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Environmental Protection Agency

# Survey of styrene

Part of the LOUS review

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Survey of styrene

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# Preface

## Background and objectives

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2011) includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic based on quantitative structure analogy relationship evaluation using computer models. For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, and information regarding ongoing activities under REACH, among others.

On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns the aromatic organic substances styrene. Styrene (CAS No. 100-42-5) was included in the list for the first time in 2004.

The main entry in LOUS for the substance is in the group "organic solvents", which presently only comprises styrene and toluene. The principal reason for the inclusion of styrene in LOUS is that the substance is on EU's priority list of substances that must be evaluated with regard to their endocrine disrupting effects.

The main objective of this study is, as mentioned, to provide background for the Danish EPA's consideration regarding the need for further risk management measures.

## The process

The survey has been undertaken by COWI A/S, the Danish Technological Institute (TI) and the National Food Institute at the Technical University of Denmark (DTU Food) from September 2013 to June 2014. The work has been followed by an advisory group consisting of:

- Lea Stine Tobiassen, Danish Environmental Protection Agency (Chairman)
- Nikolai Stubkjær Nilsen, Confederation of Danish Industry
- Helle Fabiansen, Danish Plastics Federation
- Mette Holm, Danish Veterinary and Food Administration
- Pia Vestergaard Lauridsen, Danish Working Environment Authority
- Jesper Kjølholt, COWI A/S (Project Manager)

## Data collection

The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHA's website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower) and the German Angel.
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Data on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet)
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA) and the INIRIS database.
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
  - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VRM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature.
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
- PubMed and Toxnet databases for identification of relevant scientific literature.

Besides, direct enquiries were made to Danish and European trade organisations and a few key market actors in Denmark.

# Summary and conclusions

This review report concerns the substance styrene, which is one of 40 chemical substances on the Danish Environmental Protection Agency's (DEPA) "List of Undesirable Substances" (LOUS). Styrene is listed in the group "organic solvents". All the LOUS-substances are undergoing similar reviews over the period 2012-2015.

Styrene is a liquid at ambient temperature and has a boiling point of 145 degrees Celsius. It has a characteristic pungent odour recognizable at low concentrations. The water solubility is relatively low: 320 mg/L. It is a highly reactive substance, primarily in use as a raw material for production of polymers, elastomers, and insulation materials, e.g. polystyrene and acrylonitrile-butadiene-styrene copolymers. It is also used as a component in unsaturated polyester (UP) for e.g. glass fibre-reinforced products such as boats and windmill turbines.

## Regulatory aspects

Styrene is not addressed specifically in any EU legislation concerning products, waste, environmental emissions, or occupational exposure. However, general EU legislation in the field of occupational environment also applies to styrene. A limit of 60 mg/kg has been established at EU level for migration from materials in contact with food.

The Danish legislation addressing occupational handling of styrene includes requirements for labelling of materials and working areas, training, handling and safety measures, and a National Danish occupational exposure limits (25 ppm) has been set. Also, a quality criteria for drinking water (1 µg/l at consumer's tap) has been established for styrene.

Styrene is not addressed specifically in international agreements on chemicals in the environment. Styrene is specifically mentioned in only a few eco-labelling criteria, defining requirements for imaging equipment, remanufactured toner cartridges, and hard coverings.

## Manufacture and uses

According to its REACH registration, styrene is produced in the 1,000,000 - 10,000,000 tons/year band in the EU. In 1993, European styrene production was estimated to be between 2-5 million tons but no up-to-date data on European production volume have been possible to obtain. Recent trade figures show that the European import of styrene exceeds export, resulting in a current net import of about 290,000 tons. EU consumption of styrene was about 3,808,000 tons in 1998.

Styrene is not produced in Denmark. Danish consumption ranged between 1550 – 4370 tons in 2012 according to the Product Register, while the total consumption in 2011 was about 6,500 tons, indicating a small, recent decrease in the use of styrene.

Styrene is used as a monomer for production of the following plastic materials:

- polystyrene (general purpose, GP-PS; high impact, HI-PS; and expanded EPS);
- copolymer systems (acrylonitrile-butadiene-styrene, ABS; styrene-acrylonitrile, SAN; methyl methacrylate-butadiene-styrene, MBS; and others) ;
- styrene-butadiene rubber (SBR);
- related lattices (SB Latex, for example), and
- as a component of unsaturated polyester resins (UP).

The production of polystyrene for packaging (EPS) is the largest application area of styrene in Europe, while in Denmark, unsaturated polyester resin (UP) in windmill and boat production accounts for the largest application. Since styrene is a component of many binders, it may be present in certain construction materials, fillers, paints, varnishes and adhesives.

### **Waste management**

The levels of free styrene in styrene-based polymer products are so low that the health and environmental impact from free monomeric styrene in the waste can be disregarded.

Handling of styrene-based products at the end of their useful life will differ depending on the type of product, and the chemistry and processes involved in their manufacture.

Thermoset-based products (SBR rubber and UP based) often are temporarily placed in landfills. For recycling they are later shredded in a process of one or more steps.

Thermoplastic styrene-based products can be recycled by re-melting to form new products after cleaning. However, it is assessed that, at present, thermoplastics are most often incinerated for energy recovery after use (post-consumer waste) and only internal production waste is recycled.

Styrene as waste has to be disposed of as hazardous waste and must be collected and treated by approved operators. The same is the case for products containing 20% w/w styrene or more.

Presently, there is no indication that styrene in waste should constitute a health or environmental problem, however there is a data gap regarding the amounts of styrene ending up in the waste stream.

### **Environmental effects and exposure**

Styrene is a volatile substance evaporating easily from water and soil surfaces and degrading quite rapidly in the air compartment by photooxidation, resulting in various VOC degradation products and thereby contributing to tropospheric ozone formation.

Styrene is considered easily biodegradable in water while abiotic degradation is insignificant. From the sorption characteristics, styrene is considered mobile in soil, while the bioaccumulation potential is rather low.

The toxicity of styrene to aquatic organisms such as fish and crustaceans is moderate, with short term LC/EC<sub>50</sub> values of approximately 4-10 milligrams per litre. In the terrestrial environment, the toxicity also appears to be moderate-low.

Based on the fate and effects data it can be concluded that styrene is neither PBT nor vPvB.

Styrene is assessed to be released primarily to the air compartment, partly from the many different types of productions where they are used and partly from evaporation during use of the products. Monitoring data show low levels of styrene in the environment with surface water concentrations in the sub- µg/l range. For the air compartment, Dutch monitoring data showed mean concentrations of 0.09 to 1.5 µg/m<sup>3</sup> (rural and source dominated locations, respectively).

Overall, current data do not indicate that styrene should be considered a substance of significant environmental concern.

## Human health effects and exposure

**Hazards:** Styrene is classified as an acute toxicant (class 4), a skin irritant (cat. 2), and an eye irritant (cat. 2). Furthermore, the classification has been updated based on a Danish proposal to include Specific target organ toxicity – repeated exposure, Category 1 (STOT RE 1 ;H372; Causes damage to the hearing organs through prolonged or repeated exposure) and Reproductive toxicity, Category 2 (Repr 2; H361d; suspected of damaging fertility or the unborn child).

In humans, styrene vapour is well absorbed via inhalation while uptake after dermal contact with styrene vapour is not significant. Ingested styrene is absorbed completely and the substance and/or its metabolites are widely distributed throughout the body with the highest concentrations found in fat. Styrene is metabolised extensively in humans and experimental animals; styrene and its metabolites are rapidly eliminated from the body, primarily in the urine.

Styrene is of moderate acute toxicity following inhalation, and of low acute toxicity following oral intake and dermal exposure. Following inhalation, the acute effects observed include marked signs of irritation of the eyes and nasal mucosa, general signs of central nervous system depression, and changes in the lungs.

The neurotoxicity of styrene is well-documented. As well as effects on hearing organs and colour discrimination, effects on the nervous system have also been reported.

Ototoxicity (toxicity to the hearing organs) is the most sensitive and relevant effect of styrene repeated inhalation exposure in animals. Studies on humans indicate that the sensitivity for developing hearing loss might be greater in humans than in rats. From the studies in rats, a NOAEC between 1300-2600 mg/m<sup>3</sup> for hearing loss could be ascertained. There is also epidemiological evidence that styrene causes changes in colour discrimination.

In the EU risk assessment report (RAR) for styrene, it was concluded that there is no convincing evidence of mutagenic activity or carcinogenicity of styrene with relevance for humans. IARC has concluded that styrene is possibly carcinogenic to humans (Group 2B).

For potential developmental effects, a NOAEC of 650 mg/m<sup>3</sup> was suggested in the RAR and eventually styrene was given a classification for developmental toxicity in category 2 ( Repr 2, H361d).

The RAR concluded that there is no evidence that styrene possesses significant endocrine disrupting activity on the reproductive system. However, in the EU, styrene has been placed in category 1 on the EU priority list for endocrine disruptors. EU criteria for endocrine disruption are still under development, meaning that the evaluation may need to be revisited when the criteria for endocrine disruption become available.

European occupational exposure limit values for styrene have not yet been defined. The Danish limit value for occupational exposure is 25 ppm (105 mg/m<sup>3</sup>).

WHO has established a tolerable daily intake (TDI) of 7.7 µg/kg of body weight per day (in relation to the establishment of a drinking water guideline) derived from a NOAEL of 7.7 mg/kg bw/d for reduced body weight in a 2-year drinking water study and application of an uncertainty factor of 1000. For comparison the RAR uses a NOAEL of 150 mg/kg bw/d based on hepatic necrosis observed in a 2 year cancer bioassay with mice for risk assessment using a "margin of safety" (MoS) approach.

**Exposure:** Consumers may be exposed to long-term sources of styrene, such as emissions from polymeric building materials, e.g. carpets, food, chewing gum, and (passive or active) tobacco smoking. Apart from heavy smoking, the largest exposure is stated to be emission of styrene monomers from building materials.

Consumers may also be exposed as a result of the use of styrene-containing resins or adhesives. Even though these exposures may be infrequent, they are potentially high, in particular for liquid products due their high volatility.

Occupational exposure levels have been estimated for five professional application areas of styrene: Manufacture of monomer, production of polystyrene, production of unsaturated polyester (UP)-styrene resin, production of styrene-butadiene rubber (SBR) and styrene-butadiene (SB) latex and glass-reinforced plastic (GRP) manufacture.

The highest exposure levels are found in the GRP industry, caused by the processing of the UP styrene-containing resins which involves a high degree of manual handling in either open or semi-closed moulding processes. Typical exposures (8 hour average) were estimated in the range of 1 – 60 ppm, whereas realistic worst case exposures were estimated at 1 - 100 ppm with short term exposures (15 min) reaching 180 ppm in the realistic worst case scenario. The Danish exposure limit value is 25 ppm (ceiling value).

With respect to indirect exposure via food, air and water, a daily intake of 0.058 mg/kg bw/day is estimated in the RAR. The contribution from air to this intake estimate is very high. Migration of styrene from polystyrene packaging has been documented; several studies demonstrated styrene in food items. However, food stuff concentrations are generally below 10 µg/kg and thus do not represent a major exposure pathway of human exposure.

**Risk to humans:** Short-term exposures from sporadic events such as repair work using styrene-containing resins have been assessed in the RAR as posing a risk to consumers. Long-term exposures arising as a result of emissions from polymeric building materials, including carpets, from food sources (mainly as a consequence of food packaging) and from chewing gum were reported not to cause unacceptable health risks to consumers.

According to the RAR, the production of UP-resins, GRP manufacture, and production of SBR and SB latex may cause occupational exposures to styrene monomer released from the polymeric materials that pose a health risk to workers. The risks for health effects are most pronounced in GRP manufacturing. For the remaining scenarios, the safety margins were assessed as sufficient. However, industry information suggests that exposure concentrations to styrene in the GRP industry, such as the wind power industry, have been considerably reduced during the recent years, possibly rendering the current risks to workers smaller than presented in the RAR.

No unacceptable health risks to the general population were identified in the RAR from indirect combined exposure to styrene through food, air and drinking water. However, comparing exposure estimates with the TDI established by WHO (7.7 µg/kg bw/d), a health risk through environmental exposure cannot be excluded.

### **Alternatives to styrene**

At present there are no indications that styrene will be replaced by alternative substances in the many different applications it is used for, especially the production of different types of plastics or rubber where it is used as a reactive monomer or reactive solvent.

For thermosetting plastic materials, possible alternatives to UP are either epoxies or phenol formaldehyde resins. However, such thermosetting materials are based on other hazardous

monomers because a high reactivity is required to ensure that the plastic products are fully cured and have the necessary mechanical and physical properties to be secure during use.

In most cases, in examining alternatives to UP, other thermosetting polymers that can fulfill the required technical demands simply use other monomers on the LOUS list, e.g. certain isocyanates (MDI/TDI) for thermosetting PUR, or bisphenol A for epoxies or formaldehyde, and phenol for phenol formaldehyde resins. It is assessed that in most cases it would be more expensive to change the plastic for another type, perhaps with the exception of food packaging, where there is a trend toward the use of PET instead of PS.

### **Conclusions**

The principal reason for including styrene in LOUS is that the substance is on EU's priority list of substances that must be evaluated with regard to their endocrine disrupting effects. The EU risk assessment concluded that there was no evidence of significant endocrine disrupting activity of styrene. However, EU criteria for endocrine disruption are still under development, and the evaluation may need to be revisited when the criteria for endocrine disruption become available.

Consumer exposure to styrene may be a concern in relation to both short-term exposures from repair work and long-term exposure to styrene released from polymeric building materials, including carpets, from food sources (mainly as a consequence of food packaging) and from chewing gum. Active and passive smokers are also exposed via tobacco smoke and the daily intake from intensive smoking may in some cases exceed the intake from food sources.

Certain occupational exposures also gave rise to concern in the EU risk assessment, in particular the production of UP-resins, GRP manufacture, and production of SBR and SB latex. However, industry information suggests that exposure concentrations have been considerably reduced in recent years.

No unacceptable human health risks were identified in the EU risk assessment from exposure via the environment, nor for combined exposure in the RAR. However, risk from indirect exposure cannot be excluded when comparing with the TDI from WHO.

With regard to the environment current data do not indicate that styrene should be considered a substance of significant environmental concern, although it as a VOC contributes to tropospheric ozone formation. Its environmental toxicity is moderate-low, it is readily biodegradable and it does not bioaccumulate.

At present there are no indications that styrene will be replaced by alternative substances in the many applications it is used for. Some technical alternatives do exist but they are most often based on other monomers that are also listed as undesirable and are therefore not necessarily beneficial from a human health or environmental point of view.

### **Data gaps**

A data gap is identified regarding the uses of styrene in Denmark, which due to confidentiality restrictions have not been possible to fully evaluate quantitatively. Neither has quantitative data on occurrence in waste or releases to the environment with sewage and sewage sludge been identified.

More information on the exposures related to release of styrene monomer from production and use of polymeric styrene products would be useful in order to qualify the exposure estimates for both consumer scenarios and work-related scenarios.



# Sammenfatning og konklusion

Denne rapport omhandler stoffet styren, der er et af de i alt 40 stoffer på Miljøstyrelsens Liste over uønskede stoffer (LOUS). Styren indgår (sammen med toluen) på listen i gruppen "organiske opløsningsmidler. For alle LOUS-stofferne udarbejdes tilsvarende rapporter i perioden 2012-2015.

Styren er en væske ved stuetemperatur og koger ved 145 grader Celsius. Det har en karakteristisk, skarp lugt, der er genkendelig selv ved lave koncentrationer. Vandopløseligheden af stoffet er ret lav; 320 mg/l. Styren er et meget reaktivt stof, der især anvendes som udgangsmateriale i produktion af polymerer, elastomerer og isoleringsmaterialer så som polystyren og acrylonitril-butadien-styren copolymerer. Det indgår også som komponent i umættet polyester (UP), f.eks. til glasfiberforstærkede produkter så som lystbåde og vindmøllevinger.

## Lovgivning og anden regulering

Styren nævnes ikke specifikt som kemisk stof i nogen EU-lovgivning vedrørende produkter, affald, emissioner til miljøet eller i arbejdsmiljøet. Dog er styren også omfattet af EU's generelle arbejdsmiljøregler ligesom der er fastsat en grænse på 60 mg/kg for migration af stoffet fra emballager til fødevarer. I Danmark omfatter den nationale lovgivning vedr. arbejdsmiljøet regler for mærkning af materialer og arbejdsområder, uddannelse, håndtering og sikkerhedsforanstaltninger og der er også fastsat en national dansk grænseværdi for styren i arbejdsmiljøet (25 ppm). Yderligere er der fastsat et dansk drikkevandskvalitetskrav på 1 µg/l (ved forbrugers vandhane).

Der findes heller ingen internationale konventioner eller lignende aftaler på miljøområdet, der specifik medtager styren. Stoffet nævnes i nogle få økomærkekriterier: Billedreproduktionsudstyr o.lign., tonerkassetter lavet af genbrugsmaterialer og andre inddækninger i hård plastik.

## Fremstilling og anvendelser

I følge registreringen af styren hos ECHA under REACH produceres styren i mængder mellem 1 og 10 millioner tons om året i EU. Produktionen af styren i EU var i 1993 mellem 2 og 5 millioner tons, men det har ikke været muligt at finde nye, præcise tal for produktionens omfang. Nyere handelsstatistiske data viser, at der for øjeblikket er en nettoimport af styren til EU på omkring 290.000 tons. Forbruget af styren i EU var 3.808.000 tons i 1998.

Der findes ingen produktion af styren sted i Danmark. Størrelsen af styrenforbruget i Danmark var i følge Produktregistret mellem 1550 og 4370 tons i 2012, mens det i 2011 og årene før var omkring 6.500 tons. Dette indikerer et nyligt, mindre fald i forbruget i Danmark.

Styren anvendes som monomer i produktionen af følgende polymerer:

- polystyren (general purpose, GP-PS; high impact, HI-PS; og expanded, EPS),
- copolymer systemer (acrylonitril-butadien-styren, ABS; styren-acrylonitril, SAN; methyl methacrylat-butadien-styren, MBS; m.fl.),
- styren-butadien gummi (SBR) og lignende matricer (f.eks. SB latex)
- som komponent i umættede polyester resiner (UP).

Produktionen af polystyren til fremstilling af plastemballager er det største anvendelsesområde for styren i Europa, mens umættet polyester resin er det største anvendelsesområde i Danmark, hvor det især bruges til fremstilling af vindmøllevinger og lystbåde. Da styren indgår i mange bindemidler kan det forekomme i visse byggematerialer samt i fugemasse, maling, fernis og lim.

### **Affald**

Niveauet af fri styren (monomer) i styrenbaserede polymerprodukter er så lavt, at der kan ses bort fra indvirkninger på menneskers sundhed eller på miljøet som følge af forekomsten i affald.

Håndteringen af styrenbaserede produkter i affaldsfasen vil afhænge af typen af produkt og kemien og processerne anvendt ved fremstillingen af produkterne. Varmehærdende produkttyper så som SBR-gummi og UP-baserede produkter placeres således ofte midlertidigt i affaldsdeponier, gerne med henblik på senere genanvendelse efter neddeling og fraktionering i et eller flere trin.

Termoplastisk styren kan på den anden side genindvindes ved smeltning (efter rengøring) og formning til nye produkter. Dog vurderes det, at det for øjeblikket er mest almindeligt at forbrænde termoplastiske styrenprodukter efter brug, mens kun internt produktionsaffald recirkuleres.

Styren som stof skal bortskaffes som farligt affald af godkendte operatører og det samme gælder for produkter med et indhold af styren på 20% (v/v) eller mere.

Der er for øjeblikket ikke nogen indikation af, at styrenholdigt affald skulle udgøre en fare for menneskers sundhed eller for miljøet. Der er dog mangel på kvantitativ viden om mængden af styren, der ender i affaldsstrømmene.

### **Miljømæssige effekter og opførsel samt eksponering**

Styren har et højt damptryk og fordamper let fra vand- og jordoverflader. Det nedbrydes ret hurtigt i atmosfæren ved fotooxidation til forskellige VOC'er hvorved stoffet bidrager til ozondannelse i den nederste del af atmosfæren. Styren betragtes som let bionedbrydeligt i vand, mens abiotisk nedbrydning er uden praktisk betydning. Ud fra det bindingssegenskaber må styren anses for mobilt i jord, mens dets potentiale for bioakkumulering er lavt.

Giftigheden af styren over for vandlevende organismer så som fisk og krebsdyr er moderat med typiske akutte LC<sub>50</sub>/EC<sub>50</sub> -værdier i området 4-10 mg/l. I det terrestriske miljø vurderes giftigheden også at være moderat-lavt.

Det kan ud fra de indhentede data om styrens opførsel og giftighed i miljøet konkluderes, at stoffet hverken skal klassificeres som PBT eller vPvB.

Styren frigives i hovedsagen til atmosfæren, dels fra de mange typer af produktioner hvori stoffet indgår og dels som følge af afdampning fra brugen af produkterne. Overvågningsdata viser, at niveauerne af styren i miljøet er lave med koncentrationer i overfladevand i sub- $\mu\text{g/l}$  området. I luft er der i hollandske undersøgelser fundet gennemsnitskoncentrationer på 0.09 til 1.5  $\mu\text{g/m}^3$  i hhv. landlige og punktkildedominerede områder.

Sammenfattende vurderes styren ikke at give anledning til nogen væsentlig miljømæssig bekymring.

### **Sundhedseffekter og eksponering af mennesker**

**Effekter:** Styren er klassificeret som akut giftigt (klasse 4), hudirriterende (kat. 2) og øjenirriterende (kat. 2). Endvidere er klassifikationen blevet opdateret baseret på et dansk forslag om at inddrage specifik målorgantoksicitet ved gentagen eksponering, kategori 1 (STOT RE 1, H372: Forårsager høreskader ved længerevarende eller gentagen eksponering) samt reproduktionstoksicitet, kategori 2 (Repr 2, H361d: Mistænkt for at skade forplantningsevnen eller

det ufødte barn).

Hos mennesker absorberes styrendampe i betydelig grad ved inhalation, mens optagelse efter dermal kontakt med styrendampe ikke er signifikant. Efter indtagelse absorberes styren fuldstændigt og stoffet og/eller dets metabolitter fordeles i hele kroppen med de højeste koncentrationer i fedtvæv. Styren metaboliseres i udstrakt grad i mennesker og i forsøgsdyr og stoffet og dets metabolitter udskilles hurtigt fra kroppen, primært med urinen.

Styren er moderat akut toksisk ved inhalation og har lav akut toksicitet ved oral indtagelse og dermal eksponering. Ved inhalation omfatter de akutte virkninger tydelige tegn på irritation af øjne og næseslimhinder, generelle tegn på påvirkning af centralnervesystemet samt ændringer i lungerne. Styrens neurotoksiske virkning er veldokumenteret. Ligeledes er stoffets effekt på høreorganer og farvediskrimination blevet rapporteret.

Ototoksicitet (toksicitet over for høreorganerne) er den mest følsomme og relevante effekt af styren hos dyr ved gentagen eksponering ved inhalation. Undersøgelser på mennesker tyder på, at følsomheden for udvikling af høretab kan være større hos mennesker end hos rotter. Ud fra studier med rotter kunne en NOAEC mellem 1300-2600 mg/m<sup>3</sup> for høretab beregnes. Der er også epidemiologisk dokumentation for, at styren forårsager ændringer i farvediskrimination.

I EUs risikovurderingsrapport (RAR) for styren blev det konkluderet, at der ikke er tilstrækkeligt bevis for mutagen aktivitet eller kræftfremkaldende egenskaber af styren, der har relevans for mennesker. IARC har konkluderet, at styren muligvis er kræftfremkaldende over for mennesker (Gruppe 2B).

For potentielle udviklingsmæssige effekter blev en NOAEC på 650 mg/m<sup>3</sup> foreslået i RAR'en og styren blev klassificeret som Repr, H361d.

Yderligere blev det i RAR'en konkluderet, at der ikke er bevis for, at styren udviser væsentlig hormonforstyrrende aktivitet på det reproduktive system. Imidlertid er styren blevet placeret i kategori 1 på EU's prioriteringsliste for hormonforstyrrende stoffer. EU-kriterier for hormonforstyrrende virkning er stadig under udvikling, hvilket betyder, at det vil være relevant at gentage evalueringen når disse kriterier bliver tilgængelige.

