

# Ethylbenzene: Environmental, Health & Safety Guidelines

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## Member Companies

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- Dow Europe
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- Lyondell
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- Nova Chemicals
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## Latest Version

To stay abreast of the latest developments regarding the Environmental, Health and Safety aspects of ethylbenzene, the reader is advised to visit the Styrene Producers Association section of the CEFIC web site (<http://www.cefic.be>).

## 1.0 Introduction and Purpose

The purpose of this brochure is to review environmental, health and safety aspects for ethylbenzene, i.e. how to handle the material according to current industry standards and guidelines. The Styrene Producers Association (SPA), a sector group of the European Chemical Industry Council (Cefic), encourages customers and potential users of ethylbenzene and styrene (refer to SPA's "Styrene Monomer: Environmental, Health & Safety Guidelines") to review their applications from the standpoint of human health and environmental quality. To help ensure that the product is not used in ways which are not intended or tested, producers will assist customers in dealing with ecological and product safety considerations. The supplier's Safety Data Sheet for ethylbenzene should be consulted prior to its use. The Responsible Care® commitment of the chemical industry represents efforts to assist customers in developing sound product stewardship practices in order to better safeguard workers and operations, and to protect the environment.

Ethylbenzene (CAS RN: 100-41-4; EC No.: 202-849-4; Annex I Index No.: 601-023-00-4) was first produced on a commercial scale in the 1930s by BASF (Badische Anilin und Sodafabrik) in Germany and by The Dow Chemical Company in the United States. The styrene industry, which uses ethylbenzene as a starting raw material, remained relatively insignificant until World War II. The tremendous demand for synthetic styrene – butadiene rubber (SBR) during the war prompted accelerated technology improvements and capacity expansion. This effort led to the construction of several large-scale factories, and styrene production became a significant industry. In 2002, world annual production capacity of ethylbenzene reached almost 28,000 kilotons (Kt), of which Western Europe and the United States each account for 23 %. Throughout the 1990's, most of the production capacity increase occurred in the Far Eastern countries other than Japan, where the basic petrochemical industries have undergone considerable development and expansion. In 2002 the ethylbenzene production capacity in Northeast Asia, particularly in Korea, reached 8,314 Kt, about 30 % of the world production capacity, while the Middle East accounted for 5 % (1,310 Kt) and Southeast Asia for 7 % (1,960 Kt) of the world annual production capacity (data calculated from Reference 1, see Bibliography).

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## Product Characteristics

Ethylbenzene ( $C_6H_5CH_2CH_3$ ), also known as phenylethane or alpha-methyltoluene, under ambient condition is a colourless clear liquid with a sweet, gasoline-like odour.

Chemically, it is a monocyclic alkylaromatic compound with a molecular weight of 106.

It is miscible with most of the commonly used organic solvents in any ratio, but is only sparingly soluble in water (170 ppm under ambient conditions). Spilled ethylbenzene will float on water and partition strongly towards air. Due to its high evaporation rate, no significant environmental hazards are expected. For other typical parameters, please consult Appendix 1 of this brochure.

Being rather volatile and having a flash point of 19-23 °C, ethylbenzene is classified as a highly flammable substance, which in use may form flammable/explosive vapour-air mixtures.

Short-term exposure to ethylbenzene in humans results in respiratory effects, such as throat irritation and lung constriction, irritation to the eyes, and neurological effects such as dizziness.

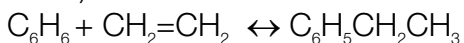
Ethylbenzene has a characteristic odour which can be detected at low concentrations (1-2.3 ppm).

## Manufacturing

Commercially, almost all ethylbenzene (> 99 %) is produced by alkylating benzene with ethylene, except for a very small fraction that is recovered from mixed C8 aromatics (xylenes) by superfractioning.

Ethylbenzene and styrene units are almost always installed together, with matching capacities. In a typical ethylbenzene-styrene complex, energy economy is realized by advantageously integrating the energy flows of the two units. The alkylation is exothermic, while the subsequent dehydrogenation to styrene is endothermic.

The reaction of benzene and ethylene takes place on an acidic catalyst (Lewis acids):



The newest technologies utilize synthetic zeolites installed in fixed-bed reactors to catalyze the alkylation in the liquid phase. Another proven route uses narrower-pore synthetic zeolites, also installed in fixed-bed reactors, to effect the alkylation in the vapour phase. A considerable quantity of ethylbenzene is still produced by alkylation with homogeneous aluminum chloride catalyst in the liquid phase, though the recent trend in the industry has been to retrofit such units with zeolite technology.

Several facilities built in the United States, Europe and Japan during the 1960's recovered ethylbenzene by fractionation of mixed xylenes (C8 aromatics) produced mainly in refinery catalytic reforming units. Mixed-xylenes capacity worldwide was 36 million tonnes in 2002. This practice has largely been discontinued, due to poor economics that result from high energy and investment costs, as well as small economies of scale (mixed xylenes only contain about 20 % ethylbenzene) in comparison to the conventional alkylation routes.

For more details on production technologies and the latest technology trends, please refer to Reference 2 of the bibliography.

## **Quality**

Commercial ethylbenzene is manufactured almost exclusively for captive use to produce styrene; only a small fraction is traded. Typically ethylbenzene has a purity of >99.5 % as determined by gas chromatography. The impurities are generally aromatic compounds in the range C6-C10 and non-aromatics in the C7-C10 range (oligomerization of ethylene, alkylation of the C6 non-aromatics in benzene).

The product specification for ethylbenzene is set to provide a satisfactory feedstock to the associated styrene unit, i.e. the levels of impurities are controlled to meet the required styrene purity specification. An assay of as low as 99 % in specifications for ethylbenzene is acceptable, provided that most of the impurities are benzene and toluene.

The majority of manufacturers have defined their sales specification according to American Standards and Test Methods ASTM D3193 "Standard Specification for Ethylbenzene". Key parameters of a typical sales specification are: a minimum purity of 99.5 wt. % and a maximum colour of 10 on the Platinum-Cobalt Scale, while the specified impurities and their concentrations depend upon the manufacturing route employed, along with plant performance characteristics.

## **Applications**

Ethylbenzene is almost exclusively (>99 %) used as an intermediate for the manufacture of styrene monomer [CAS RN: 100-42-5],  $C_6H_5CH=CH_2$ , one of the most important large-volume commodity chemicals, or in the co-production of styrene monomer with propylene oxide.

Less than 1 % of the ethylbenzene produced is used as an intermediate for the production of acetophenone, diethylbenzene and ethylanthraquinone, as a constituent of asphalt and naphtha, and as an anti-knock additive in fuels and gasolines. Of the minor uses, the most significant is in the coatings industry as a solvent (mixed xylenes) for paints, lacquers, and varnishes. Please refer to Reference 1 in the Bibliography for more details on specific application areas for ethylbenzene.

## 1.5 European Regulatory Environment

In February 2001 the European Commission issued a White Paper entitled "Strategy for a Future Chemicals Policy" (COM (2001) 88 Final), aiming at complete revision of the existing legislation on chemicals. The overall goals of the new policy are to ensure the protection of human health and environment, maintenance of the competitiveness of the European chemical industry and preventing the fragmentation of the internal market.

Following the White Paper, the European Commission presented the first draft of a new comprehensive chemicals regulation with the goal of streamlining and updating the current regulatory framework in May 2003. After a public internet consultation, the Commission modified the draft and adopted its final proposal on REACH (Registration, Evaluation and Authorisation of CHemicals) (COM 2003 0644) on 29 October 2003.

REACH will replace the legislative framework for "new" and "existing" chemicals and extend the requirements for new substances to existing ones. Existing substances available commercially between 1 January 1971 and 18 September 1981 were compiled into the European INventory of Existing Commercial Substances (EINECS) in application of Article 13 of Directive 67/548/EEC, as amended by Directive 79/831/EEC, and in accordance with the detailed provisions of Commission Decision 81/437. Among the 100,196 EINECS-listed substances is ethylbenzene. These substances could be produced and sold without meeting the comprehensive and stringent data requirements demanded for new substances. Under REACH, enterprises that manufacture or import more than one tonne of a chemical substance per year would be required to register it in a central database. Higher tonnage of manufacture will attract an increasing degree of testing. REACH would furthermore give greater responsibility to industry to manage the risks from chemicals and to provide users in the supply chain with safety information on the substances. The proposal is now being considered by the European Parliament and by the Council for adoption under the so-called co-decision procedure.

