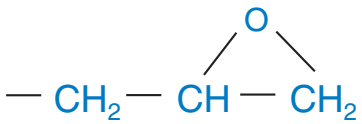
The aim of this document is to provide the reader with reference information concerning the main aspects of human health, occupational and environmental safety of epoxy products.
It is not intended to be fully comprehensive in answering all questions that might arise for the wide variety of products 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

Plastics*Europe*'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 Plastics*Europe* 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 effect 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 a condition for exposure which causes 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 is the ability of a substance to cause 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 organs or tissues 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 and depending on the degree of damage and 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 and clothing is worn.

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 tissue culture 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 adverse effects after a single exposure leading in the worst case to death of the organism. For classification purposes the degree of toxicity 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 LD_{50} or median lethal dose. The LD_{50} value is the amount of substance administered – normally expressed as dosage in mg/kg bodyweight and statistically calculated from actual data – that is likely to kill 50 per cent of a group of test animals.

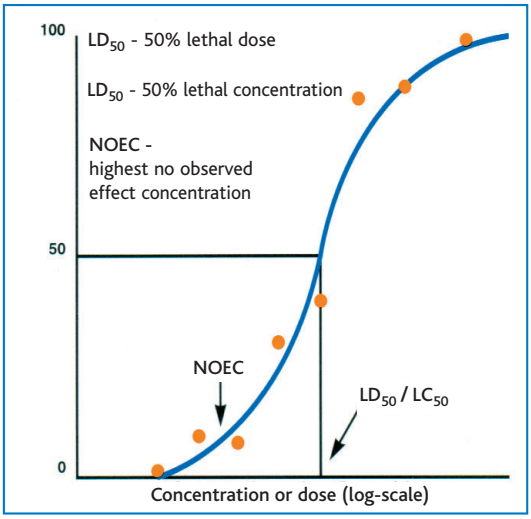
Acute toxicity by inhalation is usually expressed as the LC_{50} value or median lethal concentration. LC_{50} values are usually expressed as airborne concentration of a substance in mg/m^3 air or mg/l of air or in ppm in air and should specify the length of exposure in hours or minutes.

The dose-response relationship is illustrated in the graph on the next page.

Substances and preparations with an acute toxicity within the ranges indicated must carry the legally prescribed warning labels and the appropriate classification.

DETERMINATION OF EFFECT CONCENTRATIONS

A typical dose-response curve



Label	Very toxic T+	Toxic T	Harmful Xn
LD_{50} (mg/kg)			
Oral	≤ 25	25 - 200	200 - 2000
Dermal	≤ 50	50 - 400	400 - 2000
LC_{50} (mg/l 4h			
Inhalation			
• vapours	≤ 0.5	0.5 - 2	2 - 20
• aerosols / dust	≤ 0.25	0.25 - 1	1 - 5

The EU Directive 67/548/EEC on the Classification and Labelling of Dangerous Chemical Substances sets the above ranges for the classification of the acute toxicity in rats (right picture).

Sensitisation and Hypersensitivity

Sensitisation is an allergic or hypersensitive reaction to a substance that may develop upon repeated exposure. The degree of the sensitising effect of substances varies widely from person to person. Allergies 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 necessarily depend on the degree of exposure. Contact with trace amounts of sensitising substances can cause an allergic reaction, if the person is already sensitised.

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, thus causing adverse effects either by accumulation in target tissues or by prolonged stress of the liver and other organs. Specifically designed toxicity tests are performed in order to assess the hazard of this particular exposure type.

The substance is administered at various dose levels to groups of test animals over a prolonged period of time (weeks or months). Administration of the dose should if possible correspond to the likely route of potential exposure in humans.

The results provide the basis for determining:

- 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

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 working over a long period of time without 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 toxicity to reproduction have been the most important long-term health effects investigated. Other effects such as neurotoxicity and immuno-toxicity are now also being specifically studied as their significance is increasing.