Europæiske grænseværdier for erhvervsmæssig eksponering for styren er endnu ikke fastsat. Den danske grænseværdi for erhvervsmæssig eksponering er 25 ppm (105 mg/m<sup>3</sup>).

WHO har opstillet en værdi for tolerabel daglig indtagelse (TDI) på 7,7 µg/kg legemsvægt pr dag, og baseret på denne værdi blev en vejledende værdi for drikkevand på 20 mg/l foreslået. Til sammenligning benytter RAR'en en NOAEL på 150 mg/kg legemsvægt/d baseret på levernekrose observeret i et 2-års kræftstudie i mus i sin risikovurdering, som tager udgangspunkt i beregning af "margin of safety" (MoS).

**Eksponering:** Forbrugere kan blive eksponeret for styren gennem længere tid f.eks. gennem emissioner fra byggematerialer (f.eks. gulvtæpper), fødevarer, tyggegummi og aktiv eller passiv tobaksrygning. Ud over rygning angives den største eksponering for styren at stamme fra emission af styren som monomer fra byggematerialer. Forbrugere kan yderligere blive udsat for styren gennem anvendelse af resiner eller klæbemidler, der indeholder styren. Selv om sådanne eksponeringer ikke er hyppige kan de være kraftige når de forekommer, især fra flydende produkter på grund af den høje flygtighed af styren.

Niveauer af arbejdsmiljømæssig eksponering for styren er blevet estimeret for fem professionelle anvendelsesområder for stoffet, nemlig fremstilling af styren monomer, fremstilling af polystyren,

fremstilling af umættet polyester (UP)-styren resin, fremstilling af styren-butadien-gummi (SBR) og fremstilling af glasfiberforstærket plastik (GRP).

De højeste eksponeringsniveauer findes i GRP-industrien og er relateret til forarbejdningen af UP styrenholdige resiner, som indebærer en høj grad af manuel håndtering i enten åbne eller delvis lukkede formstøbningsprocesser. Typiske eksponeringer i løbet af 8 timer er estimeret til at ligge i området 1-60 ppm, mens realistiske worst-case niveauer vurderes at være 1-100 ppm med korttidseksponeringer (15 min.) på op til 180 ppm. Den danske grænseværdi (loftsværdi) er 25 ppm.

Hvad angår indirekte eksponering gennem fødevarer, luft og vand, er der i EU's risikovurderingsrapport (RAR) estimeret et dagligt indtag på 0,058 mg/kg bw, hvoraf en meget stor del kommer fra luften. Overførsel af styren fra fødevareremballager baseret på styren er dokumenteret i flere studier. Imidlertid er koncentrationerne i fødevarer generelt lave (mindre end 10 µg/kg) og repræsenterer således ikke en væsentlig eksponeringsvej for mennesker.

**Risiko for mennesker:** Korttidseksponeringer fra sporadisk forekommende begivenheder så som reparationsarbejder med styrenbaserede resiner er i EU's risikovurderings rapport vurderet at udgøre en sundhedsmæssig risiko for forbrugerne. Langtidseksponeringer fra byggematerialer, herunder gulvtæpper, fra kontaminerede fødevarer (fra plastemballagen) og fra tyggegummi vurderedes ikke at resultere i uacceptable sundhedsrisici for forbrugere.

I følge EUs RAR kan der ved fremstilling af UP-resiner, GRP, SBR og SB latex forekomme niveauer af eksponering for styren, der udgør en sundhedsrisiko for arbejdere. Risikoen er mest udtalt ved fremstilling af GRP. For de øvrige scenarier fandt man, at sikkerhedsmargenen var tilstrækkelig. Informationer indhentet fra industrien peger dog på, at udsættelse for styren i GRP-industrien, f.eks. ved fremstilling af vindmølevinger, er blevet betydeligt formindsket i de senere år, således at eksponeringen af arbejdere i dag typisk vil være noget mindre end vurderet i RAR'en.

Den kombinerede indirekte eksponering af den generelle befolkning for styren gennem fødevarer, luft og drikkevand er ikke fundet at give anledning til uacceptabel sundhedsmæssig påvirkning. Dog kan en sundhedsmæssig risiko ikke fuldstændig udelukkes hvis man sammenligner den TDI, som er beregnet af WHO (7,7 µg/kg bw/dag), med niveauerne i omgivelserne.

### **Alternativer til styren**

For øjeblikket er der intet der tyder på, at styren vil blive erstattet af alternative stoffer i nogen af de mange anvendelsesområder, som stoffet har, herunder i særlig grad fremstillingen af forskellige typer af plast og gummi, hvor styren anvendes som reaktiv monomer og/eller reaktivt solvent.

Inden for de varmhærdende materialer er de mulige alternativer til uP enten epoxyprodukter eller phenol-formaldehyd resiner. Imidlertid er sådanne materialer også baseret på brugen af farlige monomerer fordi en høj reaktivitet er nødvendig for at sikre en fuldstændig hærkning af produkterne samt de nødvendige mekaniske og fysiske egenskaber for at være sikre under brug.

I de fleste tilfælde viser andre varmhærdende polymerer sig blot at være baseret på andre monomerer på LOUS-listen, f.eks. visse isocyanater (MDI/TDI) for varmhærdende PUR, bisphenol A for epoxyer eller formaldehyd, og phenol for phenol-formaldehyd resiner. Det vurderes, at det i de fleste tilfælde vil være dyrere at skifte til en anden type af plastik, måske undtagen fødevareremballageområdet, hvor der synes at være en trend i retning af at bruge PET i stedet for PS.

### **Konklusioner**

Den primære grund til at optage styren på listen over uønskede stoffer er, at stoffet er på EUs liste over prioriterede stoffer, der skal vurderes med hensyn til deres hormonforstyrrende effekter. EUs risikovurdering konkluderede, at der ikke var evidens for signifikant hormonforstyrrende aktivitet af

styren. EU-kriterier for hormonforstyrrende effekt er dog stadig under udvikling, og det kan være nødvendigt at foretage en reevaluering, når kriterierne foreligger.

Forbrugernes eksponering for styren kan give anledning til bekymring i forhold til både korttidseksponering i forbindelse med reparationsarbejder og i forhold til langvarig udsættelse for styren frigivet fra polymere byggematerialer, herunder tæpper, samt fra fødevarer (hovedsagelig fra emballage til fødevarer) samt fra tyggegummi. Rygere og passive rygere eksponeres desuden via tobaksrøg, og det daglige indtag ved intensiv rygning kan i nogle tilfælde overstige indtaget med fødevarer.

Visse erhvervs-mæssige eksponeringer gav også anledning til bekymring i EU risikovurderingen, især produktion af UP-harpiks, glasfiberfremstilling og produktion af SBR og SB latex. Information fra industrien tyder dog på, at eksponeringen er blevet reduceret betydeligt i de senere år.

I EUs risikovurdering gav eksponering via miljøet ingen indikation af uacceptable sundhedsrisici for mennesker, heller ikke i forbindelse med kombineret eksponering. En risiko forbundet med indirekte eksponering kan dog ikke udelukkes, når den afledte eksponering sammenlignes med TDI-værdien fastlagt af WHO.

Med hensyn til det eksterne miljø anses styren ikke at være et stof, der giver anledning til væsentlig bekymring selv om det, i kraft af sin status som VOC, bidrager til ozondannelse i den nedre atmosfære. Giftigheden af stoffet over for organismer i miljøet er moderat-lav, det er let bionedbrydeligt og bioakkumuleres ikke.

Der er for nærværende ingen tegn på, at styren er ved at blive substitueret med andre kemiske stoffer i de mange anvendelser, stoffet har. Der eksisterer tekniske alternativer for nogle af anvendelsesområderne, men disse er typisk baseret på andre reaktive monomerer, der også anses for uønskede, hvorfor substitution ikke nødvendigvis vil være en fordel, hverken sundhedsmæssigt eller miljømæssigt.

### **Manglende oplysninger**

På grund af fortrolighedsbestemmelser har det ikke været muligt at klarlægge anvendelserne af styren i Danmark fuldstændigt eller vurdere deres betydning og omfang kvantitativt. Endvidere er der ikke identificeret kvantitative data om forekomsten af styren i affald, i udledninger af spildevand eller i spildevandsslam.

Yderligere oplysninger om afgivelse af styrenmonomer fra produktion og anvendelse af polymere styrenprodukter vil være nyttig information med henblik på at kvalificere eksponeringsestimatet for både forbrugerscenarier og arbejdsrelaterede scenarier.

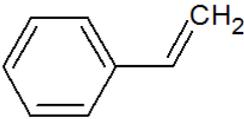


# 1. Introduction to the substance

## 1.1 Definition of the substance

This name and other identifiers of the substances included in this study are listed in Table 1.

**TABLE 1**  
NAME AND OTHER IDENTIFIERS OF THE STYRENE

Substance name	Styrene
EC number	202-851-5
CAS number	100-42-5
Synonyms	-
Molecular formula	C <sub>8</sub> H <sub>8</sub>
Structure	
Molecular weight (g/mol)	104.15

## 1.2 Physical and chemical properties

The physical and chemical properties of styrene are shown in Table 2. The listed properties mainly refer to the registration dossiers available at ECHA's website. The registration dossiers may include different values for the same parameter; in this case, a range is indicated.

Styrene as pure monomer is commercially available with a purity of 99.6 – 99.9%. Styrene often occurs in a polymerised form such as e.g. polystyrene or styrene-based rubbers. In that case, styrene is present at a maximum of 10 ppm (Arbete og hälsa 2010).

**TABLE 2**  
PHYSICAL AND CHEMICAL PROPERTIES OF STYRENE [ALL DATA PRESENTED ARE REACH REGISTRATION DATA EXTRACTED FROM ECHA'S WEBSITE IN OCTOBER 2013]

Property	Styrene
Physical state at 20°C and 1013 hPa	Colourless to yellowish liquid
Melting point (°C)	-31

Property	Styrene
Freezing point (°C)	-
Boiling point (°C)	145
Relative density at 20°C (g/cm <sup>3</sup> )	0.90 - 0.91
Vapour pressure at 20°C (hPa)	6.67
Vapour pressure at 30°C (hPa)	12.66
Surface tension at 20 °C (mN/m)	32.3; 32
Water solubility 20 °C (mg/L)	320
Log P (octanol/water) at 25 °C	2.96 (measured)

According to WHO (2000), styrene has a characteristic pungent odour, recognizable at low concentrations. The odour threshold is 0.016 ppm (70 µg/m<sup>3</sup>).

### 1.3 Function of the substance for main application areas

Styrene is a volatile organic compound primarily used as a raw material for production of polymers, elastomers, and insulation materials, e.g. polystyrene and acrylonitrile-butadiene-styrene copolymers. It is also used as a component in unsaturated polyester (UP) for e.g. glass fibre-reinforced products such as boats and windmill turbines. In UP, styrene acts both as a cross-linking agent and as a reactive solvent.

Styrene is not produced in Denmark but is rather imported for use in a variety of industrial sectors to produce a range of different polymer products.

According to the SPIN database, the reported consumption of styrene in Denmark was about 6,400 t/year in 2011. Under REACH, the substance is registered in the tonnage band 1-10 million t/year.

# 2. Regulatory framework

This chapter gives an overview of how styrene is addressed in existing and upcoming EU and Danish legislation, international agreements and by EU and Nordic eco-label criteria. The chapter primarily focuses on legislation where styrene is addressed specifically. Legislation whereby the substance is implicitly addressed, i.e. where they are included in the overall scope of a regulation/directive (e.g. due to their classification), is not listed.

In Appendix 1, an overview of legal instruments in the EU and DK is presented. The appendix gives a brief introduction to chemicals legislation, explains the lists referred to in section 2.1.3 on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), and provides a short introduction to international agreements and the EU and Nordic ecolabelling schemes.

## 2.1 Legislation

### 2.1.1 Existing legislation

Table 3 provides an overview of existing key pieces of legislation addressing styrene. For each area of legislation, the table first lists the EU legislation (if applicable) and then (as concerns directives) existing transposition into Danish law and/or other national rules. The latter is elaborated upon in the case that Danish rules differ from EU rules.

**TABLE 3**  
LEGISLATION ADDRESSING STYRENE

Legal instrument*	DK/EU	Substance (as identified in the instrument)	Requirements
<b>Regulation addressing substances and products</b>			
<b>REGULATION (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)</b>	EU	Styrene	Styrene is registered under REACH in the 1.000.000 – 10.000.000 t/y band. Styrene is not a listed chemical in the annexes regulating or restricting the manufacture and use of chemicals (i.e. Annex XIV List of chemicals of substances subject to authorisation and Annex XVII Restriction on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles)
<b>REGULATION (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006</b>	EU	Styrene, CAS No 100-42-4	Styrene is classified according to harmonised classification and labelling of hazardous substances
<b>COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food</b>	EU	CAS number 100-42-5, styrene	This regulation sets out specific rules for safe use of plastic food contact materials and articles. Styrene is included in Annex I, “1. Union list of authorised monomers, other starting substances, macromolecules obtained from microbial fermentation, additives and polymer production aids”. According to the list styrene is authorised to be used for the application “Use as monomer or other starting substance or macromolecule obtained from microbial fermentation”. No specific migration limits (mg/kg food) have been defined for styrene. Therefore the generic limit of 60 mg/kg applies to styrene.
<b>Regulation addressing emissions to the environment (Danish ministry of environment)</b>			
<b>Statutory order on water quality and monitoring of water supply systems, No. 1024 of 31/10/2011</b> [Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg, BEK nr 1024, 31/10/2011] /Danish Ministry of Environment	DK	Styrene	Annex 1C Quality requirements for organic micro-contaminations (µg/L): Output from Waterworks: 0.2 Entrance to the property: 0.2 At the consumer's tap: 0.2

Legal instrument*	DK/EU	Substance (as identified in the instrument)	Requirements
<b>Statutory order on the Transport of Dangerous Goods, No. 788 of 27/06/2013</b> [Bekendtgørelse om vejtransport af farligt gods, BEK nr 788 af 27/06/2013] /Danish Ministry of Justice	DK	Styrene monomer, stabilised	Included in the dangerous goods list – part 3, which specifies special provisions and exemptions related to transport of dangerous goods packed in limited and excepted quantities. UN No.: 2055
<b>Regulation addressing occupational environment</b>			
<b>COUNCIL DIRECTIVE 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work</b>	EU	-	The Directive sets out general rules for the working environment, imposing the duty on employers to assess any risk to the safety and health of workers arising from the presence of hazardous chemical agents at the workplace, take the necessary preventive measures and to ensure the safety and health requirements for activities involving hazardous chemical agents are met.
<b>Statutory order on working with substances and materials, No. 292 of 26/04/</b> [Bekendtgørelse om arbejde med stoffer og materialer, BEK nr 292 af 26/04/2001]	DK/EU* *	-	Implementing COUNCIL DIRECTIVE 98/24/EC.
Statutory order on youth work, No. 239 of 6 April 2005 [Bekendtgørelse om unges arbejde, BEK nr 239 af 06/04/2005]	DK	-	The statutory order prohibits that workers < 18 years work with substances that are comprised by the statutory order on measures to prevent exposure to carcinogenic substances and materials (no. 908 of 27/09/2005), organic solvents as well as materials containing 1 % or more of organic solvents.
<b>Statutory order on changing the statutory order on limit values for substances and materials, No. 986 of 11/10/2012</b> [Bekendtgørelse om ændring af bekendtgørelse om grænseværdier for stoffer og materialer, BEK nr 986 af 11/10/2012]  Amending statutory order on limit values for substances and materials, 507 of 17/05/2011	DK	100-42-5 Styrene	Occupational exposure limits: Limit value of styrene are 25 ppm (105 mg/m <sup>3</sup> ) These values are absolute limit values (L - "loftværdier"). Styrene is marked as HK: skin penetrating and carcinogen.

Legal instrument*	DK/EU	Substance (as identified in the instrument)	Requirements
[Bekendtgørelse om grænseværdier for stoffer og materialer, BEK nr. 507 af 17/05/2011]/Danish Ministry of Employment			
<p><b>Statutory order on changing the statutory order on measures to prevent exposure to carcinogenic substances and materials, No. 1175 of 11/10/2007</b></p> <p>[Bekendtgørelse om ændring af bekendtgørelse om foranstaltninger til forebyggelse af kræftisikoen ved arbejde med stoffer og materialer, BEK nr 1175 af 11/10/2007] /Danish Ministry of Employment</p> <p>Amending Statutory order on measures to prevent exposure to carcinogenic substances and materials, No. 908 of 27/09/2005 [Bekendtgørelse om foranstaltninger til forebyggelse af kræftisikoen ved arbejde med stoffer og materialer, BEK nr. 908 af 27/09/2005] /Danish Ministry of Employment</p>	DK	100-42-5 Styrene	Materials with a percentage content of more than 0.1% styrene are covered by the requirements addressing demarcation and labelling of the working area, monitoring, labelling of material, education for work with the substance, and reporting of accidents. Excepted are: cured polyester, laboratory work, and polyester casting, including plastering in the finish of polyester casting.
<p><b>Statutory order on occupational health educations, No. 1088 of 28/11/2011</b></p> <p>[Bekendtgørelse om arbejdsmiljøfaglige uddannelser, BEK nr. 1088 af 28/11/2011 ] /Danish Ministry of Employment</p>	DK	Styrene	Annex 7 - Qualification requirements when working with styrene and polyester casting Specifies that work with styrene requires certificates from specific training. It is specified which skills must be obtained through this education and who can provide the training.
<p><b>Statutory order on releases from the Danish Maritime Authority A, Technical Regulation on occupational health in ships, No. 1246 of 11/12/2009</b></p>	DK	100-42-5 Styrene	Materials with a percentage content of more than 0.1% are covered by the requirements (addressing monitoring, labelling and reporting of accidents) as specified in the statutory order No. 1246 of 11/12/2009 regarding all materials except cured polyester,

Legal instrument*	DK/EU	Substance (as identified in the instrument)	Requirements
[Bekendtgørelse om Meddelelser fra Søfartsstyrelsen A, teknisk forskrift om arbejdsmiljø i skibe, BEK nr 1246 af 11/12/2009 ] /Danish Maritime Authority			laboratory work, and polyester casting.
<p><b>Statutory order on determination of code numbers, No. 301 of 13/05/1993</b> [Bekendtgørelse om fastsættelse af kodenumre, BEK nr 301 af 13/05/1993] /Danish Ministry of Employment</p> <p><b>Statutory order on working with code-numbered products, No. 302, 13.05.1993</b> [Bekendtgørelse om arbejde med kodenummererede produkter, BEK nr. 301 af 13/05/1993] /Danish Ministry of Employment</p>	DK	Styrene (ethenylbenzene, vinylbenzene, phenylethene)	<p>The Metrological Occupational Air Requirements, called MAL [Danish: Måleteknisk Arbejdshygiejnisk Luftbehov] are defined for styrene as follows:</p> <p><b>Styrene content &gt; 0%</b></p> <ul style="list-style-type: none"> <li>- MAL-factor (m<sup>3</sup> air / 10g substance): 95</li> <li>- Content (limit weight %) / Marker number: ≥ 5% / -6 and for ≥0,1-5% / -3</li> </ul> <p>Defines minimum safety measures which have to be applied when working with code-number labelled products depending on working situations (outside, inside, large or small application areas) and processes (e.g. painting, grouting). Generally, work with styrene requires gloves, full face mask with breathing apparatus, hat, and coveralls.</p>

\* Unauthorised translation of Danish legislation instrument names into English. “Statutory order” is generally used for “Bekendtgørelse”. However, the Working Environment Authority commonly uses “Executive order”.

\*\* Statutory order which implements a European Directive into Danish legislation.

Styrene is registered under REACH. There are no restrictions under REACH on the manufacture or use of styrene. Styrene is classified according to harmonised classification and labelling of hazardous substances, as specified in the CLP regulation. Further information on the provisions under CLP and REACH are given in sections 2.1.2 and 2.1.3 below.

The EU regulation on plastic materials and articles intended to come into contact with food addresses certain applications of styrene, but does not set a specific migration limit (SML) for the substance. Therefore the generic SML of 60 mg/kg, used for all substances for which no SML or other restrictions are provided, applies to styrene.

No EU indicative occupational exposure limit (OEL) values have been defined for styrene. Styrene is, however, included in the list of recommendations by the Scientific Committee on Occupational Exposure Limit Values (SCOEL), commented upon as being an ‘on-going’ activity.

In Denmark, an OEL of 25 ppm is set for styrene. There are also several statutory orders<sup>1</sup> providing general regulation of the use of chemical substances in the working environment.

<sup>1</sup> Translation of the Danish “Bekendtgørelse”. Depending on organisation and context, other translations may be used, e.g. ‘executive order’. In this report, the translation ‘statutory order’ is used consistently.

The Danish Working Environment Authority (WEA) regards styrene as a carcinogenic substance (i.e. the substance is listed on the WEA cancer list; WEA, 2012), which resulted in Danish legislation defining, amongst others, requirements concerning labelling of the working area and material, education and training for work with the substance, as soon as the material content surpasses 0.1 % styrene. Products and mixtures containing styrene have to be labelled with code numbers according to the occupational air requirements for styrene (MAL factors), thereby also requiring the use of certain safety measure when handling the substance.

Provisions regarding monitoring, labelling and reporting of accidents also exist for occupational health on ships, according to a statutory order by the Danish Maritime Authority.

Furthermore, Danish legislation defines drinking water quality requirements (0.2 µg/L) for styrene.

## 2.1.2 Classification and labelling

### Harmonised classification in the EU

Table 4 lists the harmonized classification and labelling for styrene according to Annex VI of the CLP Regulation.

**TABLE 4**  
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION).

Index No	International chemical identification	CAS No	Classification		
			Hazard Class and Category Code(s) <sup>1</sup>	Hazard statement Code(s) <sup>2</sup>	Pictogram
601-026-00-0	styrene	100-42-5	Flam. Liq. 3	H226	
			Acute Tox. 4 <sup>3</sup>	H332	
			Eye Irrit. 2	H319	
			Skin Irrit. 2	H315	
			STOT RE1 <sup>4</sup>	H372 (hearing organs)	
			Repr. 2 <sup>4</sup>	H361d	

<sup>1</sup> Hazard Class - Flam. Liq.: Flammable liquid; Acute Tox.: Acute toxicity; Eye Irrit.: Serious eye irritation; Skin Irrit.: Skin irritation; STOT RE: Specific target organ toxicity – repeated exposure; Repr.: Reproductive toxicity

- 2 Hazard statement codes - H226: Flammable liquid and vapour; H332: Harmful if inhaled; H319: Causes serious eye irritation; H315: Causes skin irritation; H372: Causes damage to the hearing organs; H361d: Suspected of damaging the unborn child.
- 3 Minimum classification, applies when classification according to the criteria in Directive 67/548/EEC does not correspond directly to the classification in a hazard class and category under the CLP Regulation.
- 4 This classification was added with the 6<sup>th</sup> adaptation to technical progress to the CLP regulation, adopted in December 2013 and expected to be published in spring 2014 (Danish EPA, personal comm. 2014).

### Self-classification in the EU

In addition to the hazards given in the harmonized classification, the following hazard codes have been notified for styrene more than 500 times out of a total of 3059 notifications: Asp. Tox. 1 (H304), STOT SE 3 (H335), and STOT RE 1 (H372), thus indicating potential aspiration and specific target organ toxicity following single or repeated exposure. 255 out of a total of 3059 notifiers have included “Aquatic Chronic 3” in their proposal for classification of styrene.

### 2.1.3 REACH

Styrene is registered under REACH in the 1.000.000 – 10.000.000 t/y band.

For styrene, ECHA lists 135 registrants/suppliers in Europe.

The countries, where the registering companies are situated (17 countries in total), are: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Ireland, Ireland, Italy, Luxembourg, Netherlands, Poland, Spain, Sweden, United Kingdom.

### Community rolling action plan (CORAP)

Styrene is included neither in CoRAP 2012-2014, nor in the most recent draft CoRAP for 2013-2015 (ECHA, 2013a).

### Registry of Intentions

Table 5 shows the Registry of Intentions by ECHA and Member States’ authorities for restriction proposals, proposals for harmonised classifications and labelling and proposals for substances of Very High Concern (SVHC).