On 9 July 2004 the European Commission and the European chemical industry via Cefic agreed to launch a strategic partnership to test REACH in practice. Please review the following websites for more information and to stay on top of developments related to REACH:

<http://ecb.jrc.it/REACH/>

<http://europa.eu.int/comm/enterprise/reach>

<http://europa.eu.int/comm/environment/chemicals/reach.htm>

<http://www.chemicalspolicyreview.org/>

In 1993 the Council of the European Communities adopted Council Regulation (EEC) 793/93 (Existing Substances Regulation (ESR)), thereby introducing a comprehensive framework for the evaluation and control of "existing" chemical substances. The Regulation was intended to complement the already existing rules governed by Council Directive 67/548/EEC for "new" chemical substances. The evaluation and control of the risks posed by existing chemicals is carried out in four steps: data collection, priority setting, risk assessment and risk reduction.

In the data collection step, ethylbenzene was determined to be a High Production Volume Chemical (HPVC), i.e. has been imported or produced in quantities exceeding 1000 tonnes per year and produced/imported between 23 March 1990 and 23 March 1994. The data set for ethylbenzene in the required electronic format Harmonised Electronic DataSET (HEDSET) was submitted and is now managed by the International Uniform Chemical Information Database (IUCLID). According to Article 8 of 793/93 EEC, four lists totaling 141 priority substances have been published since 1994. Ethylbenzene was added to the first priority list (1179/94 EC).

Substances on priority lists must undergo an in-depth risk assessment covering the risks posed by the priority chemical to man (covering workers, consumers, and humans exposed via the environment) and the environment itself (covering the terrestrial, aquatic and atmospheric ecosystems and accumulation through the food chain). Ethylbenzene was assessed by Germany as the member state rapporteur for the environmental part only. The first in-depth discussion of this risk assessment took place at the Technical Committee on New and Existing Substances meeting in first quarter of 2004. The draft Risk Assessment Report (RAR) will be published on the European Chemicals Bureau (ECB) website (<http://ecb.jrc.it/>) in the near future. For more information on the progress made for ethylbenzene, please visit European chemical Substances Information Systems (ESIS) found on the ECB website.

The Commission Working Group on the Classification and Labelling of Dangerous Substances: Environmental Effects has agreed not to classify ethylbenzene (Annex I Index No.: 601-023-00-4) as dangerous to the environment due to its ready biodegradability (Summary Report ECBI/81/95 - Rev. 2; 27-29 September 1995). Ethylbenzene was inserted to Annex I of 67/548/EEC in Commission Directive 93/72/EEC (19<sup>th</sup> Adaptation to Technical Progress; O.J. N° L258, 16.10.1993, p. 29; O.J. N° L258A, 16.10.1993, p. 1).

Ethylbenzene is not listed in the Recommendations of the Technical Committee for Classification and Labelling and Specialised Experts for possible inclusion into the 30<sup>th</sup> Adaptation to Technical Progress (ATP) or the current 29<sup>th</sup> ATP (Commission Directive 2004/73/EC).

## **2.0 Responsible Care**

In line with regulations and the commitment to the concept of Responsible Care and its principles, ethylbenzene producers provide information regarding its safe storage, handling, use and ultimate disposal. A key document in this respect is the safety data sheet. It is an invaluable source of health and safety information, and is available in many languages. For information on specific applications of ethylbenzene, users are urged to contact the customer service center of their supplier.

### **2.1.0 Health Effects**

This section covers the effects of exposure to ethylbenzene, i.e. acute toxicity, skin and eye irritation, repeat dose toxicity and carcinogenic potential. The users of ethylbenzene are recommended to contact their suppliers for the most recent or detailed information regarding chronic hazards, reproductive and developmental toxic effects and genotoxicity.

### **2.1.1 Product Classification (Health Effects)**

According to the EU Dangerous Substances Directive the health effects of ethylbenzene are classified as “Harmful by inhalation”. The preliminary written procedure for the EU Human Health risk assessment of ethylbenzene has not yet taken place. For further details on the European Regulatory Environment please see chapter 1.5 European Regulatory Environment.

### **2.1.2 Acute Toxicity**

The available human and animal data indicate that breathing of ethylbenzene vapours at high concentrations over prolonged periods can cause central nervous system (CNS) depression resulting in dizziness, headache, drowsiness, nausea and loss of coordination. Inhalation studies in rats indicate that ethylbenzene has a moderate toxicity (lethal concentration  $LC_{50}$  (4 h) = 2-20 mg/l = 460 – 4600 ppm).

It can be concluded from animal experiments that the acute oral toxicity of ethylbenzene is low. The oral lethal dose  $LD_{50}$  (rat) is reported to be well above 2000 mg/kg body weight. As the oral toxicity is low, any small amounts of ethylbenzene accidentally ingested are unlikely to cause injury. Ingestion of large amounts of ethylbenzene may cause slight to moderate irritation of the mouth, throat and gastro-intestinal tract. After swallowing large amounts, aspiration into the lungs may cause chemical pneumonitis, which can be fatal.

The dermal toxicity of ethylbenzene is low; the  $LD_{50}$  in rabbits is above 5000 mg/kg body weight.

Note that in addition to CNS depression, in cases of high exposure in incidents and abuse, solvents may increase the sensitivity of the heart to endogenous catecholamines leading to potentially fatal cardiac conditions.

### **2.1.3 Skin and Eye Irritation**

Ethylbenzene can cause slight to moderate irritation to skin and eyes, but the effect is insufficient to trigger a classification according to EU regulations. Frequent dermal contact may lead to dryness of the skin and dermatitis.

#### **2.1.4 Sensitization**

Ethylbenzene has not been observed to cause allergic dermal reactions. The available information suggests that it has no asthmogenic potential.

### **2.1.5 Repeated Dose (Systemic) Toxicity**

The repeated exposure (non-cancer) systemic toxicity of ethylbenzene has been evaluated in laboratory animals in subchronic and chronic inhalation studies and a subchronic oral study. Overall, the liver and kidney are the target organs for the toxicity of ethylbenzene upon repeated exposures. However, chronic pathology of significance was not observed.

Specialist investigations also provide evidence of hearing loss in some experimental animal studies following repeated exposure to high vapor concentrations and the possible significance of these findings is being further investigated.

### **2.1.6 Immunotoxicity**

There is no evidence that ethylbenzene is harmful to the immune system. A screening-level immunotoxicity study in rats found no evidence of adverse effects on the functional ability of the immune system. Additionally, in the several subchronic and chronic toxicity studies that have been performed for ethylbenzene, there were no reported changes or lesions affecting immune system organs or tissues.

### **2.1.7 Developmental and Reproductive Toxicity**

Ethylbenzene is not a teratogen or reproductive toxicant and is not (selectively) toxic to the developing fetus. In laboratory animals at doses that produced toxicity to the maternal animal ( $\geq 1000$  ppm) as indicated by adverse clinical signs and reductions in body weight, ethyl benzene caused a delay in fetal development such as decreased body weights and increases in skeletal variations. No foetotoxicity was present in developmental toxicity studies at concentrations of 500 ppm or lower. Ethylbenzene, when administered at up to 500 ppm to rats, also did not adversely affect reproductive performance or offspring development over two generations. Furthermore, it has been shown that ethylbenzene is not (selectively) toxic to the developing nervous system.

### **2.1.8 Genetic Toxicity**

In *in vivo* experiments ethylbenzene was not genotoxic and not chromosome damaging. In *in vitro* mutagenicity tests ethylbenzene did not show an effect, however, in a few isolated tests positive results occurred. The *weight of evidence indicates that ethylbenzene is not genotoxic.*

### **2.1.9 Carcinogenicity**

Most national and international agencies have not classified ethylbenzene for potential genotoxicity or carcinogenicity. In Germany the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area ("MAK Commission") has classified ethylbenzene as having very low cancer potency. The International Agency for Research on Cancer (IARC) has concluded that there is inadequate evidence to classify ethylbenzene as a carcinogen in humans and sufficient evidence in experimental animals.