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 a significant step towards the formation of tumours in mammals, although an absolute correlation between mutagenicity and carcinogenicity is not proven.

The most frequently performed "in vitro" test for mutagenicity of chemical substances involves Salmonella bacteria which are also known as the "Ames test". It is sensitive, fast and inexpensive for screening purposes. Other in vitro tests use mammalian cell cultures to screen for the mutagenic potential of a substance and to obtain some indication of its carcinogenic potential. More extensive testing for mutagenicity is performed in life animals (in vivo).

The outcome of a single test is generally insufficient 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 un-repaired genetic changes (mutations) in the body's cells. Such changes can be caused by natural reasons but also by chemical substances.

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

Reproductive Toxicity

Reproductive toxicity deals with the potential influence of chemical substances on the 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.

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

Embryotoxicity

Embryotoxicity is the potential of a substance to damage or kill the embryo or foetus. To test this effect the following effects on the developing embryo are studied in pregnant experimental animals:

- Embryo mortality (embryolethal effects)
- Malformations (teratogenic effects)
- Growth retardation (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 three decades and has developed into a new discipline.

During the manufacture, processing and use of chemical substances one of the main potential ways of entry into the environment is through water, but also through air and soil. Consequently, testing for toxic effects in the environment (ecotoxicity) is generally conducted on aquatic and terrestrial 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, earthworm 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. LC_{50} value "lethal concentration" for fish, EC_{50} for reduced motility of Daphnia or the EC_{10} when the growth of bacteria is retarded by 10 per cent.

The results of these tests provide information about potential environmental damage after accidental short term exposure. The data can also help in risk assessment for longer term exposure, when information regarding the environmental behaviour 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 for the lowest 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 include also multi-generation studies providing information on the possible reproductive effects of a substance on aquatic organisms.

TOXICITY TO FISH, INVERTEBRATES AND ALGAE

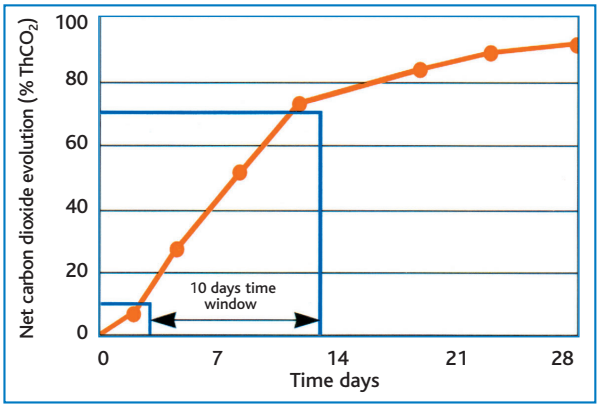
Acute aquatic toxicity categories EC_{50} or LC_{50} (mg/l)	Classification
≤ 1	Very toxic
1-10	Toxic
10-100	Harmful
> 100	None

Degradability

Apart from biodegradation, degradation by physico-chemical factors such as light, oxygen, temperature, play also 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 live 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 to cause harm. Full biodegradability means that nature gets rid of the substance in a short period of time.

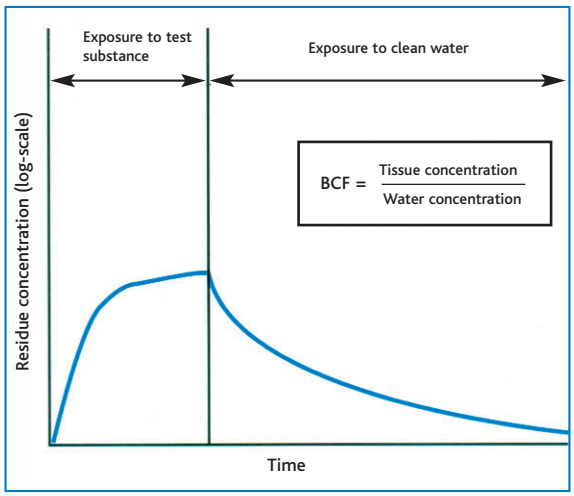
READY DEGRADABILITY - MODIFIED STURM TEST



