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2006: Styrene and Worker Protection in the Composites Industry. Fibreglass workers are exposed to styrene for long periods. This paper looks at some of the issues, including how to monitor exposure levels.

Styrene and Worker Protection in the Composites Industry

By Ken Holyoake, Managing Director of ARMATEC Environmental Ltd
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Abstract

Styrene is a key ingredient in the Composites Industry. Styrene is volatile and styrene vapour concentrations in the workplace vary from 20 ppm to 300 ppm. Styrene has a LEL (lower explosive limit) of 11,000 ppm and is not an explosion hazard in the Composites workplace where resins containing styrene are used at ambient temperatures. Styrene has adverse health effects at high concentrations and in New Zealand the WES-TWA (worker exposure standard – time weighted average) is set at 50 ppm. There is inadequate evidence for styrene to be identified as a human carcinogen but the New Zealand authority ERMA [1] has classified styrene as a "possible human carcinogen". With minimal effort, worker exposure to styrene vapour concentrations below the TWA of 50 ppm can be achieved. The effectiveness of worker protection measures can be monitored by analysing the workers urine for mandelic acid at the end of a 40 hour working week.

1. Styrene Key Ingredient in Our Industry

The chemical styrene is an essential component in the making of thousands of everyday products, providing strength, flexibility, and light weight. Examples include camper-van bodies, boats, bathroom and vanity units, chemical plant pipes and vessels, and building panels. Styrene is the volatile component of unsaturated polyester and vinyl ester resins used by the Composites Industry, and comprises between 30% and 50% of the resin. The resins change from liquids to solids during the manufacture of the composite products by a process of polymerisation. This change is produced by the action of catalysts/initiators or hardeners.

2. Styrene is Volatile

With styrene based resins, styrene vapour is given off before and during initial cure, but more than 95% of the styrene monomer is polymerised and fixed into the product during curing, even in open moulding processes.

Styrene is often called a solvent due to its strong "solvent" odour. True solvents, such as used in some thin film paints, evaporate during the drying process and are not retained in the dried paint film. Thus styrene is not an ordinary solvent, but a reactive solvent.

Anyone entering a Composites Factory using styrene based resins will immediately detect the unmistakeable odour of styrene. The odour threshold for detection of styrene is 0.05 ppm [2]. It is not unusual for this strong "solvent" odour to be interpreted as an atmosphere that has a high fire risk and one that might even explode. However when the measurements are done it is found that this isn't even a remote possibility.

3. Styrene Vapour Concentrations in the Workplace

Measurements of styrene vapour levels at Armatec operations were done using a Komyo Kitigawa AP-I precision gas detector to draw 100ml samples of air through Gastec Detector Tubes No. 124 for Styrene ($C_6H_5CH{:}CH_2$). These tubes have a measurement range of 10-1,500ppm. The results are given in Table 1. Measurements from walk through inspections of USA composites factories are given in the NIOSH website [3].

TABLE 1: Styrene Vapour Measurement in ARMATEC Workplace

Site	Location of Measurement	Resin	Styrene Concentration
AT Factory	Within 5 metres of resin sprayed	Iso	50 to 150 ppm
AT Factory	Next to resin sprayhead	Iso	100 ppm
AT Factory	Inside mixing vat during mixing	VE	300 ppm
AT Factory	Adjacent to mixing vat above	VE	20 ppm
AT Factory	General factory area	Various	20 ppm
Pulp Mill	Inside tank during lining	VE	200 ppm max
Pulp Mill	Inside pulp chest during lining	VE	250 ppm max

TABLE 2: Styrene Vapour Concentrations in USA Composites Factories

Factory	Range of Styrene Concentrations
Century Boats, Florida	20 – 60 ppm
US Marine Inc, Washington	5 – 50 ppm
Searay Boats, Tennessee	5 – 50 ppm

In the United States, ACMA [4] advises that it is unaware of any data showing styrene concentrations that exceed 700 ppm. Further ACMA advises that in a test conducted in 1985 for the Oregon Office of the State Fire Marshall, spray application of styrene-containing unsaturated polyester resin resulted in a maximum styrene concentration in air of 690 ppm.