Ethylbenzene is carcinogenic in animals following lifetime exposures to high vapor concentrations. The strongest evidence of cancer was kidney tumors found in male rats that inhaled 750 ppm ethylbenzene, a concentration that also significantly reduced the male rats' survival. There was some evidence of kidney tumors in female rats at this concentration that was detected only after extended evaluation. Exacerbation by ethylbenzene of chronic progressive nephropathy, a pathway that is considered to have no relevance for extrapolation to humans, is postulated as the mode of action underlying the development of the rat renal cancer. There was some evidence at 750 ppm ethylbenzene of liver and lung tumors in mice. The incidences of lung tumors in male mice and liver tumors in female mice were greater than those in concurrent control but were within the historical control ranges observed for these tumor types. There is evidence suggesting that increases in regenerative cell proliferation play a key role in the mouse tumor findings; the significance of these effects at non-toxic exposure levels is therefore expected to be limited.

### **2.1.10 Conclusion**

- Ethylbenzene may be harmful following brief exposure by inhalation or ingestion.
- Prolonged inhalation of ethylbenzene might cause effects on the Central Nervous System.

The carcinogenic risk to humans is estimated to be low if the workplace exposure limit is not exceeded and personal protection equipment is applied properly (see chapter 2.4.0 Occupational Health Aspects).

## **2.2.0 Environmental Effects**

Ethylbenzene degrades rapidly in the environment and does not significantly bio-accumulate. It floats on water and rapidly evaporates. It is not expected to adsorb to sediment and suspended solids in water. For details on ethylbenzene depletion from water see Appendix 2.

### **2.2.1 Product Classification (Environmental Effects)**

According to the EU Dangerous Substances Directive ethylbenzene is currently not classified as hazardous for the environment.

### **2.2.2 Partitioning to the Air Compartment**

Ethylbenzene is a volatile substance with a vapour pressure of 950 Pa at 20 °C. The relatively high Henry's Law Constant (calculated 480 – 660 Pa.m<sup>3</sup>/mol at 20 °C) indicates that evaporation from hydrosphere to atmosphere is the most significant environmental transport mechanism for ethylbenzene.

### **2.2.3 Partitioning to the Water Compartment**

Ethylbenzene has a limited water solubility of 170 mg/l at 25 °C and will float on fresh and sea water surface in case of spills. The evaporation of the floating layer will be rapid. A small portion of ethylbenzene will dissolve and decrease rapidly as a consequence of dispersion, volatilization or transformation processes such as biodegradation. For details on ethylbenzene depletion from water see Appendix 2.

### **2.2.4 Partitioning to the Soil Compartment**

Based on its low water solubility and its Organic Carbon Partitioning Coefficient ( $\log K_{oc}$ ) of 2.64, ethylbenzene is moderately mobile in soil. Volatilization from soil surfaces and biodegradation in soil are expected to be the dominant processes.

### **2.2.5 Bioaccumulation**

The n-Octanol/Water Partitioning Coefficient for ethylbenzene ( $\log P_{ow}$  is 3.13) suggests a low potential for bioaccumulation. A bio-concentration factor of 91 can be calculated from the  $\log P_{ow}$ . Some studies on the water soluble fractions of crude oil indicate that the bioaccumulation potential of ethylbenzene might be lower than predicted from the  $\log P_{ow}$ .

As the primary removal mechanism from water is volatilization, the exposure of aquatic species will be limited.

### **2.2.6 Degradation and Persistence**

Ethylbenzene is readily biodegradable and is expected to undergo full mineralisation in the aquatic environment under aerobic conditions within days to a few weeks.

Direct hydrolysis or photolysis is not expected.

In the atmosphere ethylbenzene will be degraded by photo chemically produced hydroxyl radicals with a half-life of about 2 days.

### **2.2.7 Aquatic Toxicity**

Due to the volatility of ethylbenzene relevant ecotoxicity results can only be obtained from studies using flow-through or closed systems with measurement of ethylbenzene concentrations. Short-term toxicity for vertebrates ranges from 4-12 mg/l, for invertebrates from 0.5-15 mg/l, and for algae from 3-8 mg/l.

In conclusion, ethylbenzene is toxic to aquatic vertebrates and invertebrates ( $LC_{50}$  after 48 – 96 hours is in the range of 1-10 mg/l). However, the low potential to bioaccumulate (see chapter 2.2.5 Bioaccumulation) and the lack of persistence due to ready biodegradability (see chapter 2.2.6 Degradation and Persistence) mean that ethylbenzene will not cause long-term adverse effects in the aquatic environment. For details on ethylbenzene depletion from water see Appendix 2.

### **2.3.0 Flammability Control**

Ethylbenzene is characterized as a highly flammable liquid. Ethylbenzene vapours may form an explosive mixture with air. Safe handling practices must therefore focus on necessary precautions to avoid the ignition of ethylbenzene. It is strongly advised to keep away sources of ignition (no smoking, no open flames, sparking equipment, or welding operations). Ethylbenzene can accumulate static charges; hence special attention should be paid to take precautionary measures against static discharge (spark hazard).

Suitable extinguishing media are dry extinguishing media, foam, carbon dioxide and halons. Water is considered unsuitable for extinguishing purposes. Water spray however may be used to cool fire-exposed containers and the fire affected zone until the fire is out and danger of re-ignition has passed. Accumulation of water should be avoided, because ethylbenzene may be carried across water surfaces, spreading fire and increasing the chance to contact an ignition source. Personnel are advised to stay upwind and not enter low areas where vapours (fumes) can accumulate.

### **2.3.1 Flammability**

For a fire to set off a suitable combustible material along with oxygen at a certain ratio and a source of ignition with sufficient energy are required. To prevent the possibility of a fire or its continuation, only one item of the above so-called “fire triangle” (fuel – oxygen – source of ignition) needs to be eliminated. For handling and storing ethylbenzene the commonly applied precautions against fire and explosion for combustible and flammable liquids should be followed.

Ethylbenzene has a flash point of 19-23 °C (Abel), an auto-ignition temperature of 428-435 °C and is a volatile liquid with a flammable range in air of 1.2-8.0 % vol.; this has resulted in the product being classified as highly flammable (F; R11). In terms of transport classification, ethylbenzene is a Class 3 substance with Packing Group II. See Appendix 1 of this document for further details on typical physical properties.

It should be noted that a finely dispersed spray of ethylbenzene will ignite at a considerably lower temperature than would be expected based on its flash point. Similar effects are observed if ethylbenzene is spread over a large surface area, e.g. soil (in case of spills), or fibrous insulation material (in case of leakages).

### 2.3.2 Explosive Mixtures

Precautions to prevent the formation of explosive and flammable vapour-air mixtures have the highest priority in the handling, storage and transport of ethylbenzene. In order to eliminate or minimize this hazard, ethylbenzene containers or vessels are blanketed with an inert gas, such as nitrogen, or a reduced loading speed is applied to air filled containers.

The explosion limits in air (at atmospheric pressure, measured at 140 °C) are:

- Lower Explosion Limit (LEL): 1.2 %vol.
- Upper Explosion Limit (UEL): 8.0 %vol.

Explosive vapour-air mixtures in tanks will be prevented either by maintaining the temperature below the flash point in the liquid and vapour space (by application of a safety margin of a few °C) or by blanketing the vapour space with nitrogen or another inert gas. When working under inert gas conditions it must be ensured that the oxygen level remains below 8 % so that the vapour phase remains out of the explosive range.

When tanks are inerted, it is of utmost importance to consider that such an oxygen deficient atmosphere is life threatening, as it poses the additional hazard of asphyxiation. Tank entry without air supplied respirators and proper protocols in place should be forbidden. Even inspection of the tanks from the tank hatches is considered dangerous.