In 2010, Denmark submitted a dossier for harmonised classification of styrene, which initiated the amended classification of styrene (see section 2.1.2). The dossier proposed adding the classifications STOT RE 1; H372 (nervous system) and Repr. 1B; H360D. The classification as STOT RE 1; H372 (Hearing organs) and Repr. 2; H361d was adopted by the ECHA Committee for Risk Assessment (RAC, 2012).

TABLE 5  
STYRENE IN REGISTRY OF INTENTIONS (AS OF 31 OCTOBER 2013).

Registry of	CAS No	Substance	Scope (reproduced as indicated in the Registry of intentions)	Dossier intended by:	Date of submission:
<b>Harmonised Classification and Labelling intentions</b>					
Annex XV dossiers submitted	100-42-5	Styrene	Proposed classification according to Reg (EC) No 1272/2008 (CLP): STOT RE 1; H372 , Repr. 1B; H360D	Denmark	17/12/2010

## **Candidate list**

Styrene is not on ECHA's Candidate list of substances of very high concern (SVHC) (October 2013).

## **Annex XIV recommendations**

Styrene has not been recommended for Annex XIV (Authorisation List) inclusion (ECHA, 2013b). It is notable that possible inclusion would first require uptake on the candidate list.

## **2.2 Other classifications**

IARC published a monograph on styrene in 2002 (IARC, 2002), evaluating the carcinogenicity of styrene with the following statements: "There is limited evidence in humans for the carcinogenicity of styrene" and "There is limited evidence in experimental animals for the carcinogenicity of styrene". These findings lead to the overall evaluation of styrene as a possibly carcinogenic to humans (Group 2B). This evaluation is not reflected in the European classification.

Styrene is listed in category 1 on the EU priority list for endocrine disruptors<sup>2</sup>. This category includes substances for which there is evidence of endocrine disrupting activity in at least one species using intact animals. However, the risk assessment report (RAR) on styrene concluded that there is no evidence that styrene possesses significant endocrine disruption activity (UK, 2008). Discussions on criteria for identifying a chemical substance as an endocrine disrupter are ongoing in the EU. Whether styrene is classified as an endocrine disruptor according to the EU criteria or not is a decision that therefore awaits the adoption and publication of the criteria. For further information on the topic, consult section 6.1.3/*Endocrine disruption*.

## **2.3 International agreements**

Generally, styrene is not specifically addressed in international agreements concerned with presence and/or transport of chemicals in the environment, hereunder the OSPAR Convention, HELCOM, Rotterdam Convention (PIC), and CLRTAP (Convention on Long-range Transboundary Air Pollution).

Styrene is, however, mentioned in the Basel Convention under Annex IX, which exempts certain waste from the categorisation as "hazardous waste".

By default, styrene is defined as "hazardous waste" in the Convention, since it belongs to waste category Y42 (Organic solvents excluding halogenated solvents) and is classified with the hazardous characteristic H3 "flammable liquid".

According to Annex IX, List B – 3 (Wastes containing principally organic constituents, ...), solid scrap plastic waste of non-halogenated polymers and co-polymers are not defined as "hazardous waste", even if they contain styrene, provided that the styrene content is sufficiently low that the solid plastic waste does not fall under into the category of "flammable solid".

## **2.4 Eco-labels**

Table 6 gives an overview of how styrene is addressed by the EU and Nordic eco-labelling schemes, with an indication of requirements.

Styrene is mentioned specifically in only a few Eco-label criteria, including on imaging equipment, remanufactured toner cartridges (Nordic Swan), and hard coverings (EU flower).

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<sup>2</sup> [http://ec.europa.eu/environment/chemicals/endocrine/index\\_en.htm](http://ec.europa.eu/environment/chemicals/endocrine/index_en.htm)

Since styrene is a volatile organic compound (VOC), its use and content in products is indirectly restricted or prohibited by a large number of Ecolabelling criteria, e.g. in the criteria for candles, white goods, and furniture. In many of those, styrene is – if at all - supposedly just applied as a process substance, and possible product content might due to residues or impurities.

A comprehensive overview of VOC-restricting criteria can be found in Appendix 2.

**TABLE 6**  
ECO-LABELS TARGETING STYRENE

Eco-label	Substance	Relevant criteria	Document title /number
Nordic Swan	Styrene, TVOC	A test report shall declare that the analyse results for toner powder to be used for Nordic Ecolabelled toner cartridges must be smaller or equal to the limit values listed:  Styrene: Determination limit (mg/kg): 4 Limit value (mg/kg): 40  TVOC: Determination limit (mg/kg): 100 Limit value (mg/kg): 300	Nordic Ecolabelling of Remanufactured OEM Toner Cartridges Version 5.1 • 15 June 2012 – 30 June 2016
	Styrene	The product must fulfil the maximum limit values expressed in the table below and the emission rates must be measured in accordance with the requirements described in Blue Angel: RAL-UZ 171. Emission rate (mg/h) Colour Printing Total in ready + print phase: 1.8 Emission rate (mg/h) Monochrome printing Total in ready + print phase: 1.0	Nordic Ecolabelling of Imaging equipment Version 6.0 • 20 June 2013 - 30 June 2016
EU flower	Styrene	Agglomerated stones: The emissions to air for the following parameters for the whole manufacturing process shall not exceed 2000 (mg/m <sup>2</sup> ). The styrene emission to air from natural products shall not exceed <210 mg/N m <sup>3</sup> .	Commission Decision of 9 July 2009 establishing the ecological criteria for the award of the Community eco-label to hard coverings

## 2.5 Summary and conclusions

Styrene is subject to harmonised classification under the CLP regulation. Styrene is classified as flammable, acutely toxic upon inhalation, and eye and skin irritating<sup>3</sup>. Moreover, the substance's classification has been recently adjusted and now also includes "Suspected of damaging the unborn child" and "Causes damage to organs (hearing organs)".

Styrene is not addressed specifically in any EU legislation concerning products, wastes, environmental emissions, or occupational exposure.

<sup>3</sup> H226: Flammable liquid and vapour, H332: Harmful if inhaled, H319: Causes serious eye irritation, H315: Causes skin irritation

A specific migration limit (SML) for migration of styrene from food contact materials has not been defined, resulting in the generic SML of 60 mg/kg to apply for styrene.

No Indicative occupational exposure limit has been defined for styrene yet. The Scientific Committee on Occupational Exposure Limit Values (SCOEL) has included styrene in the list of recommendations, commented upon as being 'on-going'. However, general legislation in the field of occupational environment ensuring the workers' safety and health as regards activities involving hazardous chemical agents also applies to styrene.

Danish legislation addressing occupational handling of styrene includes, amongst others, requirements regarding occupational handling of styrene, labelling of materials and working area, training, handling, safety measures and the establishment of Danish occupational exposure limits.

Styrene is not addressed specifically in international agreements on chemicals in the environment. Styrene is specifically mentioned in only a few eco-labelling criteria, defining requirements regarding the content or emissions of styrene for imaging equipment, remanufactured toner cartridges, and hard coverings. However, it is indirectly encompassed in eco-labelling criteria for a wide range of products, based on prohibition or restriction of their VOC content.

# 3. Manufacture and uses

## 3.1 Manufacturing

### 3.1.1 Manufacturing processes

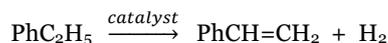
#### Styrene

The production processes of styrene are described in the European risk assessment report (ECB 2002) as follows:

*“Styrene is produced commercially from crude oil by a sequence of processes. Steam cracking of naphtha obtained from the refining of crude oil produces ethylene, propylene and a mixture of monocyclic hydrocarbons including benzene. Ethylene and benzene, fractionated from this mixture, are then reacted together in the presence of a catalyst to produce ethylbenzene.”*

Styrene (PhCH=CH<sub>2</sub>) is then manufactured from ethylbenzene (PhC<sub>2</sub>H<sub>5</sub>) by either dehydrogenation or oxidation. Some ethylbenzene may be present as an impurity in the produced styrene; ethylbenzene is the most common impurity.

In the dehydrogenation process, iron oxide is used as a catalyst, together with zinc and magnesium oxides (see equation below). Steam is added as a dilution agent and to improve the heat transfer.



The reaction is carried out at approximately 700°C and 0.8 bar. In order to prevent polymerisation of the styrene, the conversion is carried out to only 60%, and there is always a reasonable dilution. The purification of the reaction product is done by vacuum distillation. The by-product gases formed in this reaction are used as a fuel or they are flared.

The oxidation manufacturing process is described as follows: *“Styrene may be manufactured by oxidation of ethylbenzene to the hydroperoxide by bubbling air through the liquid reaction mixture. The hydroperoxide is then reacted with propylene to yield propylene oxide and a co-product, methyl phenyl carbinol, again in the liquid phase. The carbinol is dehydrated to styrene over an acid catalyst at about 225°C.”*

### 3.1.2 Manufacturing volumes and sites

Global manufacturing volumes amounted to 16.5 million tonnes in 1995 (ECB 2002).

In the EU, styrene is produced in the 1,000,000 - 10,000,000 tons/year band in the EU.

The production range in the EU Member States has been reported to be 2.22 to 4.91 million tonnes per year, and the range of import tonnages accounts for 30,000 to 150,000 tons (ECB 2002, year of statistical information not specified). A CEFIC report estimated the production and use of styrene in Western Europe (including some countries not within the EC) at 3,743,000 tonnes in 1993 (ECB 2002).

According to the PRODCOM<sup>4</sup> database, the average production in EU27 was 5,018,384 t/y in the period 2007 – 2011, and 5,114,867 tons in 2012.

In the EU, nine companies have been reported to produce or import styrene in quantities of over 1000 tonnes per annum (ECB 2002).

In a recent market analysis (Research and Markets 2012), 11 European countries are listed as styrene producing (Table 7).

Styrene producing plants are always located in the vicinity of refineries because of the manufacturing process. The typical production capacity of a styrene producing plant amounts to appr. 300,000 – 500,000 tons per year (Grønberg, pers. comm. 2014).

**TABLE 7**  
STYRENE PRODUCING COUNTRIES AND COMPANIES IN EUROPE (RESEARCH AND MARKETS 2012).

Country	Company
<b>Belgium</b>	Styrolution
<b>Bulgaria</b>	Lukoil Neftochim Burgas AD
<b>Czech Republic</b>	Synthos Dwory
<b>France</b>	Total Petrochemicals France
<b>Germany</b>	BASF AG Dow Chemical GmbH Ineos Styrenics
<b>Italy</b>	Polimeri Europa
<b>Netherlands</b>	Dow Benelux B.V. Ellba CV Lyondell Bayer Manufacturing Maasvlakte VOF Sabic Europe BV Shell Nederland Chemie BV
<b>Poland</b>	Synthos SA
<b>Romania</b>	Arpechim
<b>Spain</b>	not specified
<b>UK</b>	not specified

## 3.2 Import and export

### 3.2.1 Import and export of styrene in Denmark

Data on Danish import and export of styrene is shown in Table 8 based on data from Statistics Denmark (2013). According to Eurostat, styrene is not produced in Denmark. The calculated net import of styrene was 318 t/y on average for the period 2007-2011, and 2098 tons in 2012. This is a large deviation between the two import figures, which is not unusual for commodities. The import tonnages from 2007-2011 all range between 86 and 792 tons.

<sup>4</sup> The PRODCOM database is Eurostat's database on manufactured goods under the "Industry, trade and services" branch. Eurostat is a Directorate-General of the European Commission providing European statistical information and promoting the harmonisation of statistical methods.

**TABLE 8**  
DANISH PRODUCTION, IMPORT AND EXPORT OF STYRENE (STATISTICS DENMARK 2013, EUROSTAT PRODCOM DATABASE 2013);

CN8 code*	Substance	Import, t/y		Export, t/y		Production	
		Average 2007-2011	2012	Average 2007-2011	2012	Average 2007-2011	2012
2902 5000	Styrene	321	4,726	3.02	2,627	-	-

\* Code numbers are assigned according to the Combined Nomenclature and used for identifying goods.

### 3.2.2 Import and export of styrene in EU

Statistics on EU external trade of styrene from Eurostat are shown in Table 9. The most recent import and export figures from 2012 are lower than the average of the 4 previous years, but styrene import exceeds the export. The net consumption of styrene using the production volume of 5,114,867 tons (2012) can thus be calculated to 5,401,898 tons in 2012.

**TABLE 9**  
EU27 EXTERNAL IMPORT AND EXPORT OF STYRENE (EUROSTAT, 2013)

CN8 code*	Substance	Import, t/y		Export, t/y	
		Average 2007-2011	2012	Average 2007-2011	2012
2902 5000	Styrene	553,658	481,289	241,494	194,258

\* Code number are assigned according to the Combined Nomenclature and used for identifying goods.

## 3.3 Use

### 3.3.1 General use and function of styrene

Global and European use of styrene is described in the European risk assessment report (ECB, 2002) and the IARC monograph on styrene (IARC, 2002). Furthermore, producers and distributors as well as the Danish Plastics Federation (Plastindustrien) and Denmark's Paint and Adhesives Federation (DFL) have been contacted for information on the use and presence of styrene in different applications. Among the industries contacted were several companies involved in unsaturated polyester adhesives and coatings and a single company within expanded polystyrene production.

Globally, the major use of styrene is as an intermediate in closed systems in the chemical industry. It is the monomer that is used for production of the following materials (ECB, 2002):

- polystyrene (general purpose, GP-PS; high impact, HIPS; and expanded, EPS);
- copolymer systems (acrylonitrile-butadiene-styrene, ABS; styrene-acrylonitrile, SAN; methyl methacrylate-butadiene-styrene, MBS; and others);
- styrene-butadiene rubber (SBR);
- related lattices (SB Latex, for example), and
- component of unsaturated polyester resins (UP).

The uses listed in the registrations on ECHA's homepage comprise:

- Manufacturing of styrene
- Manufacturing of UP/VE resins and formulated resins
- Formulation
- Manufacturing of UP/VE resins (Gelcoat, Colour Paste, Putty, Bonding Paste / Adhesive, etc.)
- Formulation of polymeric mixture

- Formulation of sprayable solid surface material
- Manufacturing of formulated resins
- Toner finishing packaging
- Batch suspension polymerisation of Polystyrene (HIPS and GPPS)
- Continuous mass polymerisation of Polystyrene (HIPS and GPPS)
- Production of Expandable Polystyrene
- Production of other Styrene based polymeric dispersions
- FRP manufacturing in an industrial setting, using UP/VE resins and/or formulated resins (gelcoat, bonding paste, putty etc.)
- Production of Styrene Butadiene Latex (SBL)
- Production of Styrenic Copolymers
- Production of filled Polyols
- Production of Styrene Butadiene Rubber (SBR)
- Production of Styrene Isoprene Copolymers
- FRP (fiberglass reinforced plastic) manufacturing in an industrial setting
- Polymer processing
- Coating.

From the usage volumes in Table 10, it becomes clear that general purpose and high impact polystyrene is by far the largest application area of styrene in the European and global context. This is in agreement with the fact that packaging is the single largest application for styrene-containing resins (IARC, 2002). The data further indicate that usage of unsaturated polyester resins might have been increased, when comparing the 1993 and 1998 figures. However, interpretation of the figures should be circumspect, since they are derived from different sources.

A recent source reports the distribution of world styrene demand as follows (IHS, 2012):

- polystyrene (59.5%);
- ABS/SAN (about 17%);
- S/B copolymer latexes (5%);
- Unsaturated polyester (4.6%), and
- SBR and SBR latexes production (3.6%).

**TABLE 10**  
USE PATTERNS FOR STYRENE IN EUROPE AND WORLDWIDE.

	Europe in 1993 (tons)*	Western Europe in 1998 (tons)**	Global in 1998 (tons)**
<b>Polystyrene (GP-PS, HIPS)</b>	1,879,000	2,649,000	11,239,000
<b>Polystyrene EPS</b>	696,000		
<b>ABS</b>	397,000	433,000	2,334,000
<b>SAN</b>			
<b>SBR</b>	209,000	506,000***	1,957,000***
<b>SB Latex</b>	389,000		
<b>UP resins</b>	172,000	220,000	749,000
<b>Total</b>	<b>3,742,000</b>	<b>3,808,000</b>	<b>16,279,000</b>

\* use volumes from ECB (2002)

\*\* volumes from IARC (2002)

\*\*\* sum for copolymer systems SBR and latexes, styrene-butadiene copolymer latexes

Table 11 lists the applications of the different styrene products and demonstrates that styrene products have a wide application range for both consumers and industry.

The concentration of residual monomer in the styrene polymers or copolymers is very low, since substantially complete polymerisation can be achieved with the different polymerisation processes applied in PS, EPS, ABS, SAN, and SBR/SB production. In continuous processes, the remaining monomer in the reaction mixture is separated by volatilisation from the reaction mixture and reused, whereas in suspension processes, the reaction mixture is heated until polymerisation is complete (ECB, 2002).

According to information from the EPS-producing industry, the final concentration of residual monomer in polymerised EPS beads would be 0.1% at a maximum. However, in the final product, *i.e.* insulation material or fish packaging boxes, the residual styrene monomer is removed completely during the steaming process.

In UP, styrene is added to act as a cross-link agent and reactive diluent in the production of glass fibre-reinforced plastic. Hereby, it also functions as a solvent for the unsaturated polyester resins. The styrene content of the resins can range from 30-50% depending on the degree of cross-linking required. Low styrene emission resins are produced by lowering the styrene content or by addition of emission reducing additives. Low emission resins are used by many companies in the EU (ECB, 2002). According to information from industry, residual concentrations of styrene in the final products are negligible, since the residual monomer evaporates during curing.

**TABLE 11**  
USES OF STYRENE POLYMERS AND COPOLYMERS WORLDWIDE (ECB, 2002).

Styrene product	Industrial and consumer applications
<b>Polystyrene (GP-PS, HIPS)</b>	General packaging, furniture, electrical equipment (e.g. audio-visual cassettes) industrial mouldings (e.g. dental, medical)
<b>Polystyrene EPS</b>	Packaging, thermal insulation of refrigeration equipment and buildings
<b>ABS</b>	Interior and exterior automobile parts, drains, ventilation pipes, air conditioning, hobby equipment, casings etc.
<b>SAN*</b>	Electrical/electronic applications, automotive applications, compounding, household goods, packaging, general purpose, electrical parts, appliances, etc.
<b>SBR</b>	Tyres, radiator and heater hoses, belts and seals, wire insulation
<b>SB Latex</b>	Paper coatings, carpet backings, floor tile adhesives
<b>UP resins – glass-reinforced</b>	Building panels, marine products, household consumer goods, trucks, wind power industry**
<b>UP resins – non-reinforced</b>	Casting resins used for producing liners and seals, in putty and adhesives

\* Information on applications of SAN from UL IDES (2014)

\*\* Wind power industry is not listed in the RAR (ECB, 2002) but is also an important use in Europe

### 3.3.2 Uses in Denmark

Data on styrene registered in the Danish Product Register was retrieved in October 2013. The Danish Product Register includes substances and mixtures for professional use which contain at

least one substance classified as dangerous in concentrations of 0.1% to 1% (depending on the classification of the substance). Styrene is classified in accordance with the list of harmonised classification and labelling of hazardous substances of the CLP regulation.

The data do not necessarily provide a complete picture of the presence of the substances in mixtures placed on the Danish market, because they only comprise application in the professional sectors.

Table 12 gives an overview of the data from the Danish Product Register on the use of styrene by industry sector, which can be reported with respect for confidentiality. As shown, the major sectors are manufacture of plastic products, manufacture of engines and turbines, construction of ships, boats and similar, and maintenance and repair of vehicles. Apparently, some applications have been reported several times in different industry sectors (compare e.g. sectors C3010, C3011, and C3012). A substantial portion of the consumption is of a confidential nature as too few companies or products are registered.

Table 13, on the other hand, shows the styrene registrations in the Product Register by function. The major portions of the consumption are confidential or registered as being of “other” functions. Of the functions which can be named, construction materials, fillers, paints, lacquers and varnishes, solvents and adhesives/binding agents represent the major consumption. Note that the sums of the registered styrene consumption by sector and by function are not identical; this apparent miscalculation occurs because the designation of sectors (and functions, respectively) may have some overlap.

According to data provided by the Danish Product Register, the total import for styrene across all codes is registered as 1764-4585 t/y, the total export is 211-226 t/y, the total number of products is 746, and the total number of companies registered is 107.

The total consumption range (export subtracted from import) of ca. 1550 – 4370 t in 2012 does therefore correspond to the net import data from Statistics Denmark (2098 tons in 2012) as given in section 3.2.1. Note that the total import and export figures given above do not match the total figures given in the last line of Table 12 and Table 13 (likewise reported by the Product Register). , As mentioned, this occurs because some sectors or functions are registered more than once.

**TABLE 12**  
OVERVIEW OF REGISTRATIONS FOR STYRENE BY INDUSTRY SECTOR IN THE DANISH PRODUCT REGISTER (2012 DATA EXTRACTED FOR THIS STUDY).

Sector (NACE5)		No. of products	No. of companies	Prod/Imp range, t/y	Export range, t/y
C2220	<b>Manufacture of plastic products</b>	23	4	492	198
C2811	<b>Manufacture of engines and turbines, except aircraft, vehicle and cycle engines</b>	24	6	202 - 231	1.4 – 1.8
C3010	<b>Building of ships and boats</b>	14	3	184 - 203	0.3 – 0.7
C3011	<b>Building of ships and floating structures</b>	31	7	184 - 203	0.3 – 0.7
C3012	<b>Building of pleasure and sporting boats</b>	12	3	184 - 203	0.3 – 0.7
G4520	<b>Maintenance and repair of motor vehicles</b>	248	25	104 - 114	0 – 1.6
	<b>Unknown</b>	58	17	47	0.1
F4100	<b>Construction of buildings</b>	23	14	13 - 14	2.2 – 2.3

Sector (NACE5)		No. of products	No. of companies	Prod/Imp range, t/y	Export range, t/y
F4200	Civil engineering	23	14	13 - 14	2.2 - 2.3
T9800	Undifferentiated goods- and services-producing activities of private households for own use	58	21	0.1 - 9.2	0 - 1.5
F4399	Other specialised construction activities n.e.c.	17	11	6.8 - 7	6.4 - 6.4
F4333	Floor and wall covering	13	7	1.6 - 6.2	1.5 - 4.9
F0000	Construction	4	3	0 - 4.7	0 - 0.1
C2500	Manufacture of fabricated metal products, except machinery and equipment	12	9	0 - 4.6	0 - 0
C2561	Treatment and coating of metals	55	13	4.1 - 4.3	0 - 0
F4334	Painting and glazing	64	20	1.5 - 1.6	1.5 - 1.5
<b>Sum of confidential major sectors (rounded)</b>				1600 - 4400	10 - 20
<b>Sum of other sectors</b>				1 - 2	0 - 0
<b>Totals (rounded)</b>		<b>746</b>	<b>107</b>	<b>3020 - 5991</b>	<b>220 - 239</b>

**TABLE 13**  
OVERVIEW OF REGISTRATIONS FOR STYRENE BY FUNCTION IN THE DANISH PRODUCT REGISTER (2012 DATA  
EXTRACTED FOR THIS STUDY).

Function code (UC62)		No. of products	No. of companies	Prod/Imp range, t/y	Export range, t/y
13	Construction materials	27	12	164 - 192	0.9 - 1,4
20	Fillers	96	31	162 - 190	45 - 47
59	Paints, lacquers and varnishes	394	46	95 - 105	1.5 - 5
48	Solvents	4	4	48	2.3
2	Adhesives, binding agents	46	25	44	0.7 - 0.8
10	Colouring agents	7	3	0.62	0
45	Reprographic agents	23	7	0.2 - 0.22	0.0006 - 0.0118
61	Surface treatment	31	19	0.18 - 0.2	0.0002 - 0.0004
39	Non-agricultural pesticides and preservatives	8	3	0.0021	0 - 0.00002
14	Corrosion inhibitors	12	7	0.0002 - 0.001	0 - 0.00004
9	Cleaning/washing agents	13	8	0.0002 - 0.0009	0.00001
	Others	17	7	1041 - 2674	155
<b>Sum of confidential functions (rounded)</b>				320 - 2077	6 - 23
<b>Totals (rounded)</b>		<b>691</b>	<b>103</b>	<b>1875 - 5331</b>	<b>212 - 235</b>

It has not been possible to obtain expert estimates about which sectors or functions the substantial confidential volumes might be used.

