

Unsaturated Polyester Resin and Vinyl Ester Resin Safe Handling Guide

The European UP/VE Resin Association



Introduction

When using unsaturated polyester resins (UPR) for the production of composite parts, these resins contain styrene as the most important monomer. Styrene is classified as a dangerous substance, so certain safety precautions have to be followed.

The occupational exposure to styrene is strictly regulated in every country. In most countries a Maximum Allowable Concentration (MAC) or Threshold Limit Value (TLV) has been established which states the maximum concentration in the workplace atmosphere, to which a worker may be exposed during an 8 hour working day.

The new REACH regulation puts the responsibility for safe working with styrene in the hands of the manufacturers of styrene and their downstream users. It is therefore important for the composite industry to comply with the new legislative environment.

Apart from that, a well controlled work environment leads to a higher quality of the products and a better competitive position.

This factsheet offers a selection of possible measures that can be taken in a polyester workshop in order to control the exposure of the workers and the environment and to improve the working environment. The selection is a compilation of texts from the complete series of Safe handling Guides, which can be found on

www.upresins.org

To start: know what the risks are. Read all safety instructions, written down in the Material Safety Data Sheets. In case of doubt, ask your supplier.

The use of styrene-based UP resins is associated with several specific risks:

Flammability

The flash point of styrene is 32°C, which categorizes UP Resins as flammable liquids. So, keep them away from flames and other possible ignition sources. Fire extinguishers must be available and explosion-proof electrical installations are also required where resins are stored and used. Ensure that your operators are fully trained regularly in handling fire-fighting equipment.

Static Electricity

Static electricity can be generated when handling materials with low electrical conductivity. UP resins and glass fibres belong to this category. Insure proper earthing wherever flammable liquids or gases are present and avoid conditions that could cause static electric discharge.

Occupational exposure to styrene

In most countries a Maximum Allowable Concentration (MAC) or Threshold Limit Value (TLV) has been established which states the maximum concentration in the workplace atmosphere, to which a worker may be exposed during an 8 hour working day. The exposure to styrene should be minimized where possible by using proper ventilation in the workshop.

Safe handling of constituent materials

Constituent materials such as organic peroxides, fillers and glass fibres, have varying safety considerations. For a safe use, always consult the MSDS for more specific safety information or ask our supplier.

Organic peroxides (catalysts)

Organic peroxides are heat sensitive and thus thermally unstable. Handle them with great care. Observe the maximum storage temperature and avoid any possible contamination with dust, rust and metal particles. Always keep containers closed and follows the required storage rules strictly.

Accelerators and Promoters

Accelerators and promoters, like cobalt compounds, tertiary amines etc, should be handled carefully. Again, consult the MSDS for safety information. Accelerators and promoters can react violently with organic peroxides, so keep these products away from direct contact with organic peroxides.

Cleaning Solvents

Acetone and methylene chloride are commonly used as cleaning agents. Please observe the specific risks associated with these solvents. Acetone is used because of its excellent cleaning and solubility properties, but it is highly flammable. Methylene chloride is classified as a possible carcinogen, so avoid it whenever possible. Alternative cleaning solvents to acetone and methylene chloride are available nowadays. Where possible, switch to these modern alternative solutions.

Fillers

Most fillers used in the composite industry are regarded as inert materials, and can be treated as inert waste. But always consult the MSDS for the specific filler type for any possible restrictions.

Glass fibre

Glass fibre can be a skin irritant, so suitable skin and respiratory protection should be worn when handling glass fibres or fabric.

Composite dust

Composite dust can be generated during drilling, sawing and cutting operations. The dust may consist of particles with a size well below three microns. These very fine dust particles can create lung damage when inhaled. Always use proper dust extraction equipment.

Occupational exposure to styrene

| Process | Styrene loss % |
|---|----------------|
| Open mould processing | |
| Gelcoat spray | 10-14 |
| Spray-up, non-LSE resin | 7-10 |
| Gelcoat, brush | 6-8 |
| Filament winding | 5-7 |
| Hand Lay-up, non-LSE resin | 4-6 |
| Spray-up, LSE / LSC resin | 4-6 |
| Topcoat, spray | 4-5 |
| Topcoat, brush | 3-4 |
| Hand Lay-up, LSE / LSC resin | 3-4 |
| Pultrusion | 1-3 |
| Polymer concrete etc | 1-3 |
| Closed Mould processing | |
| Continuous lamination | 1-2 |
| SMC/BMC manufacturing | 1-2 |
| SMC/BMC processing | 1-2 |
| Closed processes (RTM/RTM Light/Infusion) | <1 |

When using unsaturated polyester (UP) resins, workers are exposed to evaporating styrene monomer. The level of allowable occupational exposure is governed, in most European countries, by maximum allowable exposure levels. The level of exposure to styrene depends very much on the used processing technique.

Different application techniques have a marked effect on the amount of styrene evaporating from the resin surface. As a guide, the table indicates the typical percentage of styrene loss in the different processing techniques.

It is essential that workplace styrene levels are regularly assessed.

A separate information bulletin is available which describes the commercially available equipment for measuring and monitoring styrene concentrations.

Keep exposure levels down

There are many ways to keep exposure levels down. Some relate to the proper choice of the raw materials, some to the process or the equipment used, and some to the awareness and the dedication of the worker.

Cleaner processing

Good housekeeping can have a major impact in keeping styrene exposure down. It also has a very positive impact on safety and operational costs. Use LSE resins wherever possible and always use a resin with the lowest possible styrene content.

Avoid open resin/gelcoat buckets and pails

Resin and gelcoat storage should always be in a separate well-ventilated room. Avoid overspray and spills during spraying/lamination. Any spillages should be removed as soon as practically possible. Avoid open waste containers and ensure that all remnants of laminates and resin contaminated rags and paper are always put in a closed container.