Ethylbenzene can form a combustible mixture with air at rather low temperatures, and therefore the necessary precautions must be taken, e.g. use appropriate design codes, and follow-up on the condition by inspection methods, repair leaks immediately, ensure that handling areas are well ventilated and install proper facilities to remove spills quickly.

It is recommended that vapours are not blown off directly to the atmosphere, but that these are routed back to the manufacturing process or routed to a vapour treatment unit. The vapour lines should be adequately protected against flame propagation.

Storage tanks and product containers that have been emptied must be flushed with water and/or steam, followed by nitrogen, and subsequently air to remove ethylbenzene vapour before they can be worked on with welding equipment or entered. Before entering a storage tank that has been flushed with nitrogen, an appropriate measurement device should be used to check for sufficient oxygen. To ensure proper measurements, any forced ventilation should be stopped. Always sample at the bottom side of the container as ethylbenzene vapours are heavier than air and will accumulate at the bottom.

### **2.3.3 Static Electricity**

The uncontrolled discharge of accumulated static electricity may generate sufficient energy to ignite ethylbenzene vapours in air.

Electrical charges can build up on poorly conductive surfaces of equipment until the dielectric strength is exceeded and a spark develops. Countermeasures to minimize this electrostatic hazard are to bond all metal objects preventing possible potential differences and to ground the entire system. Liquids in tanks with a non-conductive coating (e.g. epoxy coating) should be earthed.

When handling a static accumulator cargo, such as ethylbenzene, the product may pick up sufficient charge during transfer to constitute a hazard. The charge may arise from flowing through pipelines, and especially through filters (small mesh), and also from splashing. Submerged filling is recommended to avoid splashing. The inlet transfer line should end at or near the bottom of the tank to make electrical contact with the tank, hence to eliminate uncontrolled electrical discharge. The initial loading pipeline velocity should be kept below 1 m/sec. until the liquid level guarantees submerged filling.

In order to prevent charge accumulation, it is advised to include sufficient fluid residence time downstream of pumps and filters. The electrical resistance of the complete loading system between tank and loading arm should not exceed 10 ohms. For ships, electrically insulating flanges on the loading line as close as possible to the ship's manifold (liquid and vapour line), having a minimum resistance of 1000 ohms protect against stray currents. In the absence of in-line sampling, a waiting period of 30 minutes is sufficient between loading and sampling.

Operators wearing rubber-soled shoes, especially on floors made of insulating materials, can pick up considerable static electricity, and should exercise appropriate caution.

### **2.3.4 Ignition Sources**

There are a wide variety of sources of ignition that can be divided into two groups: electrical and non-electrical sources.

Examples of electrical sources are: electrical sparks, electrical arcs (welding), electrical discharges, stray currents and lightning. Non-electrical sources are for instance hot surfaces, flames, adiabatic compression, mechanical sparks (metal cutting or grinding) or glowing particles.

As some of these sources are difficult to avoid, consideration should be given to provide an inert atmosphere as the main measure to minimize the risk of fire or explosion of flammable vapours. It seems more prudent to control the atmosphere rather than the need for non sparking tools. The use of a metal measuring tape for tank gauging is an example of improper use of equipment.

Users of ethylbenzene should be aware that its vapours are heavier than air, i.e. they will sink to the ground accumulating in low-lying areas. These vapours may travel along on the ground to an ignition source and flash back. As a consequence, all ignition sources in the vicinity of storage or handling facilities of ethylbenzene should be eliminated.

### **2.3.5 Emergency Response Team**

Fire fighting crews must take note of ethylbenzene specific hazards. Vapours are heavier than air and therefore safe distances must be maintained. Smoke may contain ethylbenzene in addition to unidentified toxic and irritating compounds and therefore requires the use of a self contained breathing apparatus.

For a comprehensive set of product data/aspects and personal protection, please refer to the safety data sheet.

### **2.3.6.0 Fire Suppression**

Fires involving ethylbenzene can be safely extinguished with foam, dry powder, carbon dioxide or halons.

If electrical equipment such as motors, open hot plates, or open electrical switches are involved, foam should be used with caution.

### **2.3.6.1 Foam**

For extinguishing a fire and limiting evaporation, Aqueous Film Forming Foam (AFFF) or Alcohol Type Concentrate have been proven to be effective, i.e. the lower flammability limit is not attained above the layer. Because a foam layer can break down, this function must be watched and maintained. As a few centimeters of foam are sufficient to smother a fire inside a container, the contained amount of water is unlikely to trigger a so-called slop over; larger amounts may do so.

### **2.3.6.2 Water Spray**

Water spray has been proven to be the most effective way for product cooling, but its efficiency and effectiveness must be weighed against the risk of spreading ethylbenzene across the water surface, the chance of a slop over when water comes inside the tank, and the possibility to keep the product within a containment system. It is considered good practice to monitor the contained spray water; in case of contamination, send it to the waste water treatment plant. Because of its flammability and explosion hazard, ethylbenzene must be prevented from entering sewers. In case of such a release, Local Authorities must be informed immediately.

### **2.3.7 Containment**

To limit the flammability, exposure and environmental hazards, every effort must be made to contain spilled material. Therefore, in the engineering phase, a bund and optionally a remote emergency containment system should be provided for the storage tank and unloading station, to achieve a limited evaporation surface, better foam effectiveness and improved run-off control of contaminated fire and sprinkler water. Overflow of hydrocarbons such as ethylbenzene from bunds due to addition of fire water can be avoided by installing an underflow weir or siphon.

The local Water Authority should be advised if the spillage has entered a water course or external drainage system.

### **2.3.8 Community Awareness**

In the event of a fire, the emergency response plan should take into account not only the potential impact on the site operations but also the impact on the neighbouring community. The response plan should include notification to local authorities and communications to the public.

## 2.4.0 Occupational Health Aspects

The EC indicative limit values for occupational exposure of ethylbenzene are 100 ppm (442 mg/m<sup>3</sup>) as the eight hours time weight average concentration and the short-term/excursion limits (STEL) 200 ppm (884 mg/m<sup>3</sup>) (Directives 91/322/EEC and 2000/39/EC as amended). Skin designation applies. These values will be reviewed in the European risk assessment. In Germany, the "MAK Commission" (see chapter 2.1.5 Genotoxicity/Carcinogenicity) has concluded that the information is not sufficient to establish a MAK value (maximale Arbeitsplatz-Konzentration = maximum workplace concentration), but this has not passed the German regulatory bodies yet and is not legally binding at present. To limit occupational exposure the following principles should be considered in ascending order of priority: ventilation, isolation and substitution. Therefore the use of a less hazardous process will be investigated first, secondly the possibility of placing a barrier between hazard and worker (closed system; fume hood...) should be considered. Ventilation is the next option so that via engineering controls a safe workplace is maintained. Personal protective devices, such as chemical resistant clothes, goggles etc. are the types of control to be used where engineering controls cannot be made adequate.

### **2.4.1 User Label**

The user label required according to the European Dangerous Substances Directive (67/548/EEC) displays the main hazards of ethylbenzene:

- Highly Flammable (F; R11)
- Harmful by inhalation (Xn; R20)

Control and education of these hazards have the highest priority to protect the workforce against occupational hazards from chemicals. Refer to chapter 1.5 European Regulatory Environment for an update on current and future legislation.

### **2.4.2 Personal Hygiene**

Inhalation and skin contact of ethylbenzene should be avoided. Contaminated clothing should be immediately removed, and skin/eyes flushed with large amounts of water. Contaminated clothing should be laundered before re-use.

### 2.4.3 Protective Equipment

**Respiratory Protection:** In order to protect worker's health, adequate engineering controls need to be in place. For the specific conditions of use and for meeting relevant workplace-related legislation, suitable respirator protection should be selected. When used with an air filtering respirator an appropriate filter for protection against inhalation exposure to ethylbenzene is type A for organic gases and vapours with a boiling point > 65 °C and meeting standard EN 141 (to be superseded by prEN14387 in due course). If there is also the potential for a mist to be present, then a combined organic and particulate filter is appropriate. Particulate filters also come in varying levels of capacity: 1, 2 or 3 (3 being the greatest capacity). Particulate filters also come in varying efficiency classifications (P1 – low efficiency, P2 – medium efficiency, P3 – high efficiency). An example of such a combined filter is A2P3. The respiratory protection devices are compressed air line breathing apparatus for use with a full face mask, half mask or a mouthpiece assembly. The selection of an appropriate mask will be dependant on the use conditions and the likely airborne concentration.