According to information from industry, the largest application of styrene monomer is within the UP application in Denmark.

UP adhesives are used for assembling polyester- or vinylester-based glass-fibre products, such as wind turbines, boats, tanks, caravans, etc. The concentration of styrene in UP adhesives can range between 20 - 50 %, but accounts typically for about 30 - 40%. UP fillers and sealants might contain 10 - 15% styrene, depending on the viscosity requirements of the filler. Such fillers are used in e.g. car repair, but also in other industries where filling of gaps in cured fiberglass items is necessary. UP coats are for the surface treatment of glass-fibre reinforced products in order to achieve the desired surface properties, e.g. smoothness or colour. For both gel and topcoats, the same styrene concentrations apply as for UP adhesives.

There are many methods for moulding UP resins, including hand and spray lay-up (open processes), resin transfer moulding (closed process using a casting mould), sheet and bulk moulding compounds containing fibre reinforcement, filament winding and pultrusion processing (UK, 2008).

Within the windmill and boat industry, manual moulding with a spray pistol is the most common processing method for manufacturing of e.g. blades, nacelle covers (generator casings), and hulls. While most windmill manufacturers in Denmark actually use epoxy resins for production of blades, production of nacelle covers usually requires UP resins.

According to an estimate from a Danish producer, the consumption of UP has been estimated at about 5000 – 6000 tons, corresponding to a styrene consumption of about 1500 - 2400 tons, assuming a concentration range of 30 – 40%. However, this estimate is uncertain, especially with respect to the upper bound.

According to Denmark's Paint and Adhesives association (Dahl, pers. comm. 2014), styrene might be present as residual monomer in acrylate binder in polyurethane paints, water-based emulsion paints, acrylic copolymer dispersions which are used in water-based adhesives, and paints and acrylic sealants in concentrations < 0.8%. Furthermore, the substance is also used as a component of many binders.

There is no consumption of styrene for production of polymer products such as ABS or EPS beads for packaging in Denmark.

### 3.4 Historical trends in use

#### 3.4.1 European trends in use patterns of styrene

According to the data provided in the IARC monograph (2002), the use of styrene polymers increased slightly from 1985 to 1998 in Western Europe. The fractions of the different polymers have not changed significantly over the years, and polystyrene constitutes, at about 64%, the largest fraction of all styrene polymers. Estimations from more recent years could not be identified.

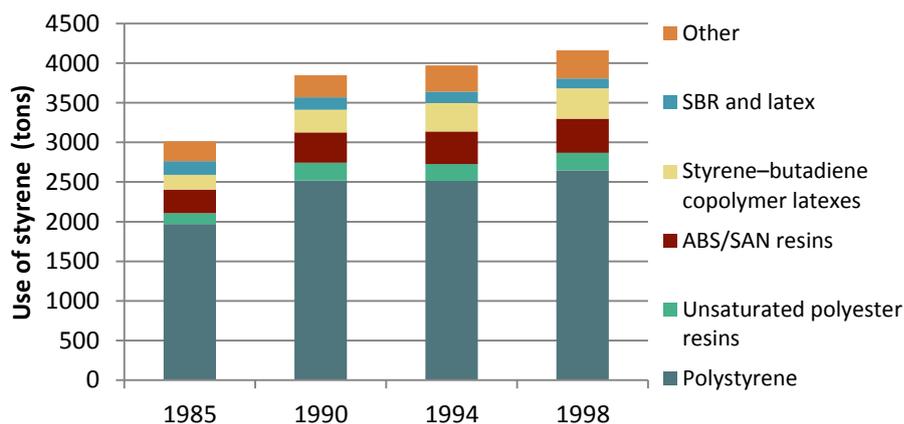


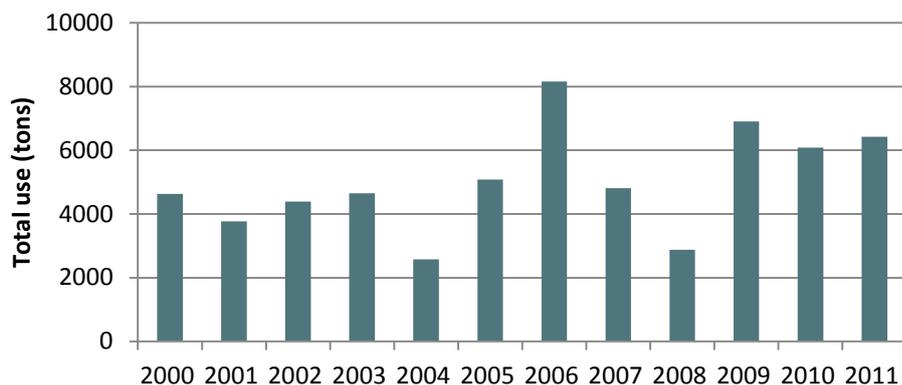
FIGURE 1  
DEVELOPMENT OF USE OF STYRENE POLYMERS IN WESTERN EUROPE (IARC 2002).

#### 3.4.2 Use pattern of styrene in Denmark

##### Styrene

The total use of styrene in mixtures in Denmark has varied between 2,000 and 8,000 t/y during the last decade, according to the SPIN database<sup>5</sup> (Figure 2). Since 2009, the total use has fairly constantly been around 6,500 t/y. However, the consumption in 2012 was in the range of 1550 – 4370 tons according to data directly from the Danish Product Register, possibly indicating a decrease in the use of styrene.

<sup>5</sup> The SPIN database provides data on the use of Substances in products and preparations in the Nordic countries. The database is based on data from the Product Registries of Norway, Sweden, Denmark and Finland and available at <http://195.215.202.233/DotNetNuke/default.aspx>



**FIGURE 2**  
TOTAL USE OF STYRENE IN MIXTURES IN DENMARK (DATA FROM SPIN DATABASE, 2014).

Several industrial players foresee that the use of styrene in Denmark might decrease in future as aspects of windmill and boat production are moved to other countries. This phenomenon, however, is mainly triggered by labour costs and not by the more restrictive Danish requirements with regard to the occupational environment.

### 3.5 Summary and conclusions

#### 3.5.1 Manufacture and consumption

Styrene is registered under REACH in the 1,000,000 - 10,000,000 tons/year band in the EU.

In 1993, European styrene production was estimated to range between 2 and 5 million tons. More recent figures indicate that European styrene production has been approximately 5,000,000 tons/year since 2007.

Recent trade figures show that the European import of styrene exceeds export, resulting in a current net import of about 290,000 tons.

EU consumption of styrene was about 3,808,000 tons in 1998, thus being considerable less than the consumption volume of approximately 5,400,000 tons in 2012.

There are no styrene production facilities located in Denmark. Danish consumption ranged from 1,550 to 4,370 tons in 2012 according to the Product Register, while the total consumption in 2011 was about 6,500 tons, indicating a small decrease in the use of styrene.

#### 3.5.2 Uses

Globally, the major use of styrene is as intermediate in closed systems in the chemical industry. Styrene is the monomer that is used for production of the following plastic materials (ECB, 2002):

- polystyrene (general purpose, GP-PS; high impact, HI-PS; and expanded EPS);
- copolymer systems (acrylonitrile-butadiene-styrene, ABS; styrene-acrylonitrile, SAN; methyl methacrylate-butadiene-styrene, MBS; and others);
- styrene-butadiene rubber (SBR);
- related lattices (SB Latex, for example), and
- component of unsaturated polyester resins (UP).

The production of polystyrene for packaging (PS and EPS) is the largest application area of styrene in Europe, followed by the production of the copolymer systems (ABS, SAN, SBR and SB latexes). The use in UP resins accounts for only a minor fraction (< 1% based on the 1998 figures) in Europe.

In Denmark, UP in windmill and boat production accounts for the largest application, while styrene polymers and copolymers are not produced in Denmark. Since styrene is a component of many binders, it might be present in certain construction materials, fillers, paints, varnishes, adhesives, and binding agents. Residual amounts are present in acrylate binders in polyurethane paints, water-based emulsion paints, acrylic copolymer dispersions, and paints and acrylic sealants in concentrations <0.8%.

# 4. Waste management

## 4.1 Introduction

Most styrene will end up as waste in the form of polymerized products with minute amounts of free styrene, if any. However, in the case that the products ending up in the waste stream are based on uncured styrene as reactive solvent, the amounts of styrene can be high and special care must be taken to prevent pollution.

However, the amount of styrene annually ending up in waste in Denmark is unknown, because:

- there is not a specific EAK<sup>6</sup> code for styrene; it falls under the EAK codes for organic solvents;
- styrene is often mixed with other compounds such as polyester or acetone when it is disposed of, and
- there are many EAK codes related to organic solvents because the EAK code system is built around industries, and there are many industries that use styrene.

Information about waste management has been based on the following:

- Technical literature;
- Internet searches;
- Contacts to industrial sector organisations: Danish Plastics Federation, Danish Coatings and Adhesives Association, and
- Contacts to companies producing thermoset fibre reinforced unsaturated polyester: (LM Windpower (wind turbine blades), Tunetanken (storage tanks) Fiberline (building and construction profiles).

## 4.2 Waste from production of styrene

Styrene is not manufactured in Denmark and, consequently, there are no associated waste streams from production of the chemical substance.

## 4.3 Waste containing styrene as reactive monomer

Waste may contain high amounts of free styrene from production sites using thermosetting glass fibre-reinforced unsaturated polyester (GUP), e.g. in the production of wind turbine blades, storage tanks, building profiles etc. where the reactive styrene monomer is left as a residue (e.g. if it is partly polymerised or deteriorated) in drums or storage tanks. This situation would mean that the substance will not be able to meet the quality criteria for production of GUP based products due to changes in viscosity and reactivity, and for this reason ends as a waste fraction.

Styrene as waste has to be disposed of as hazardous waste and must be collected and treated in plants for recovery or destruction by approved operators.

The same is the case for products containing more than 20% styrene or more (Affaldsbekendtgørelsen 1309/2012) because styrene is classified as a R36/38 substance.. On the other hand, waste

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<sup>6</sup> EAK: Det Europæiske AffaldsKatalog (European Waste Catalogue)

containing more than 20% styrene monomer will probably be very uncommon. It is expected that the classification of styrene containing products as dangerous waste will be changed to a substantially lower percentage in consequence of new classification of the substance as STOT RE1 and repr. 2.

One Danish wind turbine blade producer has stated that its annual amount of waste containing monomer styrene is on the order of 2-4 tons. It is estimated that only 2 -3% is styrene. The waste is sent to NORD as hazardous waste, code C (Karin Magelund Møller, LM Windpower, pers. comm. 2014).

Another Danish producer of tanks made from GUP has stated that the company does not have waste containing styrene monomer. If there is a faulty product, hardener is added. When it is hardened, it is sent to incineration or to a landfill depending on the amount of glass fibre present (Henrik Kjærholm, Tunetanken, pers. comm. 2014).

To prevent the release of styrene to the environment, it is important that products or raw materials containing free styrene are handled as hazardous waste in closed loops.

The styrene is decomposed by incineration and does not pollute the atmosphere because it is fully decomposed by the high incineration temperature and the stack gas filtering equipment used.

#### **4.4 Waste from manufacture and use of polymers based on styrene**

##### **4.4.1 Cross-linked polymers**

Fibre-reinforced thermosetting unsaturated polyester is used in huge amounts for composite products such as a number of different types of boats, car bodies, airplanes, caravans, containers, moulds for concrete, wind turbine blades, generator housings, process parts in chemical industry, pipe linings, skis, crash helmets, fishing rods and other reinforced consumer products (Plastteknologi, 2000).

The composite products have a long lifetime (20 – 100 years) compared to other products. Projections of waste of these composite materials, disposed of to the year 2020, have been developed by Lassen and Jensen (2002).

The projections foresee that the total volumes of composite waste from discarded products based on reinforced epoxy- and polyester thermosetting composites are 1,700-6,400 tonnes in 2000, 2,900-10,100 tonnes in 2010 and 5,700-15,300 tonnes in 2020. Included in the projections are products such as e.g. heating oil tanks left in the ground and refrigerated trailers that are exported and disposed of abroad. It should be mentioned that the projections are encumbered by high uncertainty.

Many of the wind turbines, including the UP blades that are replaced at present, are reused somewhere else, typically in Eastern Europe.

Due to the long lifetime, waste treatment and recycling in the industry is only incipient. In fact, none of the interviewed companies had yet experienced that their products were worn down. However, they have handled waste in e.g. damaged products or products not sold etc.

According to the tank producer, these products are disposed of in landfill or treated at incineration plants at the end of their useful life, depending on the amount of glass fibre. If a product has a low level of glass fibre it will be incinerated; a high level will result in disposal at a landfill (Henrik Kjærholm, 2014).

In terms of recycling of wind turbine blades, an innovation consortium GENVIND (started in 2012) in Denmark is investigating the possibility of crushing the blades and recycling the fibres in the blades. Other possibilities for recycling are pyrolysis of the polyester and recovery of the fibres.

A Danish company, Fiberline, send their faulty products to the German recycling plant Zajons where the glass fibre products are turned into useful materials for the cement industry. About 60–70% of the delivered glass fibre composites is used as raw material, whereas 30–40% is used as energy supply in cement production. The amount of composite waste from the industry is still too small to develop a business case for it.

Styrene-based cross-linked rubber is mainly SBR rubber (styrene butadiene rubber) used for tyre thread and for carpet backings. SBR rubber from tyres is recycled in plants where the tyres are mechanically shredded to rubber granulate or powder. The granulate is used for infill in artificial turf for soccer fields (approx. 100 tons per field), playing grounds and golf courses. The powder is used in new rubber compounds for tyres or other rubber goods. GENAN Business and Development in Viborg and Eldan Recycling A/S in Faaborg are both global market leaders in this shredding technology. Conveyor belts and carpet backings are expected to be incinerated or placed in landfill.

#### **4.4.2 Thermoplastic polymers**

The thermoplastic polymers (TPEs) based on styrene (SBS and SEBS) can be re-melted after use, which means that recycling of the polymers is much easier than for thermosetting polymers. The reason for this is that the TPEs are not cross-linked by chemical bonds between the polymer chains but rather by crystalline areas, which can melt. TPEs are used for a number of consumer goods, toothbrushes, sports shoes, toys, snorkels, etc. Through re-melting, it is possible to mold new products with the same shape or in another shape; a well-known example is PET Bottles (bottle to bottle).

The major portion of the styrene is used for the production of polystyrene including HIPS, shock resistant due to the incorporation of an elastic polybutadiene rubber in the polymer.

Other important plastics based on styrene are acrylonitrile butadiene styrene plastic (ABS) and SAN.

In mixed waste streams, it is important to keep the plastic products as clean as possible and, at a certain step of the recycling process, to assure that the plastics are sorted according to their chemical composition, e.g. pure PS, pure ABS and pure SAN.

A number of plastic sorting units are commercially available based on NIR infrared recognition sensor arrays; the capacity is high (approx. 3 tons per hour).

Sorting black plastics according to polymer type has so far been impossible or very expensive, but it appears that there are commercial solutions under development which can solve the problems with black plastics by using other wavelengths in the IR spectral area.

A washing step will, in most cases, be needed in the recycling process or after granulation to assure the necessary purity of the granules/flakes.

If the plastic is contaminated by chemicals or food or is exceedingly dirty, the best alternative is judged to be recycling by energy recovery in incineration plants or by feedstock recycling.

Only energy recovery by incineration is practiced in Denmark. Feedstock recycling demands huge amounts of waste to be economically profitable (20-50 tonnes per day) and is carried out in petrochemical plants.

PS and EPS might be depolymerized catalytically at higher temperatures with the formation of styrene monomer, which can be distilled to high purity and used as new raw material for styrene-based polymers (Scheirs, 1998). According to Scheirs (1998), PS completely decomposes to distillate products at 400 °C in the presence of heavy oil. The distillate obtained from waste PS comprised styrene monomer (52%), methyl-styrene (19.5%), toluene (13.6 %), ethyl benzene (11.7%) and cumene (3.3%) Heavy oil contributed 50% of the distillate.

By using base catalysis (BaO) the yield of styrene monomer and dimer is 90%. However, this process is not used in Denmark.

It is assessed that most plastics and TPEs based on styrene are currently incinerated for energy recovery, although recycling is possible.

This is also judged to be the case for EPS (known as "Flamingo") which is used for insulation and shock-absorbing packaging, but it is known that recycling is possible if the EPS is clean or washed. The Danish Plastics Federation has not been able to provide exact figures for the recycling of EPS in Denmark (pers. comm., 2014). The impression was that EPS waste was exported for recycling.

#### **4.5 Summary and conclusions**

Amounts of free styrene in styrene-based polymer products are so low that the health and environmental impact from free monomeric styrene in the waste can be ignored; for example, for food packaging there are strict rules regarding the content of residual styrene monomers, and for other products used in construction, it is judged that residual styrene has either evaporated due to the fairly low boiling point (145 °C) or polymerised due to heat or exposure to light or by oxidation.

Handling of styrene-based products by the end of their useful life is different depending on the type of product and the chemistry and processes involved in their manufacture.

Thermoset-based products (SBR rubber and UP based) often are placed in landfill (temporarily). During the recycling process they are shredded in one or more steps. It is foreseen that the amount of waste from thermoset-based products will increase in the future due to increased amounts of waste from tyres and buildings.

Thermoplastic styrene-based products can be recycled by re-melting to form new products after cleaning. However, it is assessed that, at present, thermoplastics are most often incinerated for energy recovery after use (post-consumer waste) and only internal production waste is recycled.

It is not possible to get an overview of the end-of-life waste of free unreacted styrene monomer as it has no well-defined EAK code.

Styrene as waste has to be disposed of as hazardous waste and must be collected and treated by approved operators. The same is the case for products containing 20% w/w styrene or more. It is expected that this will be changed to a substantially lower percentage in consequence of the new classification of the substance as STOT RE1 and repr. 2.

Overall, presently there is no indication that styrene in waste should constitute a health or environmental problem, however there is a data gap regarding the amounts of styrene ending up in the waste stream.



# 5. Environmental effects and exposure

This section on environmental fate, effects and exposure is largely based on the EU Risk assessment report (RAR) for styrene (ECB, 2002), which is considered still to be valid with regard to level of current knowledge. Searches for newer data have been made by consulting ECHA's registration database and US EPA's ECOTOX database but this has revealed only very few, more recent data.

## 5.1 Environmental fate

### 5.1.1 Abiotic degradation:

Hydrolysis of styrene does not take place as the substance does not possess hydrolysable groups, and photolysis in water is regarded as a marginal fate process for styrene because it absorbs very little irradiation at wavelengths above 300 nm. A photolytic half-life of 237 days has been suggested (ECB, 2002).

In the atmosphere, styrene undergoes rapid degradation by photooxidation with hydroxyl radicals and ozone. The calculated half-life of the process is about 4 hours (ECB, 2002).

### 5.1.2 Biodegradation:

A number of tests have been conducted showing that styrene is readily biodegradable in aqueous media; only in one test report did the substance fail to meet this criterion. In the EU Risk Assessment Report (RAR) for styrene (ECB, 2002), styrene is considered readily biodegradable.

Under natural environmental conditions in surface waters, styrene degrades with a half-life from 2-4 weeks while anaerobic biodegradation occurs more slowly with half-lives in the range of 4-30 weeks (ECB, 2002).

The following half-lives are used for environmental risk assessment in the RAR (ECB, 2002):

- Surface water: 15 days
- Soil: 30 days
- Sediment: 300 days
- WWTP: 0.69 hours

### 5.1.3 Environmental distribution:

Styrene has a relatively high vapour pressure and low-moderate water solubility and, hence, **volatilization** from water is considered to be an important and rapid process for removal of this substance from water. Rain-out from the atmosphere is not expected to be important (ECB, 2002).

Based on an estimated  $K_{oc}$  in soil of 352 based on the Log Pow value, styrene is considered to have a **moderate mobility in soil** (ECB, 2002).

The Log Pow of styrene is approx. 3 and an experimental BCF for fish (goldfish, *Carrassus auratus*) of 13.5 has been determined, while a BCF = 74 has been estimated based on the Log Pow (ECB, 2002). These values indicate a **rather low bioaccumulation potential** of styrene.

## 5.2 Environmental hazard

### 5.2.1 Classification

Styrene has a harmonised (CLP) classification, but it is not classified based on environmental hazards. In the self-classifications made by industry under REACH, 255 out of a total of 3059 notifiers have included “Aquatic Chronic 3” in their proposal for classification of styrene.

### 5.2.2 Environmental effects

Due to the volatility of styrene from water, as described in the environmental fate section (5.2), it is difficult to perform valid tests and obtain reliable results in standard ecotoxicity tests with this substance. Therefore, a number of acute toxicity studies identified, with styrene as test substance, and covering a range of aquatic species were disregarded (considered invalid) in the EU RAR (ECB, 2002) because they had been performed as static tests over 48-96 hours (depending on test organism). Presumably, substantial evaporation of the test substance occurred, resulting in reduced (and unknown) actual exposure concentrations.

The results of the remaining aquatic studies on fish, invertebrates and algae, considered valid or useful as supporting studies by ECB (2002), are summarised in the table below.

No chronic/long term studies with styrene were identified.

**TABLE 14**  
OVERVIEW OF DATA ON SHORT TERM TOXICITY OF STYRENE TO AQUATIC ORGANISMS IN LABORATORY STUDIES (DATA FROM ECB, 2002).

Group	Species	Study type	Endpoint	Value (mg/l)*
Fish, freshwater	<i>Pimephales promelas</i>	96 h, flow-through	LC50	10 (m)
	<i>Pimephales promelas</i>	96 h, flow-through	LC50	4.0 (m)
	<i>Onchorhynchus mykiss</i>	96 h, flow-through	LC50	5.9 (n)
	<i>Onchorhynchus mykiss</i>	24 h, flow-through	LC50	2.5 (n)
Invertebrates, freshwater	<i>Daphnia magna</i>	48 h, flow-through	EC50	4.7
	<i>Hyalella azteca</i>	96 h, flow-through	LC50	9.5
Algae	<i>Selenastrum capricornutum</i>	72 h, static	ErC50	4.9

\* (m) = measured concentration; (n) = nominal concentration

Thus, the most sensitive endpoint is the 96 h LC50 = 4.0 mg/l for the freshwater fish *Pimephales promelas* (fathead minnow). This endpoint was used in the aquatic risk assessment by ECB (2002).

In the RAR (ECB, 2002), a PNEC<sub>water</sub> = 40 µg/l for styrene was derived, applying the assessment factor AF = 100 to the LC50 value. This deviation from the AF = 1000, normally used when only acute data are available, was justified by the highly uniform toxicity values for different groups of organisms, indicating a non-specific (narcotic) mode-of-action of styrene.

For the terrestrial environment only one study, namely a standard artificial soil test according to OECD 207 with the earthworm *Eisenia foetida*, was identified by ECB (2002). This test resulted in a 14 day LC50 = 120 mg/kg soil dw. PNEC for the terrestrial environment to be used in the risk assessment was derived from the aquatic PNEC, leading to a  $PNEC_{\text{terrestrial}} = 255 \text{ mg/kg soil dw}$  (ECB, 2002). The risk of secondary poisoning caused by styrene was considered negligible.

Effects on plants and other organisms from exposure through the atmosphere are not considered likely to occur at environmentally relevant concentrations of styrene (ECB, 2002). Neither is styrene expected to contribute to low-level photochemical air pollution.

## 5.3 Environmental exposure

### 5.3.1 Sources of release

Styrene is not manufactured in Denmark and, hence, this industrial activity is not a possible source of release in Denmark. As described in Chapter 3, styrene is imported to Denmark and used for production of a considerable number of polymer products (more than 700) based on either pure polystyrene (PS), various styrene copolymers (ABS, SAN, SBR) or unsaturated polyester resins (UP). The main part of the import is used for products based on pure polystyrene (GP-PS, HI-PS, EPS) followed by copolymer products (primarily ABS) and UP.

Emission to air is considered to be the primary pathway of release to the environment, either directly from the manufacturing plants or due to residual monomer present in the products manufactured.