Keep workshop temperatures down

A high workshop temperature will increase styrene evaporation and thus exposures and emissions.

Use personal protection when necessary

Breathing protection must be worn when the exposure level exceeds the maximum allowable concentrations. Although the exposure to styrene takes place mainly through inhalation, excessive skin contact with resins should be avoided, which means always wearing protective clothing and gloves.

Switch to closed mould processing where possible

Use application techniques involving non-atomized dosing of resins, such as roller feeding or use modern spray equipment with fluid impingement nozzles. Robotized spraying is suitable when series numbers are sufficiently large.

Wherever closed moulding can be introduced it is well worth the investment. Not only will styrene emissions be substantially reduced but the finished products will have greater quality consistency. Closed moulding techniques include resin transfer moulding (RTM), resin injection (male and female moulds), or resin infusion (flexible film forms the male mould).

Low styrene emission and low styrene content resins

Low Styrene Emission (LSE) resins are produced by adding vapour suppressant additives to the resin formulation. These additives form a film over the resin surface once the moulding is left to stand. LSE additives are essentially only effective during the static phase of the process.

Another way to reduce the emission of styrene from UP resins is to reduce the styrene content of the resin. Low Styrene Content (LSC) resins are the result.

Reducing styrene emission by lowering the styrene content is most effective in the dynamic phase of the laminating process. If vapour suppressants are added to an LSC resin, a further lowering of the styrene emission can be achieved. Due to their chemical nature, resins based on DCPD (Dicyclopentadiene) or vinyl ester have an inherently lower styrene content.

LSE and LSC resins have a major influence on the emission of styrene. They may reduce the total emission by 30 - 50%, depending on application process used. And a combination of both technologies (LSC + LSE) may further reduce emissions by 10 - 20%.

Workplace ventilation

A well designed and laid out workshop contributes to higher quality, lower costs and a better workplace environment. In particular, pay attention to the following aspects:

Keep the workshop closed. A well-designed ventilation system will only be effective when the air streams are not disturbed by open windows or doors. Opening the doors in summer times to lower the temperature often results in a higher exposure to styrene.

When working with polyester resins, the bulk of the styrene vapour is generated closest to the moulding operation. It should preferably be removed from the air as close as possible to its source. This ensures the most efficient ventilation of the workshop and means that the styrene vapour can be removed at relatively high concentrations with a low air displacement volume. If the styrene vapour is allowed to diffuse through the workshop, the required ventilation capacity to remove it becomes much higher.

General Workshop Ventilation

When applying general workshop ventilation (also called dilution ventilation), the total air volume of the workshop is replaced several times per hour. This ventilation principle is relatively simple and gives a great degree of flexibility in the movement of materials and products in the workshop. General workshop ventilation is not always sufficient; especially for large mouldings like boats and silos.

Local ventilation

A more efficient method than general workshop ventilation is local ventilation. The styrene vapour is removed through ventilation hoods, installed as close as possible to the place where the styrene is generated.

Zonal ventilation

Zonal ventilation combines general ventilation with local ventilation. In this case part of the total workshop or compartment is ventilated in such a way that the styrene is removed before it is diluted into the air of the total workshop.

Spray booths are a good example of the use of zonal ventilation. A spray booth is a compartment, more or less separated from the rest of the workshop. The air stream can be better controlled and less air is necessary to remove the styrene vapour.

Styrene abatement techniques

The most effective abatement technique is to prevent the escape of styrene into the workplace and subsequently into the atmosphere. The use of low styrene emission and low styrene content resins will assist in this respect in open moulding applications.

It reduces the level of VOC emitted, compared with conventional resins. Even more effective are the use of closed mould techniques, such as vacuum infusion, RTM and hot and cold press moulding.

When styrene emission has to be controlled a number of abatement techniques exist.

Incineration

High temperature incineration or catalytic incineration (at a lower temperature) gives high efficiency of around 99% with energy recycling. To be economically viable the process must use only the combustible pollutant as fuel and require no additional fuel input (except for start up or during short stoppages). Catalytic oxidisers have the advantage of lower operating temperatures and greater destruction efficiencies than thermal oxidisers and, hence, lower running costs. However, the cost of the catalyst usually results in higher capital costs. Mini-catalytic systems can be used where the air flow-rates are low or can be used where emissions are intermittent.

Direct thermal oxidisers

Regenerative thermal oxidisers offer good destruction efficiencies (96-98%) with 90% heat recovery using gravel or ceramic beds. They can operate auto-thermally, without using extra solvent, at approximately 1g/m³ recovery of solvent. At inlet concentrations below this level additional sources of energy, gas/electricity, are required to keep the oxidiser up to temperature.

Bio-filtration systems

Bio-filtration is the bacterial oxidation of organic matter and results in the conversion of organic matter, like incineration, into carbon based gases and water vapour. Bio-filters are good at removing low concentrations of solvent but they suffer efficiency of destruction and process control. Some solvents are easily destroyed by the micro-organisms in the filters but larger molecules, like styrene, need longer residence times for destruction to occur requiring larger systems with greater area.

Adsorption and absorption onto sacrificial intermediates

These two technologies are similar with the exception of the media and they both suffer from similar disadvantages. Adsorption usually occurs onto a carbon filter whilst absorption is into a liquid. When saturated with solvent the media are removed and sent off-site for regeneration or disposal.

Concentration systems

Concentration systems are probably the best technique for low VOC abatement from exhaust levels typically found in the GRP industry. There are two types of concentration systems, rotary wheels and fluidised bed. Both remove solvents from the inlet air by adsorption onto zeolites or polymeric adsorbents and desorbs them into a hot air stream that is a fraction of the level of the original airflow.



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