**Hand Protection:** Where contact with ethylbenzene may occur, gloves classified under standard EN 374 should be used. Examples of preferred glove barrier material include: polyethylene, ethyl vinyl alcohol laminate (EVAL), polyvinyl alcohol (PVA), polyvinyl chloride (PVC or vinyl), styrene/butadiene rubber and Viton® (fluoroelastomers). Examples of acceptable glove barrier materials include: butyl rubber, chlorinated polyethylene, Neoprene, nitrile/butadiene rubber (nitrile or NBR). When prolonged or frequently repeated contact may occur, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN 374) is recommended. The selection of a specific glove for a particular application and duration in a workplace should also take into account all requisite workplace factors such as, but are not limited to: other chemicals which may be handled, physical requirements (cut/puncture protection and dexterity), as well as the instructions/specifications provided by the glove supplier. Contaminated gloves should be replaced.

**Eye Protection:** Chemical splash goggles are recommended.

**Protective Clothing:** Under usual working conditions chemical resistant gloves/gauntlets, boots and apron are recommended. If there is a risk of ethylbenzene splashing or in an ethylbenzene spillage, a chemical resistant one-piece overall with integral hood and chemical resistant gloves (see section Hand Protection) should be worn.

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#### **2.4.4 Exposure Monitoring**

The standard monitoring methods for ethylbenzene involve the use of charcoal tubes and sampling pumps followed by gas chromatography. Differences between the methods include the use of desorption media and variations in analytical tools and procedures. Personal monitors collecting air from the breathing zone should be used only where engineering controls cannot be made adequate, because they are lacking specificity and sensitivity.

Exposures to ethylbenzene can also be bio-monitored by measuring the concentration of metabolites or adducts in urine. A Biological Exposure Index (BEI) for ethylbenzene of 1.5 g/g creatinine measured as mandelic acid at the end of shift of a working week should not be exceeded.

## **2.5.0 Environmental Control**

### **2.5.1 Emergency Plan**

Facilities using and handling ethylbenzene should have developed and implemented a comprehensive spill prevention and emergency response plan.

This plan should address:

- spill detection methods,
- emergency notification procedures,
- community contacts for notification and advice on evacuation needs,
- fire prevention and protection,
- provisions for spill containment/clean-up,
- environmental protection,
- compliance with applicable local regulations or laws.

### **2.5.2 Spills & Leaks**

Because ethylbenzene is slightly soluble in water and extremely flammable at ambient temperatures, spills and leaks require prompt response to minimize the risk of fire and/or explosion, as well as to limit fugitive emissions. Ethylbenzene is considered toxic to aquatic organisms and therefore surface waters and sewage systems should be protected from spills.

### **2.5.3 Accidental Release**

In the event of a significant spill of ethylbenzene, all non essential personnel should be evacuated and all sources of ignition extinguished or removed immediately. After the appropriate personal protective equipment has been issued, the spill can be covered with fire-fighting foam to minimize emissions and the potential of fire hazards. Depending on the volume and location of the spill, it can be recovered by an inert padded vacuum truck or with solid absorbent and placed in appropriate containers for disposal. Ethylbenzene will float on water, so spills into surface water bodies may be collected using a skimmer or vacuum system. Spilled ethylbenzene can be removed safely by covering it with a suitable absorbing agent, such as sand. However, some absorbing agents, such as untreated clays and micas, may cause an exothermic reaction which could ignite ethylbenzene. Absorbing agents therefore should be tested for suitability before use on large spills. When spills occur within a bund confined area without an impervious base, water should be pumped into the area immediately. This will prevent the spilled ethylbenzene from soaking into the ground and will allow it to be pumped off the water layer for later recovery.

#### **2.5.4 Containment Aspects**

Storage and handling facilities for ethylbenzene should be designed to contain and control spills from process areas and loading/unloading operations. Soil, surface water, and ground water contamination from a spill of ethylbenzene can be minimized by the installation of curbs, sumps, and impervious containment areas. These areas should be constructed of materials such as concrete and synthetic liners. Under concrete slabs an impermeable liner is recommended and suitable sealants, e.g. epoxy, should be used on cracks and concrete joints.

### **2.5.5 Waste Classification**

Ethylbenzene containing wastes are considered hazardous if the flash point of the material is below 61 °C. Hazardous wastes may include, but are not limited to, process wastes containing ethylbenzene, ethylbenzene contaminated water, soil, debris, and empty unclean product containers.

Soil contaminated with ethylbenzene to the extent it has to be treated as hazardous waste should be excavated and transported to a secure hazardous waste treatment or disposal facility. Contaminations involving ethylbenzene may be ignitable and should be treated as hazardous until proven otherwise.

For contaminated product the preferred disposal options include sending it to a licensed incinerator or other thermal destruction device. As a service to its customers, the chemical industry can provide lists of companies which recycle or process ethylbenzene and which handle used drums.

Water contaminated with ethylbenzene may be cleaned by air stripping (to remove the bulk of the ethylbenzene), followed by biological treatment and, if required, treated with granular activated carbon. The ethylbenzene vapour should be captured by a collecting system, optionally provided with a condenser. Containers used to hold ethylbenzene must be drained and then thoroughly cleaned to be considered non-hazardous. Rinse liquid generated from washing should be collected and properly disposed of. Waste classification and compliance with laws, regional and/or local, are the responsibility of the waste generator.

## **3.0 Engineering and Operation**

### **3.1.0 General Tank Design Aspects**

In addition to the precautions for flammable liquids, the maintenance of a uniform temperature, preferably below 30 °C, is important. The use of inert gas implies that ethylbenzene vapours can be captured for treatment or recovery. Tanks should be designed and constructed in accordance with an appropriate and recognized standard of good engineering practice (e.g. British Standards (BS), German Industry Norms (DIN) and American Petroleum Institute (API) Standards) and take into account local climate conditions. Details on material compatibility with ethylbenzene are found in Appendix 3.

### **3.1.1 Construction Materials and Tank Internals**

The standard construction material is carbon steel. The insulation of storage tanks especially in hot climates is recommended. A white reflective exterior coating will increase the effectiveness of the insulation. Copper can react with organic acids and oxidation products present in ethylbenzene, eventually increasing the colour of the product. Therefore, copper and copper alloys should be avoided. Horizontal tanks can be drained more completely if they are sloped toward the drains. Floors of large vertical tanks may be tilted toward a small built-in sump with a bottom drain. Details on material compatibility with ethylbenzene are found in Appendix 3.

### **3.1.2 Pressure Rating**

The design pressure should be to API-620 or equivalent. This sets the specification for the relief system as well as minimizing breathing losses during ambient temperature changes and enabling vapour conservation measures during filling. Containment of breathing losses during a temperature rise of the contents of 20 °C should be considered. Preferably the vents should be connected to a vapour collection and recovery or treatment system and thus minimize hydrocarbon emission.

### **3.1.3 Fire Protection**

Considerations in site selection and tank spacing include proximity to other flammable material storage facilities, nearby sources of ignition, accessibility of fire fighting, and the impact of vapour cloud explosion on nearby areas. Fire monitors may be considered to provide cooling in the event of an external fire. Monitoring of oxygen levels within the head space inside the tank is one approach to ensure that oxygen levels remain below 8% at all times and thus an explosive atmosphere is avoided. A flame arrestor or pressure vacuum relief valve may be installed between the tank and any external opening if an explosive atmosphere within the vapour space is possible. All safety equipment should undergo regular maintenance and replacement to avoid fouling/plugging. The installation of a foam chamber or sub surface injection connection is also recommended for automatic fire fighting, particularly on larger tanks.