The RAR (ECB, 2002) presents Predicted Environmental Concentrations (PECs) for styrene in the main environmental compartments. At the regional level, the following PEC values are reported:

$$PEC_{\text{air}} = 0.034 \text{ } \mu\text{g}/\text{m}^3$$

$$PEC_{\text{surface water}} = 0.052 \text{ } \mu\text{g}/\text{L}$$

$$PEC_{\text{sediment}} = 0.37 \text{ } \mu\text{g}/\text{kg ww}$$

$$PEC_{\text{soil, natural}} = 0.002 \text{ } \mu\text{g}/\text{kg ww} ; PEC_{\text{soil, agricultural}} = 0.14 \text{ } \mu\text{g}/\text{kg ww}.$$

### 5.3.2 Monitoring data

#### The Danish NOVANA assessment programme

Styrene does not belong to the substances that are monitored under the Danish national environmental surveillance programme, NOVANA, either in air or in any of the other environmental compartments. Therefore, no Danish environmental monitoring data have been identified.

#### Monitoring data from outside Denmark

ECB (2002) mentions German surface water data for styrene with mean monthly concentrations from <0.01 up to 0.11  $\mu\text{g}/\text{l}$ ; data from other parts of the world (Canada, Japan) indicate levels of styrene in the sub-  $\mu\text{g}/\text{l}$  range.

For the air compartment, ECB (2003) refers briefly to Dutch monitoring results from 1979-80 at three locations (rural, suburban and source dominated) showing mean values of styrene from 0.09 to 1.5  $\mu\text{g}/\text{m}^3$  and corresponding maximum values from 0.65 to 27.7  $\mu\text{g}/\text{m}^3$ . In another Dutch study from 1986 (cfr. ECB, 2002), a level of 0.200  $\mu\text{g}/\text{m}^3$  was found in a rural area, while urban data from 1977 (also Dutch) showed a mean of <0.43  $\mu\text{g}/\text{m}^3$  with a max. of 3  $\mu\text{g}/\text{m}^3$ . Data from other parts of the world referred to by ECB (2002) appear to be at approximately the same or slightly higher level. The rural levels referred to appear to be moderately higher than the modelled regional PEC for air (0.034  $\mu\text{g}/\text{m}^3$ ).

#### **5.4 Environmental impact**

The EU RAR for styrene (ECB, 2002) concludes, with regard to the environment, that *“there is at present no need for further information and/or testing and for risk reduction measures beyond those which are already being applied already”*. This conclusion corresponds well with the PNEC values determined for styrene compared to the low concentrations found in monitoring studies (“PEC”) performed outside Denmark.

#### **5.5 Summary and conclusions**

Styrene is a volatile substance evaporating easily from water and soil surfaces and degrading quite rapidly in the air compartment by photooxidation, resulting in various VOC degradation products and thereby contributing to tropospheric ozone formation.

Styrene is considered easily biodegradable in water, while abiotic degradation is insignificant. From the sorption characteristics, styrene is considered mobile in soil, while the bioaccumulation potential is rather low.

The toxicity of styrene to aquatic organisms such as fish and crustaceans is moderate, with short term LC/EC<sub>50</sub> values of approximately 4-10 milligrams per litre. Although data is limited, the toxicity in the terrestrial compartment appears to be moderate-low with regard to earthworms and low to plant species (exposed to styrene via air).

Based on the fate and effects data, it is concluded that styrene is neither PBT nor vPvB.

Styrene is assessed to be released primarily to the air compartment, partly from the many different types of productions where they are used and partly from evaporation during use of the products for a variety of purposes, e.g. paints and other coatings, adhesives, polymers, maintenance and repair of vehicles etc.

Monitoring data show low levels of styrene in the environment with surface water concentrations in the sub- µg/l range. For the air compartment, Dutch monitoring data showed mean concentrations of 0.09 to 1.5 µg/m<sup>3</sup>, which appear to be at approximately the same or slightly higher level than monitoring data from other countries.

Thus, overall styrene is not considered to be a substance of significant environmental concern.

# 6. Human health effects and exposure

The toxicity of styrene has been intensively investigated in both humans and experimental animals and has been described in detail in the RAR for styrene, for which UK was the rapporteur Member State (UK, 2008). The data on toxicokinetics, acute toxicity, irritation, sensitization, genotoxicity and cancer are summarised in the following sections, based on the RAR.

In 2011, the Danish EPA submitted a CLH report ‘Proposal for Harmonised Classification and Labelling for styrene’ for repeated dose toxicity and for reproductive toxicity to ECHA (Danish EPA, 2011), based on which the ECHA Risk Assessment Committee published an opinion (RAC, 2012). Furthermore, WHO (2003) developed a TDI for styrene in their guidelines for Drinking Water Quality. The data on repeated dose toxicity and on reproductive toxicity are summarised in the following, based on the RAR and the Danish CLH report, and supplemented with information from RAC (2012) and WHO (2003).

## 6.1 Human health hazard

### 6.1.1 Classification

Styrene is subject to harmonised classification as a health hazard as an acute toxicant (class 4), a skin irritant (cat. 2), and an eye irritant (cat. 2) (Table 15).

**TABLE 15**  
HARMONISED HEALTH HAZARD CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International chemical identification	CAS No	Classification	
			Hazard Class and Category Code(s)*	Hazard statement Code(s)**
601-026-00-0	Styrene	100-42-5	Acute Tox. 4 *** Eye Irrit. 2 Skin Irrit. 2 STOT RE1 **** Repr. Cat. 2 ****	H332 H319 H315 H372 (hearing organs) H361d

\* Hazard Class - Acute Tox.: Acute toxicity; Eye Irrit. : Eye irritation; Skin Irrit. : Skin irritation; STOT RE: Specific target organ toxicity – repeated exposure; Repr.: Reproductive toxicity

\*\* Health hazards - H332: Harmful if inhaled; H319: Causes serious eye irritation; H315: Causes skin irritation; H372: Causes damage to the hearing organs; H361d: Suspected of damaging the unborn child.

\*\*\* Minimum classification, applies when classification according to the criteria in Directive 67/548/EEC does not correspond directly to the classification in a hazard class and category under the CLP Regulation.

\*\*\*\* This classification was added with the 6<sup>th</sup> adaptation to technical progress to the CLP regulation, adopted in December 2013 and expected to be published in spring 2014 (Danish EPA, personal comm. 2014).

### 6.1.2 Toxicokinetics

In humans, styrene vapour is well absorbed via inhalation, with an absorbed fraction of inhaled styrene of approximately 100% (at concentrations of 10-200 ppm). Following inhalation the absorption rate in humans and in rats is approximately the same, whereas the absorption rate is 2-3 fold higher in mice compared to rats. Based on an *in vitro* dermal penetration study using human skin samples, uptake after dermal contact with liquid styrene has been estimated to be approximately 2% of the applied dose. Uptake after dermal contact with styrene vapour is not significant (5% or less). No information is available on oral absorption in humans. Based on the physico-chemical properties of styrene and experimental animal information, the RAR (UK, 2008) determined an absorbed fraction of ingested styrene of approximately 100%.

Styrene and/or its metabolites are widely distributed throughout the body with the highest concentrations in fat; concentrations in brain tissues are generally higher than in blood. A study in pregnant mice has shown that styrene and/or its metabolites can cross the placenta and reach the foetus.

In humans, styrene is eliminated from the body relatively rapidly, primarily in the urine. The elimination of styrene from the blood following inhalation is biphasic, with half-lives of 0.6 hours for the first elimination phase and 13 hours for the second elimination. There is some evidence for a longer elimination half-life from human adipose tissue following repeated daily exposure to styrene.

Styrene is metabolised extensively in humans and experimental animals. The first step in the metabolism of styrene is oxidation of the aromatic ring or side-chain by the P450 enzyme system. The major metabolic route in each species is oxidation of the side chain to give the epoxide, styrene-7,8-oxide (SO). SO is either conjugated with glutathione (GSH) to give mercapturic acids, or is hydrolysed by epoxide hydrolase (EH) to phenylglycol which is further metabolised to mandelic acid, and eventually to phenyl glyoxylic acid or benzoic acid, which is excreted as its glycine conjugate hippuric acid.

Another metabolic pathway involves ring hydroxylation to give 4-vinylphenol (4-VP), and products of ring opening which are conjugated with glutathione. Other minor metabolic pathways involve side-chain oxidations to give phenyl acetaldehyde (PA) and phenylacetic acid (PAA) (via side-chain  $\beta$ -oxidation and hydroxylation), phenyl ethanol and acetophenone (via side-chain  $\alpha$ -oxidation and hydroxylation), to give products of ring-opening. The metabolites formed in the different metabolic pathways are then excreted in the urine.

According to a PBPK model, saturation of styrene metabolism in humans occurs at concentrations of approximately 850 mg/m<sup>3</sup> styrene in air.

Data from *in vitro* studies and PBPK modelling indicate significant differences in the metabolism of styrene between species.

In humans, the major part of absorbed styrene (95%) is metabolised to SO and further metabolised by EH. Approximately 5% is metabolised via the PA pathway, and only trace amounts (<1%) of SO-GSH conjugates or ring-oxidised metabolites (4-VP pathway) are recovered.

In rodents, metabolism of SO by EH is less extensive (68-72% in rats and 49-59% in mice), whereas conjugation of SO with GSH accounts for up to approximately 33% of absorbed styrene. The most significant differences between mice and rats are related to the production of phenylacetaldehyde (PA pathway: 12-22% in mice; 3-5% in rats) and to products of ring-oxidation (4-VP pathway: 4-8% in mice; <1% in rats).

### **6.1.3 Acute and chronic toxicity**

#### ***Acute toxicity***

Styrene is of moderate acute toxicity in rats and guinea pigs following inhalation and of low acute toxicity following oral intake. In rats, an inhalation LC<sub>50</sub>-value of 11,800 mg/m<sup>3</sup>/4 hours and an oral LD<sub>50</sub>-value of approximately 5000 mg/kg bw have been reported. In contrast to rats and guinea pigs, mice appear to be more sensitive to a single exposure to styrene, which is most likely due to species differences in the metabolism of styrene.

Following inhalation, acute effects observed in rats and guinea pigs include marked signs of irritation of the eyes and nasal mucosa, general signs of central nervous system (CNS) depression, changes in the lungs (congestion, haemorrhage, oedema, exudation and leukocyte infiltration). No acute dermal toxicity studies are available, but the RAR concluded that low acute dermal toxicity could be predicted based on the available toxicokinetic, toxicodynamic and physico-chemical data. Based on the available data in experimental animals, styrene is classified in terms of acute toxicity (Acute Tox. 4) with the hazard statement H332 (harmful if inhaled) (UK, 2008).

#### ***Acute effects on the central nervous system***

In humans, effects on CNS function and minor impairment in neurobehavioural test performance have been observed following inhalation of styrene; a NOAEC of 433 mg/m<sup>3</sup> (for 7 hours) was identified for CNS depression and of about 870 mg/m<sup>3</sup> (for 1 hour) for impairment in neurobehavioural test performance in the RAR.

#### ***Irritation and sensitisation***

The results of the limited studies performed in experimental animals indicate that liquid styrene is not significantly irritating to the skin after a single exposure, but that repeated exposure causes irritation. Styrene is classified as a skin irritant (Skin Irrit. 2) with the hazard statement H315 (causes skin irritation).

The results of the very limited studies from 1942, 1956, and 1996 performed in experimental animals indicate that liquid styrene and styrene vapour has the potential to cause eye irritation. In humans, styrene vapours in concentrations of approximately 1600 mg/m<sup>3</sup> were clearly irritating to the eyes; NOAECs of 935 mg/m<sup>3</sup> (for 1 hour) and of 433 mg/m<sup>3</sup> (for 7 hours) were identified for eye irritation in the RAR. Styrene is classified as an eye irritant (Eye Irrit. 2) with the hazard statement H319 (causes serious eye irritation).

Irritation to the respiratory tract (nasal) has been observed in experimental animals as well as in humans exposed to styrene vapour. Based on the human data, NOAECs of 935 mg/m<sup>3</sup> (for 1 hour) and of 433 mg/m<sup>3</sup> (for 7 hours) were identified for respiratory tract (nasal) irritation in the RAR.

The RAR concluded that the reporting of the available animal skin sensitization data (two guinea pig maximization tests) is inadequate and therefore, a clear conclusion on the skin sensitizing potential cannot be drawn from these studies. No human studies are available. The RAR concluded that styrene has no significant potential to cause skin sensitization as only one possible case of skin sensitization has been reported despite the widespread use of styrene. Similarly, the RAR concluded that styrene has no significant potential to cause respiratory tract sensitization as only two case reports of asthma have been reported despite the extensive inhalation exposure to styrene in humans. No studies in experimental animals are available.

#### ***Repeated dose toxicity***

There is a large amount of information on effects of styrene from repeated exposure of humans. The most predominant symptoms reported in worker health survey studies are eye and nasal irritation and CNS disturbance (drowsiness, headache, light-headedness). Based on all the human data available, the RAR concluded that the crucial issue in relation to the impact of styrene on the

nervous system is the need to avoid acute CNS depressant effects and associated symptomatology (UK, 2008).

A number of effects have been observed in rats and mice following repeated exposure to styrene including effects on the nasal epithelium (rat, mouse), the lung (mouse), the liver (mouse) and the central nervous system (rat, mouse). A NOAEC was not identified in the RAR for nasal epithelium damage in the rat as chronic inflammatory changes in the olfactory epithelium were seen following exposure to 215 mg/m<sup>3</sup> styrene (the lowest concentration tested) in a 2-year rat inhalation study. Similarly, a NOAEC was not identified in the RAR for lung damage in the mouse as damage to the lung epithelium was seen following exposure to 85 mg/m<sup>3</sup> styrene (the lowest concentration tested) in a 2-year mouse inhalation study. In relation to the liver, exposure to styrene in concentrations ranging from 650-1500 mg/m<sup>3</sup> has produced fatal hepatotoxicity in mice; a NOAEC was not identified in the RAR. The RAR concludes that the lung tissue findings in mice reflect a toxic response that will not occur to any significant extent in humans at relevant levels of exposure. This is also the conclusion in relation to the fatal hepatotoxic effects observed in mice. These toxic responses appear to be linked to the metabolic activation of styrene to styrene oxide, which render the mouse more susceptible than humans to lung and liver damage.

The neurotoxicity of styrene is well documented in experimental animals. Besides the effects on hearing and colour discrimination, other studies have shown a number of different effects in the nervous system (UK, 2008; Danish EPA, 2011). Based on the available animal inhalation repeated dose toxicity studies, the RAR concluded that ototoxicity is the most sensitive and relevant effect of styrene repeated inhalation exposure (UK, 2008).

The ototoxicity of styrene in the rat is well documented. Clear evidence of ototoxicity (both functional and histological) has been seen in sedentary/ordinary rats repeatedly exposed to styrene by inhalation at concentrations from 2600 mg/m<sup>3</sup>. In three different studies, no such effects were seen at 865 mg/m<sup>3</sup> for 13 weeks, or at 1300 mg/m<sup>3</sup> or 2165 mg/m<sup>3</sup> for four weeks (UK, 2008; Danish EPA, 2011). Based on the data from studies in experimental animals (rat), a NOAEC for potential ototoxic effects of styrene of 2165 mg/m<sup>3</sup> was suggested in the RAR (UK, 2008). From the studies in rats a NOAEC between 1300-2600 mg/m<sup>3</sup> for hearing loss can be identified (Danish EPA, 2011). The available human data indicate a relationship between styrene exposure and hearing loss as well as effects on vestibular reflexes in some workers. The observed ototoxicity in animals may therefore also be relevant to humans. In addition, the human studies indicate that the sensitivity for developing hearing loss might be substantially greater in humans than in rats, as one study indicated that exposure to styrene at concentrations below 87 mg/m<sup>3</sup> produced high-frequency hearing loss (Danish EPA, 2011).

Twelve epidemiological studies investigating colour discrimination in workers exposed to styrene provide evidence that styrene causes changes in colour discrimination. The most recent study (cited as Gong et al., 2006) showed that exposure to styrene would impair colour vision even if the exposure concentration was lower than 43 mg/m<sup>3</sup>. The ocular effects of styrene in experimental animals have not been studied in depth, but there is one study showing effects on the number of the large amacrine cells as well as on the content of neuramines and glutathione of the retina of rats exposed repeatedly to 1300 mg/m<sup>3</sup> styrene for 12 weeks. (Danish EPA, 2011). Based on the human data, a NOAEC for changes in colour vision of 216.5 mg/m<sup>3</sup> was suggested in the RAR (UK, 2008).

In 2011, the Danish EPA submitted a proposal for classification of styrene for repeated dose toxicity (STOT RE 1) with the hazard statement H372 (causes damage to the nervous system through prolonged or repeated exposure by inhalation) (Danish EPA, 2011). In the RAC opinion on the Danish classification proposal, it is concluded that there is sufficient evidence of repeated dose toxicity to warrant classification as STOT RE 1. However, the RAC considered the effects of styrene on colour vision in humans as supportive of the STOT classification, but the degree to which this

effect can be considered to be adverse is difficult to establish based on the proposal. Therefore, the RAC concluded that the hazard statement H372 should be rephrased (causes damage *to the hearing organs* through prolonged or repeated exposure by inhalation) (RAC, 2012).

### **Mutagenicity/genotoxicity**

*In vitro* assays with bacterial test systems and with yeast, and mammalian cell studies (chromosome aberration, sister chromatid exchange (SCE), unscheduled DNA synthesis) have yielded both negative and positive results. Metabolic activation (presumably to styrene oxide) is required for the *in vitro* genotoxic activity of styrene.

The results from the *in vivo* chromosome aberration studies following single or repeated exposure to styrene up to concentrations and/or doses causing systemic toxicity were generally negative. Similarly, styrene did not show a genotoxic potential up to concentrations and/or doses causing systemic toxicity in most of the *in vivo* micronucleus assays. An increase in micronucleus frequency was observed in styrene-treated mice (3 studies); the RAR concluded, however, that these findings should not be regarded as convincing evidence of mutagenicity *in vivo*. Styrene did not induce DNA repair in hepatocytes of female mice in an *in vivo* unscheduled DNA synthesis study (inhalation). In general, the SCE results have been positive in the wide range of tissues examined; the RAR concluded, however, that the significance of the SCE findings in relation to mutagenicity is clearly reduced as the results of the concomitant chromosome aberration and/or micronucleus assays involving the same animals and, in some cases, the same tissues were negative in most cases.

Styrene at high doses lead to DNA strand breakage in various tissues of mice, but not of rats; the RAR concluded, however, that the significance of these findings is unclear given the repeated failure of styrene to demonstrate mutagenic activity in standard clastogenicity assays. DNA binding studies indicate an interaction with DNA leading to various covalently bound DNA adducts in various organs from rats and mice exposed to styrene. Based on standard regulatory tests, the RAR concluded that there is no convincing evidence that styrene possesses significant mutagenic/clastogenic potential *in vivo*.

Based on the large number of studies aimed at investigating the genotoxic potential of styrene in humans by examination of various endpoints in styrene exposed workers, the RAR concluded that there is no convincing evidence that styrene possesses significant mutagenic/clastogenic potential *in vivo* or has shown mutagenic activity in humans.

Overall, the RAR concluded that there is no concern for mutagenicity of styrene (UK, 2008).

The main metabolite styrene-7,8-oxide is a direct acting mutagen in several *in vitro* test systems but shows contradictory results *in vivo*. IARC concludes based on results from both animal studies and humans that styrene exposure can result in low levels of DNA adducts and DNA damage in individuals who possess the capacity to activate styrene metabolically to its epoxide metabolite, styrene 7,8-oxide. These results may be relevant for other organs than the lung.

### **Carcinogenicity**

Increased risks for lymphatic and haematopoietic neoplasms have been observed in some epidemiological studies of workers exposed to styrene. The RAR considered, however, that the findings were not robust and could be due to chance, bias or confounding by other occupational exposures. Therefore the RAR concluded that there is no clear and consistent evidence for a causal link between specific cancer mortality in humans and exposure to styrene.

The results of the inhalation and oral carcinogenicity studies in rats indicate that styrene is not carcinogenic to rats. Styrene-7,8-oxide (SO) has been shown to be carcinogenic in long-term oral studies in rats (WHO, 2003). The relevance of the carcinogenic effect of styrene in the lungs of mice

has been extensively discussed and is most likely due to species differences in the metabolism of styrene. Therefore the RAR concluded that the overall weight of evidence indicates that the lung tumours observed in mice are unlikely to be of any relevance for human health at relevant levels of exposure.

Styrene has been evaluated for carcinogenicity by IARC in 2002 (IARC, 2002). The Working Group considered it likely that the proposed mechanism for tumour formation in the mouse lung involving metabolism of styrene to 7,8-oxide (SO) in mouse Clara cells (non-ciliated bronchiolar epithelial cells) is not operative in human lungs to a biologically significant extent. However, based on the observations in human workers regarding blood SO, DNA adducts and chromosomal damage, the Working Group was of the opinion that it cannot be excluded that this and other mechanisms are important for other organs. IARC concluded that styrene is possibly carcinogenic to humans (Group 2B). The RAR reflected that pointing to a possible carcinogenic potential of styrene in other organs is highly speculative and overall, the RAR concluded that there is no concern for carcinogenicity of styrene in humans (UK, 2008).

### ***Reproductive toxicity***

No effects on fertility and reproductive performance were observed in rats exposed to styrene at concentrations up to 2165 mg/m<sup>3</sup> in a well-conducted two-generation inhalation study. The other relevant studies available did not show convincing evidence that styrene can impair reproductive performance, produce testicular toxicity or sperm abnormalities, or adversely affect the reproductive organs. (UK, 2008; Danish EPA, 2011). The RAR concluded that the data available indicate that styrene does not have the potential to impair fertility and reproductive performance in animals (UK, 2008).

In the rat, styrene did not cause significant effects on conventional developmental toxicity parameters (i.e. malformations, death) at inhalation exposure concentrations of up to approximately 2600 mg/m<sup>3</sup> styrene or oral exposure of up to 250 mg/kg bw/day. In a well-performed two-generation study including developmental neurotoxicity assessment, in the F<sub>2</sub> offspring, a pattern of pup developmental delays both before and after weaning (decreased pup weights, delays in attaining some pre-weaning developmental landmarks, slight shift in the normal pattern of motor activity, delayed preputial separation, decreased swimming ability, small reductions in forelimb grip strength) were seen postnatally in rats following inhalation exposure levels of 1300-2200 mg/m<sup>3</sup>. Significantly decreased pup body weight (up to 10%) has been observed during the lactation period in the two-generation study following an inhalation exposure level of 650 mg/m<sup>3</sup> (UK, 2008; Danish EPA, 2011).

In humans, the epidemiological studies, particularly focusing on developmental effects, have generally been negative and provide no reliable evidence for styrene exposure-related adverse effects in relation to spontaneous abortions, congenital abnormalities, birth weight, menstrual disorders, male fertility or sperm quality within the exposure ranges investigated. However, most of the epidemiological studies lacked adequate exposure information and were considered to be too small to be conclusive. It is concluded that there is no clear evidence of an effect of styrene on human reproduction, but data are too limited to exclude the possibility for effects (UK, 2008; Danish EPA, 2011).

Taking into account all of the available information, a NOAEC for potential effects of styrene on development of 650 mg/m<sup>3</sup> was suggested in the RAR (UK, 2008).

Denmark's proposal for classification of styrene included classification for reproductive toxicity (Repr. 1B) with the hazard statement H360d (may damage the unborn child when exposed via inhalation) (Danish EPA, 2011). In the RAC opinion on the Danish classification proposal, it is concluded that there is sufficient evidence for developmental effects to warrant classification as

Repr. 2 with the hazard statement H361d (suspected of damaging the unborn child) (RAC, 2012). The conclusion is based on indications of effects on development, but these effects are “rather inconsistent” and do not therefore qualify as the ‘clear evidence’ required by CLP classification with Repr. 1B. Furthermore, a possible relationship between the effects could not be completely ruled out (RAC, 2012).

### ***Endocrine disruption***

The information on endocrine disruption included in the RAR (UK, 2008) is summarized below.

In female styrene-exposed group workers, the serum prolactin and human growth hormone levels were statistically significantly higher, by about two fold, compared with control group values. No significant differences were observed between the two groups in the levels of thyroid stimulating hormone (TRH) and gonadotrophins. The RAR reflected that, in the absence of confirmation of the results and explanation of the findings and their biological significance, these differences could be considered to be a reliable reflection of styrene toxicity.

In another study, the serum prolactin level was reported to be statistically significantly higher in female styrene-exposed workers compared to the control group.