Accumulation

Bioaccumulation or bio-concentration describes the ability of a substance to accumulate in the environment. The most common method used to assess the potential of a material to concentrate in aquatic organisms is the so-called Octanol/Water partition coefficient log Pow (logarithmic ration of concentration in octanol to concentration in water at equilibrium). A substance with a log Pow coefficient >3 may have the potential to bio-accumulate. However, such calculations do not allow to make corrections for metabolism of substances which may influence its log Pow and therefore its potential to bio-accumulate. Therefore, tests in animals or plants have to be conducted to establish the real bioaccumulation potential of such chemicals.

BIOCONCENTRATION FACTOR (BCF)



More recently, bioaccumulation and persistence in the environment have become major issues in the EU and the USA. So-called PBT chemicals (persistent, bio-accumulating, and toxic) and vPvB (very persistent, very bio-accumulative) 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 (LD_{50} > 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 tests; no carcinogenic potential is associated with these epoxy systems. These epoxy systems are not toxic to reproduction.

Unmodified solid resin grades (Mn > 700) are not readily bio-available and their acute toxicity is very low (LD_{50} > 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. When crushed to a fine powder the materials should be treated as forming an irritant dust. No mutagenic and no carcinogenic potential are associated with solid resin systems, and they are not 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".

Cycloaliphatic Epoxy Resins

Most commercially available resins of this type have toxicological properties similar to those of liquid bisphenol A and bisphenol F based epoxy resins. This type of epoxy resins is of low acute toxicity, but shows mild to moderate potential for skin, eye and respiratory tract irritation. In addition, a skin sensitising potential is associated with these resins. However, extra care needs to be taken with blends of certain cycloaliphatic resins with bisphenol A and bisphenol F resins because of possible effects resulting in potential skin carcinogenicity.

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".

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.

Curing Agents

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.

The risk of vapour exposure increases with the volatility of the amine and the 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 which have been identified as 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 hardeners via inhalation and especially the dermal route.

Polyaminoamides

This product group has a low acute oral toxicity (LD_{50} >34 g/kg) and low irritating effects on skin and mucous membranes compared to the aliphatic and cycloaliphatic amine hardeners. They are the least critical 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 to be irritating to skin, eyes and mucous membranes.

Anhydrides

Most anhydride curing agents are strong irritants for skin, eyes and the respiratory tract. Some of them may even cause burns. Anhydrides with high vapour pressure at normal processing and curing temperatures have a strong sensitising effect in the respiratory tract, such as trimellitic anhydride.

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 represent the most frequently occurring health hazard. The inhalation of filler dust – even so-called nuisance dust – may be detrimental to the respiratory tract.

The processing of glass fibres in combination with epoxy resins and hardeners present 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.

4.2. Environmental considerations

Ecotoxicology of Epoxy Products

Liquid epoxy resins and some reactive diluents are not readily biodegradable, although its epoxy functional groups are hydrolysed in contact with water, they have the potential to bio-accumulate 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 the air should be controlled. For specific details the relevant SDS should be consulted.
Uncured solid resins on the other hand are not readily bio-available, not toxic to aquatic and terrestrial organisms, not readily biodegradable, but hydrolysable.

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. Fire retarded resins containing halogenated compounds should also be treated as special waste. Accidental spillage 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 is 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, appropriate 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 workroom air occurs.

For operations with increased risk of forming hazardous vapours, such as spraying, lay-up or casting and curing 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 formation 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. Occupational 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 occupational exposure limits (OEL).

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). 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.

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

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.

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 unexposed 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:

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This guide has been developed by the members of the Epoxy Resins Committee (ERC) of Plastics*Europe*, the Association of the Plastics Manufactures in Europe. The Association has more than 60 member companies, producing over 90% of polymers across the EU's 25 member states plus Bulgaria, Croatia, Norway, Romania, 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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