### **3.1.4 Uniform Temperature Control**

Efficient mixing is important to achieve a uniform temperature. Therefore, inlet, outlet and re-circulation connections are usually located near the bottom of the tank and can be reversed so that the product is pumped from the bottom and discharged through the swing pipe below the liquid surface. If desired, cooling the content from the bottom up can be achieved via the swing pipe, i.e. ethylbenzene can be withdrawn below the liquid surface and returned to the bottom. It is stressed that return of product to the tank should always be below the liquid level, to prevent static electric charge buildup (refer to chapter 2.3.3 Static Electricity for more details), and that a reliable siphon break should be provided in dip pipes. It goes without saying that in warm climates, a chiller will be a minimum requirement to maintain the desired storage condition.

### 3.1.5 Lines and Valves

The following are recommended engineering practices for ethylbenzene:

- lines smaller than 25 mm in diameter should not be used,
- a minimum of flanged connections is preferred because of leak potential,
- lines should not be buried because of the difficulty of checking for leakage,
- all lines should be sloped so they can be completely drained for maintenance,
- newly installed lines should be pressure tested by an approved method before insulation.

Thermal expansion in blocked ethylbenzene lines which are exposed to the sun without relief protection can cause high pressure, which can result in failure of gaskets, pump seals, and pump housings. If burial is preferred, the regulatory requirements to protect soil and ground water should be observed. A dip pipe should extend to the bottom of the tank and be provided with a pinch hole (siphon break). The electrical continuity across connections should be checked to ensure grounding. Lines constructed of carbon steel are acceptable, but copper, bronze, or plastic should not be used. Large lines are usually joined by welded flanges, while for smaller lines threaded joints are satisfactory. Ethylbenzene can dissolve pipe dope and thus cause product colouration and contamination. To avoid this, the pipe threads can be wrapped with PTFE [poly(per)tetrafluoroethylene] tape. As with all transport equipment, caution should be taken with the choice of valve. All valves should be protected against climatic extremes, shock and mechanical stress. A fusible airline or equally effective safety shutoff valve should be installed to close off lines in case of excessive external heat. Emergency block valves for isolation of equipment by remote activation may be considered on storage tanks, unloading stations and long pipelines holding large amounts of ethylbenzene. Plug cocks and ball valves, lined with fluoro-elastomer, give excellent service with stainless steel balls. Gate valves are less satisfactory, but usually cheaper, and may be used. Lubricated plug cocks and non-lubricated ball-type valves are satisfactory. The piping system should use either ball valves or plug valves. Gate valves may be considered for applications with infrequent use. The piping system should use plug valves rather than ball-valves for all manually and infrequently operated valves. To limit emissions from packed glands, bellow valves may be considered. Drain line valves should be provided with a cap or end-flange. Valves must be protected against freezing, heat shock, or mechanical stress.

Details on material compatibility with ethylbenzene are found in Appendix 3.

### **3.1.6 Pumps**

Most pumps are suitable for ethylbenzene, except those having copper, bronze, or plastic parts. (Details on material compatibility with ethylbenzene are found in Appendix 3). Centrifugal pumps with enclosed impellers and mechanical seals are the most widely used, but displacement pumps and rotary pumps are satisfactory. A canned or magnetically driven pump may be considered to comply with tight fugitive emission regulations. All metal should be properly grounded to avoid static accumulation. As deadheading will cause heat build up a minimum flow line should be installed. In addition to mechanical reliability aspects, environmental performance parameters should be considered in the selection process for seals. For mechanical seal components it is recommended to specify the stationary face (e.g. tungsten carbide) and rotating face (e.g. carbon). Tandem seals with barrier fluid are recommended.

### **3.1.7 Tank Pits**

A containment system is a basic requirement for ethylbenzene storage to:

- limit the spreading of a product spill and thus limit the flammability and environmental hazard,
- control run-off during fire fighting,
- provide a barrier against soil and groundwater contamination,
- allow spilled product to be effectively covered with foam.

An under storage leak detection system is recommended. For containment the storage size, configuration and hydraulic load due to sprinkler water and rainwater and whether foam will be the standard medium/practice for fire extinguishing should be considered. To contain the ethylbenzene in such a situation, a siphon or under-flow weir may be considered.

### **3.1.8 Loading and Unloading Facilities**

A remote impoundment for flammables could be considered.

### **3.1.9 Drainage**

Installation design should allow for recirculation and complete drainage, and subsequently flushing with inert gas.

### **3.1.10 Accessories**

#### **Gaskets and O-rings**

For flanged connections at ambient conditions it is recommended to use gaskets of PTFE [poly(per)tetrafluoroethylene] or graphite with a reinforced rim inside. O-rings in ethylbenzene service should be made from a co-polymer of fluorinated ethylene and fluorinated propylene. Rubber or other ethylbenzene soluble materials and PTFE encapsulated O-rings should be avoided. For gland sealing, graphite (optionally PTFE) is the material of choice.

#### **Filters**

Since small amounts of foreign matter may enter a storage tank from various sources, a filter in the transfer piping between tank and processing equipment is recommended. A replaceable cartridge or filter is recommended. Suitable materials are polyester and nylon. Especially for seal-less pumps, an inline basket strainer is recommended. The strainer will have adjacent isolation valves and connections for blowing it clear, for safe removal and cleaning.

#### **Flexible Transfer Hoses**

To avoid product contamination, the most important aspects for transfer facilities are easy cleaning and product compatibility. Therefore lightweight aluminum pipe and swing joints, with seals of fluoroelastomer are preferred. Composite hoses, which are static-conductive, and flexible metal hoses (woven metal type) are satisfactory, but they require more care and attention to keep them properly clean and to prevent damage or breakage during use. Hoses from fluoro-olefin elastomers give the best service and are the most widely used of the composite hoses. Neoprene elastomer synthetic hoses do not have sufficient resistance to aromatics and are therefore not recommended for ethylbenzene service. Multi-layered polypropylene and PTFE hoses are flexible and chemically resistant, and are therefore recommended materials. Because ethylbenzene can attack the interior of a hose, it should never be allowed to stand in any of the composite hoses. All residual ethylbenzene should be drained, and all intermittently used transfer lines should be thoroughly cleaned to prevent formation of undesirable reaction products. All transfer lines and hose connections should be properly grounded to prevent build up of static electricity. Regular preventive maintenance is recommended for flexible transfer lines.

Further details on material compatibility with ethylbenzene are found in Appendix 3.

## 4.0 Transport

For transport by road, rail, air, inland waterway and by sea packaged up to bulk container, ethylbenzene (UN 1175) is classified as a flammable liquid in class 3, Packing Group II.

Road transport of ethylbenzene is regulated in Europe by The European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) which can be consulted online at

<http://www.unece.org/trans/danger/publi/adr/adr2005/05ContentsE.html>

In Europe, rail transport is regulated by the "Réglement concernant le transport International ferroviaire des marchandises Dangereuses (RID)" and inland waterway transport by the "Accord Européen au transport international des marchandises Dangereuses par voie de Navigation du Rhin (ADNR)".

Air transport of ethylbenzene is regulated by the International Civil Aviation Organisation Technical Instructions (ICAO TI).

Marine transport of packaged ethylbenzene is regulated by the International Maritime Dangerous Goods Code (IMDG Code).

Bulk marine transport of ethylbenzene is regulated by the International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IBC Code).

## **4.1 Rail Transport**

For general information on the requirements for the design, construction and testing of standard rail tank cars for the carriage of liquid chemicals in bulk please visit [http://www.cefic.org/files/Publications/Rail\\_FINAL%204092003.pdf](http://www.cefic.org/files/Publications/Rail_FINAL%204092003.pdf)

## **4.2 Road Transport**

For guidelines on the standardization of equipment for road transport of chemicals please visit the following websites:

[http://www.cefic.org/files/Publications/Road\\_FINAL%2003092003part1.pdf](http://www.cefic.org/files/Publications/Road_FINAL%2003092003part1.pdf)

[http://www.cefic.org/files/Publications/Road\\_FINAL%2003092003part1.pdf](http://www.cefic.org/files/Publications/Road_FINAL%2003092003part1.pdf)

## 4.3 Emergency Response

### 4.3.1 Emergency Response Intervention Card – ERICard

The Emergency Response Intervention Cards (ERICards or ERIC's) provide guidance on initial actions for trained fire crews when they first arrive at the scene of a chemical transport accident without appropriate and reliable product-specific emergency information. ERICards are intended for land-transport accidents involving a substantial amount of product and therefore may not be appropriate for accidents in other situations.