No evidence of any treatment-related effects on uterine weights or tissue histopathology was observed in an uterotrophic assay in rats administered doses of up to 200 mg/kg subcutaneously once a day for 3 consecutive days.

Plasma prolactin levels were significantly increased in female rats exposed by whole body inhalation to 650 mg/m<sup>3</sup> styrene vapour (8 hours/day for 10 days) compared to control females; no significant change was observed in male rats exposed similarly. As well, no differences in blood serum levels of prolactin were observed in male rats exposed to styrene by inhalation at concentrations of 0, 645, 2150 or 6450 mg/m<sup>3</sup>, for 6 hours/day on 5 consecutive days; or following a single intra-venous injection of 5.8 mg styrene over 1 hour. In the absence of information on the normal background levels of prolactin in the rat, the RAR considered that the relatively minor increase in plasma prolactin in female rats is unlikely to be of toxicological significance (UK, 2008).

A decrease in plasma testosterone level was observed in mice given an oral dose of 12 mg/kg bw/d styrene in drinking water for 4 weeks. The RAR considered that the full toxicological significance of this finding is unclear given the absence of histopathological findings in the testes, the absence of background information on the possible normal range of testosterone levels that might be expected in young mice, and the absence of such effects at low dose levels in other well documented studies (UK, 2008).

An exposure-related increase in oestrus cycle was reported in mice exposed by inhalation to 62.5 to 500 ppm styrene for 90 days (no further details are provided as only an abstract was available). The RAR noted that it is not clear from the abstract whether or not all exposure levels produced such effects.

No evidence for oestrogenic or androgenic activity of styrene was observed in *in vitro* studies (UK, 2008).

Overall, the RAR concluded that there is no evidence that styrene possesses significant endocrine disruption activity (UK, 2008).

However, styrene has been placed in category 1 on the EU priority list for endocrine disruptors<sup>7</sup>. This category includes substances for which there is evidence of endocrine disrupting activity in at least one species using intact animals. The rationale for placing styrene in category 1 on the priority list is given below.

Effects on the pituitary, in the form of elevation in prolactin level and enhanced TRH stimulated prolactin secretion in female styrene-exposed workers, have been reported. Two of the three references mentioned in the database on the endocrine disruptors present on the EU priority list have also been included in the RAR (in the section addressing neurotoxic effects of styrene in humans) and are described above.

In addition, severe impairment of the immunological defence system was indicated by reduced blood complement titre and depressed leukocyte phagocytic activity in rabbits exposed to a dose of up to 250 mg/kg bw for up to 216 days. This reference, a Russian article from 1969 (in Russian), is not included in the RAR.

The WHO 'Environmental Health Criteria' on styrene (EHC 26 from 1983) is also mentioned as a reference in the database on the endocrine disruptors.

Within the EU, discussions on criteria for identifying a chemical substance as an endocrine disruptor are ongoing. Whether or not styrene is classified as an endocrine disruptor according to the EU criteria is a decision that awaits the adoption and publication of the criteria.

#### 6.1.4 No-effect levels

Based on the previous sections, the no-observed-adverse-effect-concentrations (NOAEC) are summarised in Table 16.

The concentration of 433 mg/m<sup>3</sup> is the lowest NOAEC reported for acute effects on the central nervous system.

With respect to repeated dose toxicity, a NOAEC of 1300 - 2600 mg/m<sup>3</sup> was identified for hearing loss in rats. Hearing effects in humans have been suggested to occur at considerably lower concentrations (below 87 mg/m<sup>3</sup>), but a NOAEC for hearing effects in humans has not been established. The lowest NOAEC for humans has been determined at 216.5 mg/m<sup>3</sup> for changes in colour vision.

In relation to repeated oral exposure, a NOAEL of 150 mg/kg/day for hepatic necrosis was identified from a 2 year cancer bioassay with mice. The RAR also notes that extrapolation to humans requires careful consideration of the mouse's metabolism and its high sensitivity for liver toxicity as compared to e.g. the rat.

**TABLE 16**  
NO OBSERVED ADVERSE EFFECT CONCENTRATIONS OF STYRENE

Organism	Exposure	Effect	NOAEC/NOAEL	Reference
Human	Inhalation (7 hours)	CNS depression	433 mg/m <sup>3</sup>	UK, 2008
Human	Inhalation (1 hour)	Impairment in neurobehavioural test performance	870 mg/m <sup>3</sup>	UK, 2008
Human	Inhalation (1 hour)	Eye irritation	935 mg/m <sup>3</sup>	UK, 2008

<sup>7</sup> [http://ec.europa.eu/environment/chemicals/endocrine/index\\_en.htm](http://ec.europa.eu/environment/chemicals/endocrine/index_en.htm)

Organism	Exposure	Effect	NOAEC/NOAEL	Reference
Human	Inhalation (7 hours)	Eye irritation	433 mg/m <sup>3</sup>	UK, 2008
Human	Inhalation (1 hour)	Respiratory tract (nasal) irritation	935 mg/m <sup>3</sup>	UK, 2008
Human	Inhalation (7 hours)	Respiratory tract (nasal) irritation	433 mg/m <sup>3</sup>	UK, 2008
Rat	Inhalation (4 weeks)	Ototoxicity	2165 mg/m <sup>3</sup>	UK, 2008
Human	Inhalation (8 hr TWA)	Changes in colour vision	216.5 mg/m <sup>3</sup>	UK, 2008
Rat	Inhalation (2-generation study)	Developmental effects	650 mg/m <sup>3</sup>	UK, 2008
Rat	Inhalation (several studies)	Hearing loss	1300-2600 mg/m <sup>3</sup>	Danish EPA, 2011
Mouse	Oral (5 days a week for 78 weeks)	Mortality and hepatic necrosis	150 mg/kg/day	UK, 2008
Rat	Oral (5 days a week for 78 weeks)	Hepatic necrosis	1000 mg/kg/day	UK, 2008

### **Occupational exposure limit values**

Occupational exposure limit values for styrene for selected European countries are presented in Table 17. Until now, there has been no European indicative occupational exposure limit value available for styrene (see chapter 2.1).

**TABLE 17**  
OCCUPATIONAL EXPOSURE LIMIT VALUES FOR STYRENE FOR SELECTED COUNTRIES

	Limit value 8-hours		Limit value short term		Reference
	Ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>	
Denmark*	25	105	-	-	Danish statutory order No. 986 of 11/10/2012
Germany**	20	86	40	172	GESTIS database, 2014

\* Absolute limit values ("loftværdier") which may not be exceeded at any time.

\*\* The short-term values are average values for exposures of 15 min, which may occur 4 times during a shift with at least 1 min between the exposures.

### **Tolerable daily intake**

WHO has established a tolerable daily intake (TDI) of 7.7 µg/kg bw derived from a NOAEL of 7.7 mg/kg bw/d for reduced body weight in a 2-year drinking water study (cited as Litton Bionetics, 1980) in rats applying an uncertainty factor of 1000 (100 for intra- and interspecies variation and 10 for carcinogenicity and genotoxicity of the reactive intermediate styrene-7,8-oxide) (WHO, 2003).

In a drinking water study in rats from 1985 mentioned in the RAR (cited as Beliles et al., 1985; most likely related to the study mentioned in WHO, 2003), a slight (around 10%) but statistically significant reduction in bodyweight was observed in females at 21 mg/kg bw/d after 2 years. No

effects were observed at concentrations in drinking water of 125 ppm (corresponding to 7.7 mg/kg bw/d for male rats). However, in the absence of other findings, the RAR concludes that there is no clear evidence of toxicity in this study, and therefore it is not used for the establishment of a NOAEL, or for further risk characterisation. Instead, the RAR uses the oral NOAEL of 150 mg/kg/day for hepatic necrosis from a 2 year cancer bioassay with mice for the risk characterisation.

However, using significantly reduced body weight as a relevant adverse effect for establishing the NOAEL of 7.7 mg/kg bw/d as basis for risk characterization and derivation of a TDI is in accordance with EU methodology.

## **6.2 Human exposure**

Human exposure data for both consumer and worker exposures are provided in the RAR (UK, 2008). With respect to the working environment, the information has been supplemented by the Danish Working Environment Authority and through contact to Danish companies in the UP industry.

### **6.2.1 Direct exposure**

#### **Consumers**

Potential consumer exposure is described as follows (UK, 2008):

*“Consumers may be exposed through the release of residual styrene monomer from polymeric styrene products. This exposure may follow emission into the atmosphere from materials such as carpet backing and underlay, or migration from food wrappings into food. Consumers may also be exposed to the monomer if they use styrene-containing resins for filling or repair of wood, glass fibre or metal, or use styrene based adhesives. The resin exposures may be infrequent and acute but are potentially high – comparable to equivalent work in an occupational setting. Styrene is also present in the diet from natural sources, from chewing gum and tobacco smoke.”*

Exposures were estimated using measured and modelled data from the above sources.

Because of assumptions and partly insufficient data, there are some uncertainties in the calculations of human uptake. However, it was attempted to differentiate between continuous low-level exposures to styrene and the short-term, sporadic exposures which may arise from certain consumer activities such as repairing. The extent of absorption following exposure, and consequent uptake, was considered in the risk characterisation of the RAR (UK, 2008).

In the RAR, several studies (mostly from North America published in the period 1969 – 1995) on indoor and ambient air concentrations of styrene were reviewed. Low concentrations of styrene have been reported for indoor air as a result of emissions from flooring materials. It was suggested that flooring materials emitted most of the styrene within the first two weeks of manufacture (up to 200 µg/m<sup>3</sup>), while after a month the emissions appeared to fall dramatically (“almost nothing”). Styrene butadiene rubber (SBR), which is used for products such as carpet backing, was the only polymer reported to contain residual levels of styrene. In the studies providing both indoor and ambient data, indoor air levels of styrene were greater than levels in ambient air, sometimes linked to smoking (depending on the information available).

Exposure from long-term low-level sources is therefore made up of the following components:

- Emissions from polymeric building materials, incl. carpets (inhaled) - 5 µg/m<sup>3</sup> (80 µg/day);
- Food (swallowed) - 3 µg/day, and
- Chewing gum (swallowed) - 8 µg/day.

Exposure arising from tobacco smoking is included for comparison:

- Passive smoking of tobacco (inhaled) - 9 µg/day, and

- Heavy smoker (20 cigarettes/day) (inhaled) - 400 µg/day.

Sporadic exposures following specific events/activities are as follows:

- New carpet (inhaled) - 2 mg/event
- Liquid resin (inhaled) - 413 mg/event
- Liquid resin (on the skin surface) - 11,000 mg/event
- Resin paste (inhaled) - 68 mg/event
- Resin paste (on the skin surface) - 5,500 mg/event
- Boat building (inhaled) - 4,330 mg/event
- Boat building (on the skin surface) - 1640 mg/event.

For an adult consumer, the combined long-term exposure may arise through the release of residual styrene monomer from polymeric building materials (80 µg/day), via food (3 µg/day) and from chewing gum (8 µg/day) and would thus result in a total exposure of about 90 µg/day (1.3 µg/kg bw/day). The sporadic exposures are not included in this estimate, but are considered in the risk assessment by the RAR (UK, 2008).

### ***Occupational exposure***

In the RAR (UK, 2008), occupational exposure estimates have been derived from measured data, usually provided by the industry, and by means of the predictions from the EASE (Estimation and Assessment of Substance Exposure) model.

Occupational exposures have been estimated for five application areas of styrene, hereunder:

- Manufacture of monomer;
- Production of polystyrene;
- Production of unsaturated polyester (UP)-styrene resin;
- Production of SBR and SB latex, and
- Glass-reinforced plastic (GRP) manufacture.

In the following sections, the exposure levels for the different application areas of styrene, as well as the origin of measured data, are summarised.

#### *Manufacture of monomer*

Styrene monomer is produced in a batch process within a largely enclosed system.

The exposure estimates based on industry information ranged from 0 – 7.2 ppm (8-hr TWA) in the different working areas of the plant, with most median concentrations being ≤ 0.06 ppm.

With the EASE model, RWC (Reasonable Worst Case) short-term inhalation exposures of 6.6 - 50 ppm were predicted for different working operations.

Dermal exposure was likewise estimated for a RWC task, resulting in a predicted exposure estimate of 0.1 mg/cm<sup>2</sup>/day.

#### *Production of polystyrene*

Potential airborne exposure to styrene may occur during the polymerisation process, process sampling, spillage, storage activities and maintenance. According to industry information, the styrene monomer is stored in bunded tanks and delivery to the plant is by fixed line. The handling of the raw material is thus minimal and the possibility of leakage is low.

The 8-hr TWA based on measured data ranges from 0.01-15.8 ppm with geometric means of ≤ 0.4 ppm (figures based on data from the 1980s). In order to estimate typical and RWC exposures to reflect the current situation, the RAR included considerations from other exposure scenarios.

### *Production of UP-styrene resin*

The UP-styrene resins are produced within a largely enclosed system, as reported by one producing company. There may be some styrene vapours released during the blending process but these are controlled by local exhaust ventilation (LEV). Occupational exposure to styrene may occur during discharge from the blender into storage or when drumming off. However, the filling point above the drum is provided with LEV and the employees generally wear respiratory protective equipment. The company monitored short-term background concentrations in different working areas during production. All short-term measurements were below 50 ppm, with arithmetic means being  $\leq 10$  ppm. Measured long-term exposures ranged between 2-6 ppm (8-hour TWA).

Short-term exposures were also predicted with EASE. The predicted RWC range was 20 to 50 ppm and the 15 minute TWA was 5.3 - 13.3 ppm.

### *SBR and SB Latex Production*

SBR is produced by manufacturing companies throughout the EU in closed systems using approximately 25% styrene and 75% butadiene. Both styrene and butadiene are copolymerised in a continuous polymerisation process. After termination of the polymerisation process, unreacted butadiene and styrene are recovered from the latex. The potentially highest exposures to airborne styrene may occur during monomer recovery, sampling and venting to atmosphere. Personal samples, provided from a SB latex producer, during these activities gave exposure levels to airborne styrene of up to 6.5 ppm 8-hr TWA with the majority below 2.5 ppm 8-hour TWA. More recent data (2005) show a maximum 8-hr TWA of 2.7, with the 95<sup>th</sup> percentile at 2.6 ppm.

At another site, personal exposures and background concentrations of less than 5 ppm 8-hr TWA have been obtained with the majority of concentrations being less than 1.0 ppm 8-hour TWA. Highest exposures were measured during maintenance operations at the site, resulting in 8-hr TWA of up to 10 ppm.

### *GRP Manufacture and UP-styrene use*

According to information from the Danish Working Environment Authority, there were 9200 people working in the wind power industry in Denmark in 2003. It was estimated that about half of the workforce is occupied in the production area (UK, 2008). According to industry information from Denmark, these figures are substantially lower nowadays and may account for a third or a quarter of the 2003 numbers.

In the GRP industry, styrene exposures are higher than those found in monomer and polymer production. This is because the processing of the styrene-containing resins involves manual handling in either open or semi-closed moulding processes. In the RAR (UK, 2008), working operations for GRP manufacture are described as follows:

*“In the GRP industry, there are two categories of fabrication, namely contact moulding and machine moulding. Machine processes are generally used for the production of small to medium sized items such as containers, sheets and tubes. Contact moulding operations are often manual and can involve hand lay-up or spray up lamination to deposit UP-styrene resin and fibre glass onto the surface of a prepared mould. In hand lay-up the UP-styrene resin is applied direct to the laminate by spraying and then covering with fibreglass mat by hand. In spray-up, both the resin and chopped fibreglass are applied simultaneously to the mould. The laminate is then rolled out manually to remove any entrapped air bubbles. The operations are repeated until the correct thickness is obtained. After a few hours, curing is usually complete. Edges may be trimmed during or after the curing process.*

*With these open moulding techniques the operators work very near the moulds and there is considerable potential for exposure to evaporating styrene. The concentration of styrene in the*

*working atmosphere will vary according to the amount of resin used, the area of surface fabrication, duration of work process, temperature and whether LEV is provided. Often, work practices are poor, with operators leaning over large work pieces or working between the work piece and LEV, thus rendering any LEV present ineffective. In open moulding up to 10% of the styrene contained in the resin may volatilise into the workplace and, without appropriate controls, airborne exposures can be high.”*

The RAR also states that there is an increasing use of semi-enclosed processes such as the RTM (Resin Transfer Moulding) process, and sheet and bulk moulding compound (SMC & BMC) processes. These techniques can significantly reduce exposure because they reduce the amount of time the operator is in contact with the resin. The techniques usually include the use of moulds and resin pressure feeding of the moulds, which removes the need for the operator to hand-work the resin into the mould. Even though occupational exposures can still occur due to residual styrene evaporation during mould opening/closing, the semi-enclosed resin moulding processes do provide a significant improvement over open moulding techniques.

Low styrene emission (LSE) resins also help to reduce exposures. It is reported in the RAR (UK, 2008) that these resins can cause problems with delamination between layers, but this problem has now been largely overcome and they are used extensively.

A large number of studies and monitoring activities on long- and short-term exposures in GRP production have been reviewed in the RAR. Selected comprehensive studies and the latest studies are referred to below.

A CEFIC report from 2005 (cfr. UK, 2008) came to the following conclusions:

- *“Open mould operations show the highest exposure of workers to styrene with gel coating being the activity with the highest exposure. The wealth of data on open mould operations show that keeping the workers exposure below the specified MAC value has proved to be very difficult.*
- *Conversely in all data coming from closed mould injection operations the styrene concentration stays well below the MAC value.*
- *SMC/BMC operations also typically show a high variation in styrene concentrations. The highest values are obtained during SMC moulding when SMC sheets are laid in the press, essentially the “open mould” part of the operation.”*

The CEFIC report from 2005 reported in the RAR collected long-term exposure data from 8 European countries including Denmark on different UP operations for GRP production. It is emphasized in the RAR that the data are derived from different methodologies and do not all present 8-hr TWA, which requires some caution with respect to their comparability.

Measured concentrations of styrene ranged from 0.2 – 374 ppm (min. – max. range) for hand lay-up with average concentrations ranging from 17.1 – 55.4 ppm. The corresponding Danish values were 0.3 – 282.7 ppm (min. – max. range) and 31.9 ppm (average).

For spray lay-up, concentrations were generally higher with min. and max. concentrations ranging from 0.7 - 380 ppm, and average concentrations from 11.7 – 105.9 ppm. Here the Danish exposure concentrations were among the highest: 49.1 – 186.9 ppm (min. – max. range) and 105.9 ppm (average).

In gel coating, concentrations are slightly lower than in hand lay-up with min. and max. concentrations ranging from 0.1 - 193.2 ppm, and average concentrations from 11.5 – 47.3 ppm. The Danish exposure concentrations appear to be representative of the European averages of 3 - 133.2 ppm (min. – max. range) and 28.8 ppm (average).

Long-term exposure values for selected countries are derived from measured data in RTM, SMC/BMC production, SMC/BMC moulding, filament winding, and pultrusion operations. The exposure levels in these processes were generally lower than in the three processes mentioned before and therefore not elaborated upon here.

Short-term data for hand and spray lay-up, as well as gel coating from the period 1990 – 2002, indicate that exposure concentrations do not differ significantly from the long-term data with 4 – 219 ppm (min. – max. range) and average concentrations of 60.25 ppm.

According to industry information, open production systems for moulding operations essentially do not exist in Danish industry anymore. This can be explained by the following:

- Production processes involving open systems such as spray-up or hand lay-up have been moved out of Denmark;
- Open techniques have been substituted with closed systems, such as vacuum injection methods (RTM), using negative and positive forms or sheeting, and
- Spray-up operations (apparently only used by a single company in Denmark) are conducted by robots, not by humans.

Coatings, in contrast, are always applied in open systems. However, exposures are significantly reduced, because (personal communication with industry):

- Of use of resins which contain vapour suppressant additives or simply have a reduced styrene content (LSE resins);
- Operators always wear fresh-air masks and the coating is applied in separate coating compartments with exhaust ventilation, thus also reducing styrene concentrations in other parts of the production, and
- In some companies (10 -20 %) coating operations are performed by robots.

Measured dermal exposure data are sparse. The potential exposure of the hands was evaluated in a single study by attaching a cotton/charcoal patch at the inner and outer side of cotton gloves resulting in a RWC value of 8 mg/cm<sup>2</sup>/day and a typical value of 1.2 mg/cm<sup>2</sup>/day (UK, 2008).

In summary, the exposure of employees in the industries producing monomer, polystyrene, UP-styrene resin and SBR and SB latex is much lower than that experienced by employees in the GRP manufacturing industry. In the monomer, polymer and copolymer-producing industries, manufacturing processes are largely enclosed with breaches for sampling, drum filling, and coupling and uncoupling of pipework for tanker loading. Where breaches occur, exposure is often controlled by the use of local exhaust ventilation. Exposure experienced during maintenance activities is suggested to be one of the highest. The use of respiratory protective equipment further reduces actual exposure to styrene (UK, 2008).

Within the GRP industry in the EU and Denmark, there is a much wider range of exposures experienced by workers. The higher exposure experienced by the GRP manufacturing industry compared to the other users of styrene is a reflection of the work methods, which in many cases are open, labour-intensive processes. More modern semi-enclosed processes are available, but open moulding techniques were stated to remain widespread (UK, 2008). According to Danish industry information, open moulding techniques essentially do not exist anymore in Denmark.

Table 18 provides an overview of the typical and realistic worst-case exposures values, commonly derived from consideration of both measured data and EASE prediction, which were used for the risk assessment in the RAR (UK, 2008). Note that the concentrations are given in ppm (1 ppm = 4.33 mg/m<sup>3</sup>).

**TABLE 18**  
EXPOSURE LEVELS FROM TYPICAL AND REALISTIC WORST-CASE SCENARIOS AS PROVIDED IN THE RAR (UK, 2008).

Application of styrene	Inhalation				Dermal (mg/cm <sup>2</sup> /d)	
	Long-term (ppm, 8-hr TWA)		Short-term (ppm, 15-min TWA)			
	Typ.	RWC	Typ.	RWC	Typ.	RWC
Manufacture of monomer	0.1	1	1	15	0.1	0.1
Production of polystyrene	0.1	1	1	15	0.1	0.1
Production of UP-styrene Resin	3	20	9	50	0.04	0.4
SBR and SB Latex Production	1	5	1	15	0.1	0.1
GRP Manufacture and UP-styrene use	40	100	60	180	1.2	8

Abbreviations - TWA: Time weighted average; Typ.: typical; RWC: Realistic worst case

#### *Exposure to styrene from other work processes*

Exposure to styrene from dust released during sanding/grinding processes is not addressed in the RAR. According to the Danish Working Environment Authority, the styrene monomer can reform from cured materials during sanding/grinding. This is a relevant exposure pathway, e.g. in the windpower industry, which is the main application area of styrene in Denmark. Furthermore, workers may be exposed to styrene during handling of uncured waste from production of UP resins (WEA, 2014; personal communication).

#### **6.2.2 Indirect exposure**

##### ***Styrene in food contact materials***

Styrene may migrate into food from polystyrene packaging. Migration of styrene from food contact materials has not been addressed separately in the RAR. A risk assessment on styrene in food from EFSA is not available.

WHO (2003) reviewed exposure to styrene in food and drinking water for the development of guidelines for drinking-water quality. The report states that styrene has been found in food which was packaged in polystyrene containers, especially yoghurt (2.5 – 34.6 µg/kg). In other milk products and honey, some tens of micrograms were found up to 120 days after packaging. An Australian survey cited in the WHO report (2003) detected styrene in yoghurt (85% contained less than 50 µg/kg, maximum 100 µg/kg), and in margarine (90% contained less than 10 µg/kg). Another study found concentrations of 1 to 200 µg/kg in 133 different types of polystyrene packed foods. In meat products, styrene was present in the outermost layers, but could not be detected after cooking (WHO, 2003).

A British study on dietary exposure to chemical migrants from food contact materials used styrene as a model substance to estimate uptake with a probabilistic approach (Holmes et al., 2005). The authors found uptake levels of 0.037–0.041 µg/kg bw/day resulting from styrene concentrations in food from a typical “food basket” diet of an adult. The estimate is in good agreement with earlier findings (Holmes et al., 2005). It is, however, not differentiated as to whether the styrene concentration originates from environmental food concentrations or from packaging migration.