ERICards apply to product groups, hence should not serve as substitutes for specific product information obtained from a reliable source (e.g. safety data sheet, reference databases or industry experts). For this reason, using ERICards requires sound judgement taking into account the particular circumstances of each accident.

#### ERICard relevant for ethylbenzene:

Substance:	ETHYLBENZENE
UN Number:	1175
HIN:	33
ADR Label:	3
ADR Class:	3
Classification Code:	F1
Packing Group:	II
ERIC:	3-11
Emergency Response Information:	HIGHLY FLAMMABLE LIQUID.

#### 1. Characteristics.

- Gives off dangerous fumes.
- Flash point below 23°C.
- Hazardous to eyes and air passages.
- Immiscible or partly miscible with water (less than 10%), lighter than water.

#### 2. Hazards.

- Heating of container(s) will cause pressure rise with risk of bursting and subsequent explosion (BLEVE).
- May form explosive mixture with air.
- Gives off toxic and irritant fumes when heated or burning.
- The vapour may be invisible and is heavier than air. It spreads along the ground and may enter sewers and basements.
- May be narcotic and cause unconsciousness.

#### 3. Personal Protection.

- Self contained breathing apparatus.
- Chemical protection suit if risk of personal contact.
- Consider wearing standard fire fighting clothing underneath the suit.

## 4. Intervention Actions.

### 4.1 General.

- Keep upwind.
- No smoking, eliminate ignition sources.
- PUBLIC SAFETY HAZARD - Warn people nearby to stay indoors with doors and windows closed. Stop any ventilation. Consider evacuation of people in immediate danger.
- Minimise number of personnel in risk area.

### 4.2 Spillage.

- Stop leaks if possible.
- Contain spillage by any means available.
- Check explosive limits.
- Use low sparking hand tools and intrinsically safe equipment.
- Absorb liquid in sand or earth or any other suitable material, or cover with foam.
- If substance has entered a water course or sewer, inform the responsible authority.
- Ventilate sewers and basements where there is no risk to personnel or public.

### 4.3 Fire (Involving the Substance).

- Keep container(s) cool with water.
- Extinguish with foam - dry powder, subsequently secure with foam blanket.
- Do not use water jet or fog (spray) to extinguish.
- Use water spray to knock down fire fumes if possible.
- Avoid unnecessary run-off of extinguishing media which may cause pollution.

## 5. First Aid.

- If substance has got into eyes, wash out with water for at least 15 minutes and seek immediate medical attention.
- Persons who have been in contact with the substance or have inhaled fumes should get immediate medical attention. Pass on all available product information.
- In case of burns, immediately cool affected skin for as long as possible with cold water. Do not remove clothing adhering to skin.
- Remove contaminated clothing immediately and wash affected skin with soap and plenty of water.

## 6. Essential Precautions for Product Recovery.

- Ensure proper earthing of pumping equipment.
- Use flame proof pump(s). If electrically driven, minimum class T3.
- Use mineral oil resistant equipment.
- Recover spilled product in vented container fitted with absorption filter.

## 7. Precautions after Intervention.

### 7.1 Undressing.

- Drench contaminated suit and breathing apparatus with water/detergent before removing facemask and suit.
- Use chemical protection suit and self contained breathing apparatus while undressing contaminated co-workers or handling contaminated equipment.
- Contain decontamination run off.

## 7.2 Equipment Clean Up.

- Drench with water/detergent before transporting from incident.

### **4.3.2 Transport Emergency Cards or Tremcards**

One of the specific requirements of ADR (see section 5.4.3) not applicable to other modes of transport for the consignor is to provide "instructions in writing" to truck drivers. These instructions, for which the format and required content have been established, should enable the truck driver to be aware of the dangers of the products transported and to take the necessary actions in case of an accident or emergency. They must be provided in a language that the driver is able to read and understand, as well as in the languages of all the countries of origin, transit and destination. The standard written instructions developed by Cefic are known as Transport Emergency Cards or Tremcards.

Instructions on how to obtain the ethylbenzene Tremcard in various languages are found on the Cefic website at:

<http://www.cefic.org/Templates/shwStory.asp?NID=27&HID=382&PHID=381>

A specimen of Cefic's Tremcard for ethylbenzene is provided below.

## **5 REACH and Styrene**

### **5.1 What is the purpose of this page?**

Under the REACH legislative system (**R**egistration, **E**valuation and **A**uthorisation of **C**hemicals) all companies working with chemical substances have specific obligations. This page is an initiative of the Styrene Producer Association (SPA) to assist the styrene industry, including downstream users with respect to the implementation and compliance with the REACH legislative framework. SPA is a sector group of Cefic, the Council of European Chemical Industry Federations.

## **5.2 How is the SPA organised for REACH?**

SPA set up a REACH Task Force to develop and implement a REACH compliance strategy. One of its responsibilities is to prepare the formation of a registration consortium of manufacturers, importers, data owners and downstream users of styrene and ethyl-benzene, open to non-SPA members that will help future registrants to meet their Substance Information Exchange Forum (SIEF) obligations and make joint submissions.

### **5.3 What are SIEFs and what is their role with consortia?**

A SIEF, or a **S**ubstance **I**nformation **E**xchange **F**orum, will be defined for each substance that is pre-registered between June 01<sup>st</sup> and December 01<sup>st</sup> 2008. The REACH legislation does not provide details on how SIEFs should operate. SPA identified a need to create consortia that will offer to coordinate the work done in the SIEFs for styrene and to some extent for ethyl-benzene. Participation of a SIEF member in a consortium is voluntary. Conditions for membership of a consortium will be fair and non-discriminatory.

#### **5.4 What does SPA recommend to EU Manufacturers, Importers (M/I) and Downstream Users (DU) of styrene and ethyl-benzene?**

SPA recommends that EU Manufacturers, Importers, or M/I, (represented by their "Only Representative"), Downstream Users (DU) of styrene and ethyl-benzene and Data Owners do the following:

- Understand the legislation and its guidance and determine if they need to register the production, importation or use of these two substances (and if applicable pre-register; the pre-registration period will begin on 1 June 2008 and will end on 1 December 2008);
- Determine from the information given on this page, if they are likely to belong to a SIEF together with SPA members;
- Decide whether they will wait for the publication by the European Chemical Agency (EChA) (list of SIEFs) or whether they prefer to contact SPA proactively to declare their interest in joining the styrene or ethyl-benzene REACH Registration Consortium.

Downstream Users are encouraged to contact their suppliers for any additional information.

Downstream Users should be aware that REACH created several obligations and rights with respect to the substances they use. One of these obligations is to provide substance use exposure information to be included in the registration dossier, if the use is also to be registered. Cefic recommends to the extent possible that the definition and standardization of exposure scenarios be coordinated by downstream users with their respective trade associations. Should these trade associations identify within their industry exposure scenarios linked to the use of styrene or ethyl-benzene, they should also contact SPA.

## **5.5 What are the benefits for M/I in informing SPA of their intent to pre-register styrene or ethyl-benzene or for DU in informing SPA of their uses?**

There are several important reasons to inform SPA of the intent to pre-register and subsequently, to possibly register styrene or ethyl-benzene, and/or to inform SPA of their uses, including:

- The time allocated by the REACH Regulation for the organisation of the consortia and its relationship with the respective SIEF is very short; by proactively notifying SPA of their interest, non-SPA member companies will benefit from better preparation;
- If M/I, DU or Data Owners have physico-chemical, toxicological or ecotoxicological data on styrene or ethyl-benzene, these data can be more readily incorporated into the existing database of studies lowering the overall cost by allowing an earlier decision not to undertake additional testing, thereby avoiding testing whenever possible and in accordance with guidelines;
- Begin work as soon as possible to establish "sameness" of the substances added to the SIEF (see RIP 3.10 for details).

## **5.6 What about Confidentiality?**

SPA staff is prepared to address questions concerning the confidentiality of information provided by any third party expressing an interest in joining a styrene or ethyl-benzene REACH registration consortium.