A British survey from 1999 cited in the RAR (UK, 2008) found concentrations of up to 14 µg/kg, resulting in uptake levels ranging between 0.03 and 0.04 µg/kg/day for a 70 kg adult. The

uppermost value of this range was used for the risk characterisation in the RAR. Styrene levels were highest in the food sample groups of ‘oils and fats’.

Gelbke et al. (2014), representing several large international chemical companies, state that the amount of styrene monomer may reach about 500 mg/kg PS in current styrene based polymer grades. They further refer to migration tests with food simulants under standardized conditions, reflecting most closely the conditions of use for the polymers GP-PS, HI-PS, and EPS. For GP-PS and HI-PS, migration of styrene was generally below 100 µg/kg, but reached 75–590 µg/kg in olive oil after 10 days at 40°C. Lower concentrations (≤ 40 µg/kg) were found for EPS, extracted for 10 days at 5°C in sunflower oil (Gelbke et al., 2014).

These figures are in accordance with results of an American study, where the authors found styrene concentrations of 9.3 to 3100 mg/kg in polystyrene packaging, and 2.6 to 163 µg/kg in the analysed food items comprising yoghurt, baked goods, and meats (Genualdi et al., 2014).

The studies thus support the idea that consumers may be exposed to styrene due to migration from food packaging polymers. The relative contribution of styrene inherently contained in the food item and styrene migrated from packaging material is not known.

### ***Environmental concentrations and human uptake***

Table 19 gives the predicted environmental exposures to styrene and the daily human doses arising from releases from production and uses as reported in the RAR (UK, 2008). The releases to the environment and the resulting biota concentrations (in fish, plant roots, plant leaves, meat, and milk) have been estimated with an environmental distribution model (EUSES; parameters log Kow=3.02, BCF=74, oral absorption rate=1 and inhalation absorption rate=1). The modelled data show that the daily human intake (consumption and inhalation rates are not stated in the RAR) at the regional level is  $1.6 \times 10^{-5}$  mg/kg/day (corresponding to 0.016 µg/kg/day), while the highest local exposure (for the scenario of styrene production) is 0.11 mg/kg/day (110 µg/kg/day).

**TABLE 19**  
CALCULATED DAILY CONCENTRATIONS FOR INDIRECT EXPOSURE VIA THE ENVIRONMENT

Scenario	Air (mg/m <sup>3</sup> )	Drinking water (µg/l)	Human dose* (mg/kg bw/day)
Production	99	930	0.11
Processing: GP, HI-PS	97	1.1	0.024
EPS	47	1.9	0.013
ABS/SAN	29	1.2	0.009
SB rubber/latex	31	1.3	0.009
UP resin	18	2.9	0.006
Use of: GP, HI-PS	0.12	0.026	$3.3 \cdot 10^{-5}$
EPS	0.67	0.026	$1.5 \cdot 10^{-4}$
ABS/SAN	0.06	0.026	$2.0 \cdot 10^{-5}$
SB rubber/latex	0.23	0.026	$5.6 \cdot 10^{-5}$
UP resin use	59	0.66	0.016
Regional	0.034	0.026	$1.6 \cdot 10^{-5}$

\* Derived from uptake of food (modelled concentrations in fish, plant roots, plant leaves, meat, and milk), air, and drinking water.

In addition to the calculated levels, a few environmental concentrations based on measured data were provided. A British survey (cited in the RAR) detected styrene at levels of up to 14 µg/kg in 20 food groups. Based on the levels of styrene in each food group and daily consumption estimates for each food group, the highest daily dietary intake of styrene, per person, is estimated to be 0.04 µg/kg bw/day for a 70 kg adult. For air, a value of 80 µg/m<sup>3</sup> downwind from a GRP processing site has been measured and is the value used in the risk assessment. For exposure through water, the measured value of 10 µg/l has been chosen as a conservative measurement (UK, 2008).

Using these measured concentrations, a body burden via environmental sources of 0.058 mg/kg bw/day from food, air and water has been estimated in the RAR. The RAR states that contribution from air to this estimate is very high (UK, 2008), but further details on the derivation of the estimate are not provided. Note that this intake estimate covers oral and inhalation uptake.

### **6.2.3 Bio-monitoring data**

Styrene is metabolised extensively in humans and experimental animals. As described in section 6.1.2, the major metabolic route of styrene is oxidation of the side chain to give the epoxide, styrene-7,8-oxide (SO). Subsequent metabolites include mercapturic acids, mandelic acid, and phenylglyoxylic acid.

Therefore, styrene exposure has commonly been determined by measuring SO levels in blood and mandelic acid levels in urine samples in occupational environments. Levels of styrene in blood have also been measured to reflect recent exposure. Other urinary biomarkers are phenylglyoxylic acid, mercapturic acid derivatives, and hippuric acid (UK, 2008).

Recent studies documenting styrene exposure in worker or consumers over time have not been identified.

## **6.3 Human health impact**

### **6.3.1 Consumers**

Consumer exposure to styrene can arise as a result of emissions from polymeric building materials, including carpets, from food sources (mainly as a consequence of food packaging), from chewing gum, from newly laid carpets, from the use of styrene containing resins for filling or repair of wood, glass fibre or metal, from the use of styrene-based paste and from boat building.

Several scenarios evaluating sporadic exposures have been evaluated as posing a risk to consumers, i.e. leading to the conclusion (iii) *There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account*. The scenarios posing the most unacceptable risk was boat building, with respect to acute CNS depression, eye and respiratory tract irritation, effects on the ear and on colour vision following repeated exposure and developmental toxicity. Unacceptable risk was also identified for the use of styrene containing liquid resins in relation to eye and respiratory tract irritation, effects on the ear and on colour vision following repeated exposure and developmental toxicity, and to the use of styrene-based paste in relation to developmental toxicity.

For all other scenarios and effects, the safety margins were assessed as sufficiently high, leading to conclusion (ii) *There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already*.

That means consumers are not at risk due to long-term exposures arising as a result of emissions from polymeric building materials, including carpets, from food sources (mainly as a consequence of food packaging) and from chewing gum. None of the long- or short-term scenarios resulted in unacceptable risks in relation to sensitization, mutagenicity, carcinogenicity and effects on fertility.

The same applies for the considerations of the RAR on the combined exposure of consumers who might also be exposed via the environment. Even the worst case exposure estimate from the styrene production scenario provided sufficient safety margins in the comparison with the relevant no-effect levels.

The Danish EPA has published results from a number of surveys on selected consumer products that might contain problematic substances, or products that consumers are highly exposed to. Some reports focus on the content of chemicals in the products; others also include releases to indoor air and migration studies. Two surveys include exposure and risk assessment of styrene in different consumer products. In the report "Overall health assessment of chemicals in the indoor climate from selected consumer products" (Jensen and Knudsen, 2008) potential indoor concentrations of eight selected volatile chemicals, including styrene, which have been included in different consumer surveys, are estimated. Concentrations were estimated in three model rooms: a hall/utility room, a kitchen/family room and a children's room, based on pragmatic model calculations with some assumptions and simplifications. Because the available data in the DEPA reports have different character and aim, they are not equally reliable, and are not necessarily produced with the purpose of assessing indoor climate.

The following products releasing styrene to the indoor air in a children's room were included in the calculations: computer, monitor, play station, decorative lamp, television, and rechargeable batteries. The calculated concentrations of styrene added up to 22 µg/m<sup>3</sup> for new products and 8 µg/m<sup>3</sup> for used products. Possible contributions up to approx. 772 µg/m<sup>3</sup> from incense, children's tent, and tubular pearls should be added to these values. The report concludes that the total concentration is close to the WHO air quality guidance value for styrene indicated as 800 µg/m<sup>3</sup> (24 hours). The reported Reference dose is 0.2 mg/kg bw/d, which is somewhat above a Dutch Tolerable Daily Intake (TDI) of 120 µg/kg bw/d referred to in the report and even more so for the TDI of 7.7 µg/kg bw/d established by WHO and referred to in section 6.1.4 of the present report. Jensen and Knudsen (2008) further conclude that child exposure to a concentration of 20 µg/m<sup>3</sup> in 6 hours a day result in an intake of 7 µg styrene/kg bw/d, which is below various danger limits and without health effects. However, in the worst case scenario for the children's room with use of incense etc. there will be a 20% excess of the Reference dose.

Another consumer report investigated the exposure to styrene from various baby products intended to come into direct or close contact with baby skin. Products included breast feeding pillows, baby carriers, nursing pillows, baby mattresses, aprons to perambulators, and disposable foam washcloths (Thønning et al., 2008). Based on the results from chemical analyses, migration tests and estimated releases and exposures of children 0-1 years old, and a worst case oral uptake of 0.0017 µg/kg bw/d and a NOAEL of 200 mg/kg bw/d (effect on erythrocytes in beagle dogs), it was concluded that there was no risk for human health from skin contact and oral intake in the worst case exposure scenario. The same conclusion was made with regard to inhalation of released amounts of styrene from the breast feeding pillow measured in a climate chamber.

### **6.3.2 Workers**

Five occupational scenarios have been evaluated in the RAR: manufacture of the monomer, production of UP-resins, production of polystyrene, production of SBR and SB latex, and GRP manufacture.

The two scenarios involving UP resins (production of UP-resins and GRP manufacture) were evaluated as posing a risk to workers, leading to the conclusion (iii) that *"There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account."* Unacceptable risks were identified with respect to acute CNS depression, skin, eye and respiratory tract irritation, and effects on the ear and colour vision discrimination, following

repeated exposure and developmental toxicity for the GRP manufacture scenario. Conclusion (iii) also applies to production of UP-resin in relation to effects on the ear following repeated exposure and developmental toxicity, and to production of SBR and SB latex in relation to developmental toxicity.

The two UP-related scenarios were also the only ones where the estimated exposure concentrations exceeded the available occupational limit values in the typical and/or reasonable worst case scenarios. However, information from the UP industry in Denmark suggests that exposure concentrations in the Danish wind power industry are considerably lower than those estimated in the RAR due to the widespread use of low emission techniques, which, according to information from industry, have been implemented in recent years.

For the remaining scenarios, the safety margins were assessed as sufficient, expressed by conclusion (ii) *There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already*. Conclusion (ii) also applies to all scenarios in relation to sensitisation, mutagenicity, carcinogenicity and effects on fertility.

### **6.3.3 Indirect exposures**

Both the modelled uptake estimates (0.11 as the highest local exposure and  $1.6 \cdot 10^{-5}$  as regional exposure) and the estimate based on measured data (0.058 mg/kg bw/day) were assessed in the risk assessment on indirect exposure via food, drinking water and air.

The total uptake via ingestion from the main long-term sources of exposure has been estimated in the RAR, and is relevant for comparison with the oral no-effect levels. The total oral exposure resulting from the conservative uptake estimates in the RAR on food (3 µg/d), chewing gum (8 µg/d) and drinking water (10 µg/l), would add up to a daily exposure of 0.44 µg/kg bw/d assuming a consumption of 2 l drinking water and a human body weight of 70 kg. Comparing this value with the oral NOAEL given in the RAR (150 mg/kg/d), the resulting ratio of approximately 300 000 (150 mg/kg/d divided by 0.44 µg/kg bw/d) appears to provide a sufficient safety margin. The daily oral exposure of 0.44 µg/kg bw/d is therefore also considerably lower than the TDI of 7.7 µg/kg bw/d.

No unacceptable human health risk was identified through indirect exposure via the environment and, neither the contributions from drinking water nor food alone are expected to pose a risk to human health.

### **6.3.4 Total body burden**

The estimated total body burden via environmental sources of 0.058 mg/kg bw/day (corresponding to 58 µg/kg bw/day) from food, air and water does exceed the TDI of 7.7 µg/kg bw as developed by the WHO considerably. However, caution should be applied when comparing these figures, because the body burden originates mainly from inhalation, while the TDI is derived from an oral exposure rat study. Lack of derivation data on the body burden estimate also complicates its interpretation. The body burden estimate, being derived from measured data, is likely to be overestimated, because the air concentration (main contribution to the body burden) 80 µg/m<sup>3</sup> was measured downwind from a reinforced plastics processing site. Food and water contributions are likewise based on highly conservative estimates. Due to the uncertainties regarding realistic exposure levels from in particular indirect exposures (air, food and water), a refined risk assessment as well as an evaluation of the TDI would be desirable for assessing possible risk via environmental sources.

## **6.4 Summary and conclusions**

### **6.4.1 Human health hazard**

Styrene is classified as an acute toxicant (class 4), a skin irritant (cat. 2), and an eye irritant (cat. 2).

Furthermore, the classification has been updated based on a Danish proposal to include STOT RE 1 (H372; Causes damage to the hearing organs through prolonged or repeated exposure) and Repr 2 (H361d; suspected of damaging the unborn child).

In humans, styrene vapour is well absorbed via inhalation. Uptake after dermal contact with styrene vapour is not significant (5% or less). The RAR concluded that ingested styrene is absorbed completely. Styrene and/or its metabolites are widely distributed throughout the body with the highest concentrations in fat; the concentrations in brain tissues are generally higher than in blood. Styrene is metabolised extensively in humans and experimental animals; styrene and its metabolites are rapidly eliminated from the body, primarily in the urine. There are considerable differences between animal and human metabolism which need to be considered when evaluating the relevance of animal studies in relation to human health, depending on exposure route and effect.

The toxicity of styrene has been intensively investigated. Styrene is of moderate acute toxicity (in rats and guinea pigs) following inhalation, and of low acute toxicity following oral intake and dermal exposure. Following inhalation, acute effects observed include marked signs of irritation of the eyes and nasal mucosa, general signs of central nervous system depression, and changes in the lungs.

Repeated exposure to liquid styrene can cause skin irritation. Styrene vapour can cause eye irritation as well as irritation to the respiratory tract (nasal). Styrene has no significant potential to cause skin sensitization or respiratory tract sensitization.

The neurotoxicity of styrene is well-documented in humans and in experimental animals. Besides effects on hearing organs and colour discrimination, other effects on the nervous system have also been reported. Based on the large amount of information on effects of styrene from repeated exposure in humans, the need to avoid acute CNS depressant effects and associated symptomatology is regarded as crucial in relation to the impact of styrene on the nervous system.

Ototoxicity is the most sensitive and relevant effect of styrene repeated inhalation exposure in animals. The available human data indicate a relationship between styrene exposure and ototoxicity. The observed ototoxicity in animals may therefore also be relevant to humans. In addition, the human studies indicate that the sensitivity for developing hearing loss might be greater in humans than in rats. From the studies in rats, a NOAEC between 1300-2600 mg/m<sup>3</sup> for hearing loss could be identified. Regarding the Danish proposal for classification of styrene for specific target organ toxicity, the Risk Assessment Committee concluded that there is sufficient evidence of ototoxicity to warrant classification. The data led to attribution of a classification as STOT Re1; H372 with specific reference to hearing loss.

A number of epidemiological studies investigating colour discrimination provide evidence that styrene causes changes in colour discrimination. Based on human data, a NOAEC for changes in colour vision of 216.5 mg/m<sup>3</sup> was suggested in the RAR. However, the degree of adversity of this effect was disputed by RAC and thus not included in the basis for classification.

The RAR concluded that there is no concern for mutagenicity of styrene.

IARC concluded that styrene is possibly carcinogenic to humans (Group 2B). In contrast, the RAR concluded that there is no concern for carcinogenicity of styrene in humans.

For potential developmental effects, a NOAEC of 650 mg/m<sup>3</sup> was suggested in the RAR. Regarding the Danish proposal for classification of styrene for reproductive toxicity, the Risk Assessment

Committee concluded that there is sufficient evidence of developmental effects to warrant classification as Repr 2, H361d.

The RAR concluded that there is no evidence that styrene possesses significant endocrine disrupting activity on the reproductive system based on data showing impairment of the immunological system and effects on prolactin level. However, in the EU, styrene has been placed in category 1 on the EU priority list for endocrine disruptors. EU criteria for endocrine disruption are still under development, meaning that the evaluation may need to be revisited when the criteria for endocrine disruption become available.

European occupational exposure limit values for styrene have not yet been defined. The Danish limit value of 25 ppm (105 mg/m<sup>3</sup>) is slightly higher than the German long-term limit value of 20 ppm.

WHO has established a tolerable daily intake (TDI) of 7.7 µg/kg of body weight per day and, based on this limit, a guideline value for drinking water of 20 µg/L was put forth.

#### **6.4.2 Human exposure**

Consumers may be exposed to long-term sources of styrene, such as emissions from polymeric building materials, e.g. carpets, food, chewing gum, and (passive or active) tobacco smoking. Apart from heavy smoking, the largest exposure is stated to be emission of styrene from building materials.

Consumers may also be exposed when using styrene-containing resins or adhesives. Even though these exposures may be infrequent, they are potentially high.

Occupational exposures have been estimated for five application areas of styrene:

- Manufacture of monomer;
- Production of polystyrene;
- Production of unsaturated polyester (UP)-styrene resin;
- Production of SBR and SB latex, and
- Glass-reinforced plastic (GRP) manufacture.

The highest exposures are found in the GRP industry, caused by the processing of the UP styrene-containing resins which involves a high degree of manual handling in either open or semi-closed moulding processes. In contrast, manufacture of monomers and polymers is conducted in largely closed systems.

Maximum air concentrations of up to 380 ppm (8-hr TWA) have been measured for spray-up processes with UP, while average concentrations of UP working processes do not usually exceed 50 ppm. Within the GRP industry in EU and Denmark, possible exposures experienced by workers range over 4 orders of magnitude. Measured dermal exposure data are sparse.

Semi-enclosed production techniques, such as Resin Transfer Moulding, and sheet and bulk moulding compounds exist and can significantly reduce exposure. Another possibility for reducing exposure is through the application of low styrene emission resins, if technically possible.

With respect to indirect exposure via food, air and water, a daily intake of 0.058 mg/kg bw/day is estimated in the RAR. The contribution from air to this estimate is very high.

Migration of styrene from polystyrene packaging has been documented and several studies demonstrate styrene in food items. It is, however, usually not differentiated whether the detected styrene originates from environmental food concentrations or from packaging migration. In any

case, concentrations in food are generally below 10 µg/kg, even though concentrations of up to 200 µg/kg have been measured, and therefore do not represent a major exposure pathway.

### **6.4.3 Human impact**

Short-term exposures from sporadic events such as repair work with styrene-containing resins have been assessed in the RAR from 2008 as posing a risk to consumers. Long-term exposures arising as a result of emissions from polymeric building materials, including carpets, from food sources (mainly as a consequence of food packaging) and from chewing gum were reported not to cause unacceptable health risks to consumers.

The production of UP-resins, GRP manufacture, and production of SBR and SB latex may cause occupational exposures that pose a health risk to workers, according to the RAR. The risks of health effects are most pronounced in GRP manufacturing. For the remaining scenarios, the safety margins were assessed as sufficient. However, industry information suggests that exposure concentrations in the GRP industry, such as the wind power industry, have been considerably reduced in recent years, possibly rendering the current risks to workers smaller than presented in the RAR. Updated systematic data on exposures in the occupational environment would be required in order to decide whether occupational risks still exist.

Unacceptable human health risks were identified neither through indirect exposure via the environment, nor for combined exposure in the RAR. However, comparing exposure estimates with the TDI established by WHO (7.7 µg/kg bw/d), a health risk through environmental exposure cannot be excluded. Uncertainties in the prediction of exposures from e.g. polymeric materials relevant for both consumer and occupational exposure scenarios, as well as a discrepancy between the NOAEL values identified as relevant for risk characterisation and derivation of a TDI suggest that a refined risk assessment re-evaluating the exposure estimate and the TDI would be desirable.

# 7. Information on alternatives

## 7.1 Introduction

Styrene is a reactive solvent or monomer for the production of plastics and rubber or other polymer based products either as thermosetting UP and SBR rubber, or thermoplastic plastics like PS and ABS. Styrene is also used as monomer in some glues/adhesives and as a component in many binders.

According to EU occupational health and safety legislation, companies that use hazardous substances in their production are obliged to look for alternatives to these substances and substitute them with less hazardous substances where feasible.

When considering alternatives, the first step will always be to look for other chemical substances of lower hazard which meet the legal and technical requirements, are compatible with the production process, and can be adequately controlled and disposed of with existing control and waste disposal measures. The substitution should result in safer products with the required performance and at the same time the alternative must be commercially available in sufficient amounts.

In the case of thermosetting plastic materials, identification of less toxic alternatives is often difficult because the curing reaction demands a high chemical reactivity - which usually implies that the substance also is capable of reacting/doing damage within the human organism. This concept should be kept in mind throughout this chapter.

Information collection on alternatives has been based on the following:

- Technical literature;
- Internet searches, and
- Contacts to trade organisations.

Searches on the Internet were carried out by using the words "substitution" and "alternatives" in combination with the substance name, as well as using the name of the plastics or rubber based on styrene (e.g. polystyrene, ABS, SBR).

The following trade organisations have been contacted:

- Danish Plastics Federation, and
- Danish Coating and Adhesive Association.

Personal communications have been made to three producers of products based on UP. The products are for use in the wind turbine and building/construction industry.

## 7.2 Identification of possible alternatives

### 7.2.1 Styrene and styrene-based polymers

In order to identify alternatives to styrene-based polymers, there is a number of requirements that have to be fulfilled, e.g. the alternatives must have comparable mechanical functions such as strength, flexibility etc. for each type of use.

### **7.2.2 Production of wind turbines and building/construction products (fibre reinforced)**

Wind turbine blades are currently made either from fibre-reinforced unsaturated polyester or from fibre-reinforced epoxy resins. Therefore, a substitution possibility already exists for styrene-based polyester, but it must be kept in mind that epoxy resin chemistry also includes the use of unwanted chemical substances and that the processes are different and would require modification of moulding process equipment.

LM Windpower has some ongoing R&D on substitution of styrene, but so far has not found a better alternative. Epoxy has been used in some production lines, but trouble with durability and heavy composite materials led to the phase-out of epoxy products. Acrylates are also known by LM Windpower and Fiberline A/S as possible substitutes. However, this compound group also has occupational health and safety issues with its use. The companies generally prefer styrene because it is inexpensive, well-documented and the precautions are known and implemented (Karin Magelund Møller 2014, Benedikte Jørgensen 2014).

In the Technical Paper “Non-Styrene Options For Cured In Place Plastic Pipe” (CIPP) (More, 2011), the possibility to replace styrene-based polyester and vinyl ester resins in CIPP applications with other CIPP resins is discussed. The conclusion is that vinyl toluene-based unsaturated polyester or vinyl ester resins are the most economic alternatives to styrene-based CIPP resins.

It is stated that the higher odour threshold, higher boiling point and lower vapour pressure make them less likely than styrene-based resin to cause odour issues. Epoxy resins are also mentioned as alternatives, but they are much more expensive than the styrene-based polyester and vinyl ester resins. Other reactive monomers that can be used to replace styrene are not mentioned in the paper by their chemical names, but it is mentioned that they are much more expensive than a standard styrene-based resin.

In general thermosets such as unsaturated polyester (UP), epoxies (EP) and phenol-formaldehyde resins (PF) are used where their strength and durability can be utilized. Important to consider is that these materials are preferred for highly demanding applications and have long “end of life” expectancies of 25 – 100 years or more. This high durability is caused by the tight crosslinking of the polymeric networks which stabilize against chemicals, heat and weathering and give high mechanical strength. Making crosslinking demands highly reactive monomers. This is the reason why it is not possible to substitute UP with other thermosets to reduce the use of hazardous substances: they use other reactive and hazardous substances for the above reason. Epoxies have better mechanical properties but are more expensive than UP. PF has very high temperature and fire resistance, but can only be used in darkly coloured products as it get yellow due to weathering.

### **7.2.3 Production of tyres**

For tyres it is unrealistic to conceive of the replacement of SBR rubber with other types of rubber as the thread in all tyres is based on SBR rubber mixed with butadiene rubber (BR) or natural rubber (NR).

### **7.2.4 Thermoplastic styrene-based products**

#### ***Foamed products***

EPS and XPS are used as insulating materials in the building industry. Other insulation materials may also be an option, e.g. inorganic glass fibre or stone wool, as well as insulating materials based on natural fibres. Use of polyurethane foam may also be considered as an alternative to EPS as insulating material, but it is more expensive.

### Solid products

Polystyrene-based technical plastics are used in e.g.:

- cabinets in products such as refrigerators and consumer electronics, and
- high quality toys like LEGO bricks.

Polystyrene-based packaging products include:

- drinking cups, and
- packaging for yoghurt, eggs etc.

Polystyrene, ABS, SAN and other styrene-based thermoplastics may be replaced by other and more expensive plastic materials, e.g. polyethylene terephthalate (PET), but, in most cases, the alternatives will be more expensive or have inferior technical performance properties.

It should be mentioned that LEGO bricks are still manufactured from ABS plastic because of the very good dimension stability etc. of the bricks.

For special purposes e.g. electrical motors and transformers, DuPont has developed an unsaturated polyester with low emissions and free from monomers.

In other applications, thermosetting plastics such as phenolic resins or polyurea may be used as substitutes (Bech, 2014). However, phenolic resins, for example, are based on formaldehyde and phenols which are also on the list of unwanted substances.

It must be stressed that the substitution of UP with epoxy or other thermosetting plastics cannot be done without changing the process equipment, as the chemical processes are different and require specialised processing equipment.

### **7.3 Human health and environmental aspects of alternatives**

The classification of alternatives to styrene according to the CLP Regulation (harmonised classification and/or self-classification by registrants) is listed in the table below. It is noted that a number of the possible technical alternatives are classified in category 2 as carcinogenic, mutagenic or toxic to reproduction, or suspected of having endocrine disrupting properties.

**TABLE 20**  
CLASSIFICATION OF ALTERNATIVES TO STYRENE

**TABLE 1**  
CLASSIFICATION OF ALTERNATIVES TO STYRENE

Alternative substance	EC number	CAS number	Hazard Class and Category Code(s)	Hazard Statement Code(s) <sup>1</sup>
Methylene diphenyldiisocyanate (MDI)	247-714-0	26447-40-5	Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2 Acute Tox 4 * Resp. Sens. 1 STOT SE 3 Carc. 2 STOT RE 2 *	H315 H317 H319 H332 H334 H335 H351 H373 **
Toluene-diisocyanate (TDI)	247-722-4	26471-62-5	Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2 Acute Tox. 2 * Resp. Sens. 1 STOT SE 3 Carc. 2 Aquatic Chronic 3	H315 H317 H319 H330 H334 H335 H351 H412
Bisphenol A	201-245-8	80-05-7	Skin Sens. 1 Eye Dam. 1 STOT SE 3 Repr. 2	H317 H318 H335 H361f ***
Diglycidyl ether of bisphenol A (BADGE)	216-823-5	1675-54-3	Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2	H315 H317 H319
Phenol	203-632-7	108-95-2	Acute Tox. 3 * Acute Tox. 3 * Skin Corr. 1B Acute Tox. 3 * Muta. 2 STOT RE 2 *	H301 H311 H314 H331 H341 H373 **
Formaldehyde	200-001-8	50-00-0	Acute Tox. 3 * Acute Tox. 3 * Skin Corr. 1B Skin Sens. 1 Acute Tox. 3 * Carc. 2	H301 H311 H314 H317 H331 H351
Terephthalic acid (PET) <sup>+</sup>	202-830-0	100-21-0	Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	H315 H319 H335

#### **7.4 Historical and future trends**

It is expected that the use of styrene for thermosetting plastics will increase dramatically due to increasing demand by new markets (China, Brazil etc.). As well, there will be a demand for more tyres using SBR rubber in the threads.

For thermosetting materials there is some substitution of styrene-based thermoplastics with other plastics, e.g. PET instead of PS, that may occur. However, e.g. LEGO bricks are still made from ABS plastic e.g. because of the high dimension stability and shatterproofness.

It is foreseen that improvements still will be exploited with regard to creating a safe working environment in the industries using UP/fibre reinforced UP in their production by better protection clothes and breathing protection, better exhaust and closed production loops.

#### **7.5 Summary and conclusions**

It is concluded that, at present, there are no indications that replacement of styrene for the many different applications it is used for, especially for the different types of plastics or rubber where it is used as reactive monomer or reactive solvent, will occur. For example, the threads of all of the tyres in the world are all based on SBR rubber (Styrene Butadiene Rubber) and approximately 70 % of all SBR rubber is used for this purpose.

For thermosetting plastic materials, the alternatives to UP are either epoxies or phenol formaldehyde resins. However, these thermosetting materials are both based on other hazardous monomers because a high level of reactivity is needed to be sure that the plastic products are fully cured and have the necessary mechanical and physical properties to be secure during use.

In most cases, when looking at alternatives to UP, other thermosetting polymers which can fulfill the technical demands just use other monomers on the LOUS list, e.g. certain isocyanates (MDI/TDI) for thermosetting, PUR or bisphenol A for epoxies or formaldehyde, and phenol for phenol formaldehyde resins. In most cases it will be more expensive to change the plastic for another type, perhaps with the exception of food packaging where there is a trend towards the use of PET instead of PS.



# 8. Abbreviations and acronyms

ABS	Acrylonitrile-butadiene-styrene
ADI	Acceptable daily intake
AF	Assessment Factor
BCF	Bioconcentration factor
BMC	Bulk moulding compound
CEFIC	European Chemical Industry Council
CIPP	Cured In-Place Plastic Pipe
CLH	Harmonised Classification and Labelling (report)
CLP	Classification, Labelling and Packaging Regulation
CNS	Central Nervous System
CoRAP	Community Rolling Action Plan
CRLTAP	Convention on Long-Range Transboundary Air Pollution
DEFRA	Department for Environment, Food and Rural Affairs (UK)
DEPA	Danish Environmental Protection Agency
DFL	Trade organisation for the paint and adhesives industry in Denmark
DNEL	Derived No-Effect Level
DT	Degradation time
DTU	Technical University of Denmark
EASE	Estimation and Assessment of Substances Exposure (model)
EC <sub>n</sub>	Effect concentration where n % of the organisms tested show the effect
ECB	European Chemicals Bureau
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
E-PRTR	European Pollutant Release and Transfer Register
EPS	Expanded polystyrene
EQC	Equivalent level of concern
EU	European Union
FRP	Fibre-reinforced plastic
GP-PS	General purpose polystyrene
GRP	Glass-reinforced plastic
GUP	Glassfibre-reinforced unsaturated polyester
HELCOM	The Helsinki Commission (the Baltic Marine Environment Protection Commission)
HIPS	High Impact Polystyrene
IARC	International Agency for Research on Cancer
IR	Infrared
K <sub>ow</sub>	Octanol/water partitioning coefficient
K <sub>oc</sub>	Organic carbon/water partitioning coefficient
K <sub>p</sub>	Partial pressure equilibrium constant
LC	Lethal effect concentration
LD	Lethal Dose
LEV	Local exhaust ventilation

LOAEC	Lowest Observed Adverse Effect Concentration
LOUS	List of Undesirable Substances (of the Danish EPA)
LSE	Low Styrene Emission
MAL	Måleteknisk Arbejdshygiejnisk Luftbehov
MBS	Methyl methacrylate-butadiene-styrene
MSWI	Municipal solid waste incinerators
MWWTP	Municipal waste water treatment plant
NMC	Nation Mean Concentration
NOAEL	No observable adverse effect level
NOEC	No observable effect concentration
NOVANA	Danish national monitoring and assessment programme
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PBPK	Physiologically Based Pharmacokinetic (modelling)
PBT	Persistent, Bioaccumulative and Toxic
PEC	Predicted environmental concentration
PET	Polyethylene terephthalate
PF	Phenol-formaldehyde
Ph	Phenyl
PIC	Prior Informed Consent (Convention) (the Rotterdam Convention)
PNEC	Predicted no effect concentration
Pow	Octanol-water partitioning coefficient
PS	Polystyrene
PUR	Polyurethane
QSAR	Quantitative Structure and Activity Relationship
RAC	Risk Assessment Committee (ECHA)
RAR	Risk Assessment Report (EU)
RATG	Risk Assessment Task Group of the American Chemistry Council's Petroleum Additives Panel
RED	Reregistration Eligibility Decision
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RTM	Resin Transfer Moulding, process in glass-reinforced plastic production with unsaturated polyester
RWC	Reasonable Worst Case
SAN	Styrene-acrylonitrile
SB	Styrene-butadiene
SBL	Styrene-butadiene latex
SBR	Styrene-butadiene rubber
SMC	Sheet moulding compound
SIDS	Screening Information Data Sets
SPIN	Substances in Products in the Nordic Countries (database)
SPT	Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries
STP	Sewage treatment plant
SVHC	Substance of Very High Concern
TGD	Technical guidance document
ThOD	Theoretical oxygen demand
TDI	Tolerable daily intake
TPE	Thermoplastic polymers
UP	Unsaturated polyester
VE	Vinyl ester
VOC	Volatile Organic Compounds
WEA	Danish Working Environment Authority
WWTP	Wastewater Treatment Plant

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## Appendix 1: Background information to chapter 2 on legal framework

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 3.

### EU and Danish legislation

Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

#### There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvring as to the form and means of implementation. However, there are great differences in the space for manoeuvring between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.
- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulate to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

### Chemicals legislation

#### REACH and CLP

The REACH Regulation<sup>8</sup> and the CLP Regulation<sup>9</sup> are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP

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<sup>8</sup> Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

<sup>9</sup> Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

### **(Pre-)Registration**

All manufacturers and importers of chemical substance > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered dead-lines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

### **Evaluation**

A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

### **Authorisation**

Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

### **Restriction**

If the authorities assess that there is a risks to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

### **Classification and Labelling**

The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.
2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publish the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

### **Ongoing activities - pipeline**

In addition to listing substance already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

### **Community Rolling Action Plan (CoRAP)**

The EU member states have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when a given substance is expected to be evaluated.

### **Authorisation process; candidate list, Authorisation list, Annex XIV**

Before a substance is included in REACH Annex XIV and thus being subject to Authorisation, it has to go through the following steps:

- It has to be identified as a SVHC leading to inclusion in the candidate list<sup>10</sup>
- It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
- It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

### **Registry of intentions**

When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intentions in relation to Annex XV dossiers divided into:

- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

for the three types of Annex XV dossiers.

## **International agreements**

### **OSPAR Convention**

OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

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<sup>10</sup> It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. [Decisions and recommendations](#) set out actions to be taken by the Contracting Parties. These measures are complemented by [other agreements](#) setting out:

- issues of importance
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out.
- guidelines or guidance setting out the way that any programme or measure should be implemented
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

### **HELCOM - Helsinki Convention**

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the [Helsinki Convention](#).

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

### **CLRTAP - Convention on Long-range Transboundary Air Pollution**

Since 1979 the Convention on Long-range Transboundary Air Pollution (CLRTAP) has addressed some of the major environmental problems of the UNECE (United Nations Economic Commission for Europe) region through scientific collaboration and policy negotiation.

The aim of the Convention is that Parties shall endeavour to limit and, as far as possible, gradually reduce and prevent air pollution including long-range transboundary air pollution. Parties develop policies and strategies to combat the discharge of air pollutants through exchanges of information, consultation, research and monitoring.

The Convention has been extended by eight protocols that identify specific measures to be taken by Parties to cut their emissions of air pollutants. Three of the protocols specifically address the emission of hazardous substances of which some are included in LOUS:

- The 1998 Protocol on Persistent Organic Pollutants (POPs); 33 Parties. Entered into force on 23 October 2003.
- The 1998 Protocol on Heavy Metals; 33 Parties. Entered into force on 29 December 2003.
- The 1991 Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes; 24 Parties. Entered into force 29 September 1997.

### **Stockholm Convention on Persistent Organic Pollutants (POPs)**

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

### **Rotterdam Convention**

The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

### **Basel Convention**

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

### **Eco-labels**

Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

**EU flower**

The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

**Nordic Swan**

The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" (<http://www.ecolabel.dk/>). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).

**Blue Angel (Blauer Engel)**

The Blue Angel is a national German eco-label. More information can be found on: <http://www.blauer-engel.de/en>.

## Appendix 2: Ecolabel criteria styrene as a VOC

TABLE 21  
ECO-LABELS TARGETING STYRENE

Eco-label	Substances	Relevant criteria	Document title /number
Nordic Swan	VOC (styrene)	The product may contain a limited quantity only of volatile organic compounds (VOC) that may contribute to the formation of photochemical smog, measured as POCP. Products with a VOC content of < 1.2% do not need to undergo POCP calculation since the requirement will be fulfilled even in a worst case scenario. The maximum content of VOC in the product is 12 g ethylene equivalents/ kilo of product.	Nordic Ecolabelling of Car and boat care products Version 5.2 • 21 March 2012 – 31 March 2016
	Organic solvents, TVOC	The content of organic solvents must not exceed 1% by weight of the candle. Alternatively, reference may be made to test results, which show the Total Volatile Organic Compounds (TVOC) in the candle to be less than 1200 µg/m <sup>3</sup> of air measured in a test chamber for 24 hours and using gas chromatography/mass spectrometry (GC/MS).	Nordic Ecolabelling of Candles Version 1.3 • 13 December 2007 – 30 June 2015
	VOC	The following substances must not be actively added to the chemical products mentioned elsewhere in the criteria, e.g. cleaning products, paints, lacquers, adhesives, sealants used in final assembly of white goods and surface treatment): <ul style="list-style-type: none"> <li>- volatile organic compounds at more than 1% by weight</li> <li>- volatile organic compounds (VOCs) at more than 5% by weight in surface treatment agents</li> </ul>	Nordic Ecolabelling of White Goods Version 5.0 • 20 June 2013 - 30 June 2017
	Volatile organic compounds	The use of volatile organic compounds for textile cleaning is prohibited.	Nordic Ecolabelling of Alternative Dry Cleaning Version 1.4 • 23 March 2006 – 31 March 2014
	Volatile organic compounds	Solvents for impregnation and surface treatment: Pressure impregnation is not permitted. The emission of volatile organic compounds (VOC) resulting from impregnation shall not exceed 11 kg/m <sup>3</sup> .	Nordic Ecolabelling of Windows and Exterior Doors Version 3.4 • 4 November 2008 – 31 December 2014

Eco-label	Substances	Relevant criteria	Document title /number
	<p>Volatile organic compounds and volatile aromatic compounds</p>	<p>Prohibited substances and additives</p> <ul style="list-style-type: none"> <li>- volatile aromatic compounds that exceeds 1% by weight</li> <li>- volatile organic compounds (VOC) that exceed the limit of 130 g/l chemicals used for surface treatment</li> <li>- Volatile aromatic compounds (VAH) must not be added directly to the product. Ingoing compounds containing VAH can be added if the total content of VAH in the final product does not exceed 0,1% by weight.</li> </ul>	<p>Nordic Ecolabelling of Toys Version 2.0 • 21 March 2012 – 31 March 2016</p>
	<p>Styrene, TVOC</p>	<p>A test report shall declare that the analyse results for toner powder to be used for Nordic Ecolabelled toner cartridges must be smaller or equal to the limit values listed:</p> <p>Styrene: Determination limit (mg/kg): 4 Limit value (mg/kg): 40</p> <p>TVOC: Determination limit (mg/kg): 100 Limit value (mg/kg): 300</p>	<p>Nordic Ecolabelling of Remanufactured OEM Toner Cartridges Version 5.1 • 15 June 2012 – 30 June 2016</p>
	<p>Volatile organic compounds</p>	<p>Printing pastes must not contain more than 5% volatile organic compounds (VOC).</p>	<p>Nordic Ecolabelling of Textiles, hides/skins and leather Includes products for apparel and furnishings Version 4.0 • 12 December 2012 – 31 December 2016</p>
	<p>Volatile organic compounds and aromatic solvents</p>	<p>The following substances must not be added to the chemical product or the material used:</p> <ul style="list-style-type: none"> <li>- aromatic solvents in the chemical product, more than 1% by weight</li> <li>- VOC (volatile organic compounds) more than 3% by weight.</li> </ul> <p>The content of Volatile Organic Solvents, VOC, in the production of surface treatments must be either: 1) below 5% by weight, or 2) not in excess of 10g/m<sup>2</sup> of the surface</p>	<p>Nordic Ecolabelling of Panels for the building, decoration and furniture industries Version 5.2 • 17 March 2011 – 30 June 2015</p>

Eco-label	Substances	Relevant criteria	Document title /number
	Solvents, aromatic	The content of solvents with a vapour pressure of more than 2.5 kPa at 20 °C or an aromatic content in excess of 1% by weight in the finished products must not exceed a total maximum quantity of 1% by weight.	Nordic Ecolabelling of Industrial cleaning and degreasing agents Version 2.5 • 13 October 2005 – 31 March 2016
	Volatile organic compounds and volatile aromatic compounds	VOC content shall not exceed the following limits (g/L including water): Interior Matt (walls/ceiling) (Gloss <25@60°) - 15; Interior glossy (walls/ceiling) (Gloss >25@60°) - 60; Interior trim and cladding paints for wood and metal including undercoats - 90; Interior trim varnishes and wood-stains, including opaque woodstains - 75; Interior minimum build woodstains - 75; Primers – 15; Binding Primers – 15; Pack performance coatings - 100; Two-pack reactive performance coatings for specific end use such as floors - 100; Decorative effect coatings – 90  Volatile aromatic hydrocarbons shall not be directly added to the product before or during tinting (where applicable); however ingredients containing VAH may be added up to such a limit that the VAH content in the end product will not exceed 0.1% (m/m).	Nordic Ecolabelling of Indoor paints and varnishes Version 2.3 • 4 November 2008 – 31 March 2015
	Styrene	The product must fulfil the maximum limit values expressed in the table below and the emission rates must be measured in accordance with the requirements described in Blue Angel: RAL-UZ 171. Emission rate (mg/h) Colour Printing Total in ready + print phase:1.8 Emission rate (mg/h) Monochrome printing Total in ready + print phase: 1.0	Nordic Ecolabelling of Imaging equipment Version 6.0 • 20 June 2013 - 30 June 2016

Eco-label	Substances	Relevant criteria	Document title /number
	Volatile organic compounds	The following substances must not be actively added to chemical products, for example, cleaning products, paints, lacquers, adhesives or sealants used in final assembly of heat pumps and surface treatment: <ul style="list-style-type: none"> <li>- volatile organic compounds (VOC) at more than 1% by weight.</li> <li>- volatile organic compounds (VOC**) at more than 5% by weight in surface treatment agents</li> </ul>	Nordic Ecolabelling of Heat pumps Version 3.0 • 13 March 2013 - 31 March 2017
	Volatile organic compounds	The individual product's total concentration of volatile organic compounds must not exceed the following limits: <ul style="list-style-type: none"> <li>- Wash-and-wax care products and wash polish: VOC &lt; 0.5 w/w%</li> <li>- Base coat polish, floor polish and floor wax: VOC &lt; 5.0 w/w%</li> <li>- Polish removers and wax removers : VOC &lt; 20.0 w/w%</li> </ul>	Nordic Ecolabelling of Floor care products Version 4.1 • 15 June 2012 – 31 December 2015
	Volatile organic compounds	The emissions of VOCs during polymerisation of polyester, expressed as an annual average, shall not exceed 1.2 g/kg of produced polyester resin.	Nordic Ecolabelling of Fabric cleaning products containing microfibers Version 2.1 • 12 October 2010 – 31 March 2016
<b>EU Flower</b>	Volatile organic compounds	The final products of all-purpose cleaners and sanitary cleaners (as sold) shall not contain more than 6 % (by weight) of volatile organic compounds with a boiling point lower than 150 °C. Alternatively, for concentrated products to be diluted in water, the total concentration of volatile organic compounds with a boiling point lower than 150 °C shall not exceed 0,2 % (by weight) in the washing water. The final products of window cleaners (as sold) shall not contain more than 10 % (by weight) of volatile organic compounds with a boiling point lower than 150 °C.	COMMISSION DECISION of 28 June 2011 on establishing the ecological criteria for the award of the EU Ecolabel to all-purpose cleaners and sanitary cleaners
	Volatile organic compounds	The emissions of VOCs during polymerisation and fibre production of polyester, measured at the process steps where they occur, including fugitive emissions as well, expressed as an annual average, shall not exceed 1,2 g/kg of produced polyester resin.	Commission Decision of 9 July 2009 establishing the ecological criteria for the award of the Community Ecolabel for textile products

Eco-label	Substances	Relevant criteria	Document title /number
	Volatile organic compounds and volatile aromatic compounds	<p>VOC content shall not exceed the following limits (g/L including water):</p> <p>Interior Matt (walls/ceiling) (Gloss &lt;25@60°) - 15;</p> <p>Interior glossy (walls/ceiling) (Gloss &gt;25@60°) - 60;</p> <p>Interior trim and cladding paints for wood and metal including undercoats - 90;</p> <p>Interior trim varnishes and wood-stains, including opaque woodstains - 75;</p> <p>Interior minimum build woodstains - 75;</p> <p>Primers – 15;</p> <p>Binding Primers – 15;</p> <p>Pack performance coatings - 100;</p> <p>Two-pack reactive performance coatings for specific end use such as floors - 100;</p> <p>Decorative effect coatings – 90.</p> <p>Volatile aromatic hydrocarbons shall not be directly added to the product before or during tinting (where applicable); however ingredients containing VAH may be added up to such a limit that the VAH content in the end product will not exceed 0,1 % (m/m).</p>	Commission Decision of 13 August 2008 establishing the ecological criteria for the award of the Community eco-label to indoor paints and varnishes
	Volatile organic compounds and volatile aromatic compounds	<p>VOC content shall not exceed (g/l including water):</p> <p>Coatings for exterior walls of mineral substrate – 40;</p> <p>Exterior trim and cladding paints for wood and metal including undercoats - 90 ;</p> <p>Exterior trim varnishes and wood-stains, including opaque woodstains - 90 ;</p> <p>Exterior minimum build woodstains - 75 ;</p> <p>Primers (for exterior use) - 15 ;</p> <p>Binding Primers (for exterior use) - 15 ;</p> <p>Pack performance coatings - 100 ;</p> <p>Two-pack reactive performance coatings for specific end use such as floors – 100.</p> <p>Volatile aromatic hydrocarbons shall not be directly added to the product before or during tinting (where applicable); however ingredients containing VAH may be added up to such a limit that the VAH content in the end product will not exceed 0,1 % (m/m).</p>	Commission Decision of 13 August 2008 establishing the ecological criteria for the award of the Community eco-label to outdoor paints and varnishes

Eco-label	Substances	Relevant criteria	Document title /number
	Volatile organic compounds	The emissions of VOCs during polymerisation and fibre production of polyester, measured at the process steps where they occur, including fugitive emissions as well, expressed as an annual average, shall not exceed 1,2 g/kg of produced polyester resin.	Commission Decision of 30 November 2009 on establishing the ecological criteria for the award of the Community Ecolabel for textile floor coverings
	Styrene	Agglomerated stones: The emissions to air for the following parameters for the whole manufacturing process shall not exceed 2000 (mg/m <sup>2</sup> ). The styrene emission to air from natural products shall not exceed <210 mg/N m <sup>3</sup> .	Commission Decision of 9 July 2009 establishing the ecological criteria for the award of the Community eco-label to hard coverings
	Volatile organic compounds	Emissions to air: The following criterion must be met: $(P_{\text{VOC}} - R_{\text{VOC}}) / P_{\text{paper}} < 5$ [kg/tonnes] Where: P <sub>VOC</sub> = the annual total kilograms of VOC contained in the purchased chemical products used for the annual total production of printed products R <sub>VOC</sub> = the annual total kilograms of VOC destroyed by abatement, recovered from printing processes and sold, or reused P <sub>paper</sub> = the annual total tonnes of paper purchased and used for the production of printed products  Volatile solvents from the drying process of heat-set offset and flexography printing shall be managed by means of recovery or combustion or any equivalent system. In all cases where no legislative measures apply, the emissions of VOC to air must not exceed 20 mg C/Nm <sup>3</sup> .	Commission Decision of 16 August 2012 establishing the ecological criteria for the award of the EU Ecolabel for printed paper.



## Survey of styrene

This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The survey concerns the aromatic organic substance styrene. This substance was included in the LOUS list in 2004. The report defines the substance and present information on the use and occurrence of styrene internationally and in Denmark, information on existing regulation, on environmental and health effects, on monitoring and exposure, on waste management and on alternatives to the substance.

Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Kortlægningen omhandler det aromatiske organiske stof styren. Rapporten definerer stoffet og indeholder blandt andet en beskrivelse af brugen og forekomsten af styren internationalt og i Danmark, om eksisterende regulering, en beskrivelse af miljø- og sundhedseffekter af stoffet, af monitoringsdata, af affaldsbehandling samt alternativer til stoffet.



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