## **5.7 When will SPA set up a Consortium?**

It is expected that a consortium will be set up on 1 June 2008.

## 5.8 What SPA will not do

SPA will not provide "helpdesk" services to non-members to help them understand their obligations under the REACH Regulation. The role of SPA is strictly limited to facilitating the formation of a consortium of future SIEF members with an interest in styrene or ethyl-benzene. Cefic, national chemical industry trade federations, EChA and the national authorities have set up several websites and contacts to help parties concerned understand their respective obligations.

For more information on REACH, visit the following websites:

[Cefic REACH information page](#)

[European Commission information page](#)

[European Chemical Agency](#)

For more information on the formation of styrene or ethyl-benzene consortia contact:

Dr. Paul-Michael Bever

Cefic

Phone: +32 (2) 676 7227

e-mail: [pmb@cefic.be](mailto:pmb@cefic.be)

or

Celine Oostens

Phone: +32 (2) 676 7262

## Cefic Tremcard - Instructions in Writing

Class - 3

LOAD

Ethylbenzene

PG - II  
HI No - 33  
UN - 1175

### Name of substance(s):

- Colourless liquid or paste - Usually with perceptible odour.
- Immiscible with water.
- Lighter than water.

### NATURE OF DANGER

- Highly flammable.
- May form explosive mixture with air, particularly in empty uncleaned receptacles.
- The vapour may have narcotic effect.
- May evaporate quickly.
- The vapour may be invisible. The vapour is heavier than air and spreads along ground.
- Heating will cause pressure rise with risk of bursting and subsequent explosion.

### PERSONAL PROTECTION

- Protective gloves.
- Protective footwear.
- Eyewash bottle with clean water.

### INTERVENTION EQUIPMENT

- Shovel.
- Broom.
- Sand or other absorbent.

### GENERAL ACTIONS BY THE DRIVER

- Stop the engine.
- No naked lights. No smoking.
- Mark roads with self-standing warning signs and warn other road users or passers-by.
- Keep public away from danger area. Keep upwind.
- Notify police and fire brigade as soon as possible.

### ADDITIONAL AND/OR SPECIAL ACTIONS BY THE DRIVER

- Any action only if without personal risk.
- Stop leaks if without risk.
- Contain or absorb leaking liquid with sand or earth or other suitable material.
- Avoid direct contact with substance.
- Vapour may create explosive atmosphere.
- Avoid making sparks.
- Prevent liquids entering water courses, sewers, basements and workpits.
- If substance has entered a water course or sewer or been spilt on soil or vegetation, inform police.
- Warn everybody: Explosion hazard.

**FIRE (information for the driver in case of fire)**

- Do not attempt to deal with any fire involving the load.

**FIRST AID**

- If substance has got into the eyes, immediately wash out with plenty of water. Continue treatment until medical assistance is provided.
- Remove contaminated clothing immediately and wash affected skin with soap and water.
- Seek medical treatment when anyone has symptoms apparently due to inhalation, swallowing or contact with skin or eyes.
- In case of burns immediately cool affected skin as long as possible with cold water.

**SUPPLEMENTARY INFORMATION FOR EMERGENCY SERVICES**

- Keep container(s) cool by spraying with water if exposed to fire.
- Extinguish with waterspray or preferably with foam or dry chemical.
- Do not use water jet.
- Sewers must be covered and basements and workpits evacuated.
- Use low-sparking handtools and explosion-proof electrical equipment.

**Additional Information**

EMERGENCY TELEPHONE:

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### **Reference 1.**

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### **Reference 2.**

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### **Reference 3.**

European Union Environmental Risk Assessment Ethylbenzene Report Draft dated 4th September 2004. Bundesanstalt für Arbeitsschutz und Arbeitsmedizin.

## Appendices

### Appendix 1: Typical Physical Properties of Ethylbenzene

Property (condition, method)	
Appearance / Physical Form	Liquid
Colour	Transparent colourless
Odour	Sweet, aromatic
Odour Threshold	1-2.3 ppm
Molecular Weight	106.17
Density (20 °C)	868 kg/m <sup>3</sup>
Boiling point (1013 hPa)	136.2 °C
Freezing point	-95 °C
Kinematic viscosity (10 °C)	0.9 mm <sup>2</sup> /s (cSt)
Kinematic viscosity (60 °C)	0.5 mm <sup>2</sup> /s (cSt)
Dynamic viscosity (10 °C)	0.78 m•Pas (cP)
Dynamic viscosity (20 °C)	0.68 m•Pas (cP)
Dynamic viscosity (60 °C)	0.43 m•Pas (cP)
Thermal conductivity (10 °C)	0.137 W/m °C (1.37x10 <sup>-3</sup> J//s•cm•K)
Thermal conductivity (60 °C)	0.101 W/m °C (1.01x10 <sup>-3</sup> J//s•cm•K)
Relative vapour density (air = 1)	3.7
Vapour pressure (10 °C)	500 Pa
Vapour pressure (20 °C)	950 Pa
Vapour pressure (60 °C)	7400 Pa
Electrical conductivity	123 pS/m
Flash point (Abel CC)	19-23 °C
Auto ignition temperature	428 – 435 °C
Explosion / Flammability limits in air: lower at 140 °C	1.2 % vol/vol
Explosion / Flammability limits in air: upper at 140 °C	8 % vol/vol
Solubility in water (25 °C)	0.17 kg/m <sup>3</sup>
Surface tension (25 °C)	29-30 mN/m
n-octanol/water partition coefficient (log Pow)	3.15
Refractive index (n <sub>D</sub> , 25 °C)	1.4959
Relative evaporation rate (butyl acetate = 1 min.)	0.84
Dielectric constant (25 °C)	2.4
Critical density	2.67 mmol/cm <sup>3</sup>
Critical volume	374 cm <sup>3</sup> /mol
Critical pressure	3.701 MPa
Critical temperature	343.05 °C

## Appendix 2: Ethylbenzene Depletion from Water

Ethylbenzene has been classified as readily biodegradable in surface water and waste water treatment plants (WWTP). The following table shows the derived rate constants and half lives in different compartments (Reference 3).

Rate constants and half lives due to biodegradation of ethylbenzene

	Rate constant	Half life
Surface water	$4.7 \times 10^{-2} \text{ d}^{-1}$	15 d
WWTP	$1 \text{ h}^{-1}$	-
Soil	$2.31 \times 10^{-2} \text{ d}^{-1}$	30 d
Sediment	$2.31 \times 10^{-3} \text{ d}^{-1}$	300 d

Using a Koc of 432, a Henry constant of  $617 \text{ Pa}\cdot\text{m}^3 \text{ mol}^{-1}$  and a rate constant of  $1 \text{ h}^{-1}$ , the following distribution of ethylbenzene in WWTP was calculated with Simple Treat 3.0.

Summary of distribution in sewage treatment plant.

	% of total
air	46.7
water	5.4
sludge	3.7
degraded	44.2
total removal	94.6

## **Appendix 3: Material Compatibility**

### **Recommended Materials:**

For containers or container linings: mild steel, stainless steel

For container paints: epoxy paint, zinc silicate paint

**Non-metallic materials** such as thermosets, thermoplastics and elastomers may be suitable for use as lining, gasket or seal depending on the material specification and intended use (fluid/service temperature). The material must be impermeable and must not be weakened or otherwise affected by the fluid.

### **Non-metallic materials resistant to ethylbenzene:**

Thermosets: Epoxy, Epoxy-Novolac

Thermoplastics: PVDF, PTFE, PFA, ETFE (Tefzel®), ECTFE (Halar®)

Elastomers: FKM (Viton), FFKM (Kalrez®), FMVQ (Fluorosilicone)

### **Materials to Avoid:**

Copper and copper alloys

Strong oxidizing agents

### **Non-metallic materials not resistant to ethylbenzene (not suitable for the storage / long term contact)**

Thermosets: Vinyl Ester, Polyester

Thermoplastics: PVC, CPVC, PP, PE

Elastomers: Nitrile/Buna\_N (NBR), Butyl (IIR), EPDM, Neoprene (CR)

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