Therefore the hazard we are dealing with is a styrene concentration in the air of up to 700 ppm, and more likely up to about 300 ppm. The maximum will vary from site to site due to different manufacturing methods, resins with differing amounts of styrene, and differing ventilation systems.

4. Explosion and Fire Risk with Styrene

Once alight styrene based resins, both in the liquid form and as cured products, burn with a thick black toxic smoke. When a composites factory is entered and the unmistakeable “solvent” odour of styrene is detected, one reaction is to think that the whole atmosphere is likely to explode and the facility burn. Is this possible or even likely?

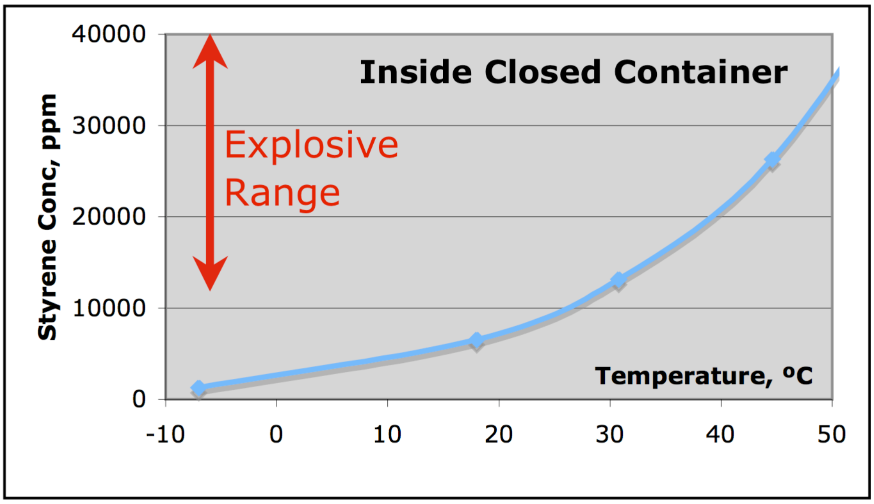
For a vapour based explosion to occur, there have to be two ingredients: (1) an explosive vapour atmosphere, and (2) a source of ignition. Without either of these two an explosion is impossible. Styrene forms an explosive vapour atmosphere in air when the styrene concentration lies between the LEL (lower explosive limit) of 11,000 ppm and the UEL (upper explosive limit) of 61,000 ppm.

With the maximum ever recorded styrene concentration in air in a composites facility of 700 ppm as discussed in section 3, when compared to the LEL of styrene of 11,000 ppm, it is plainly obvious that there is not only no explosive atmosphere due to styrene, but that there is no chance of one being present as it is only 6.4% of the LEL. A styrene vapour explosion cannot occur in a composites manufacturing facility, and so electrical fitting s do not need to be flameproof or fire rated.

A fire test was done with 100 ml of styrene placed in a 2 litre metal container and a flame introduced. Ignition did not occur automatically. When the flame was held in the styrene, it did catch fire, but extinguished itself when the flame was withdrawn.

The place with the highest possible styrene vapour concentration is in a closed container containing styrene liquid. In this situation, with the vapour in equilibrium with the liquid, the vapour concentration is temperature dependent (see fig 1).

FIG 1: Styrene Vapour Concentration Inside Closed Container [5]



From fig 1, an explosive atmosphere forms inside a closed drum of styrene when the temperature exceeds 27ºC. Therefore, if drums of styrene and resin containing styrene solutions are stored in cool places, an explosion cannot occur if a spark accidentally entered the drum. Good work practice is of course keep lids on containers whenever possible to make doubly sure this cannot occur. These closed containers are generally kept within a dangerous goods store. It is also relevant that resins are less hazardous than styrene itself because of their higher viscosity, their ability to form thin films and because they contain 30% to 50% styrene.

5. Comparison with Acetone

Acetone is widely used in the Composites Industry as a cleanup solvent, albeit in very small quantities. It is common practice to have small containers of acetone readily available for workers to clean their tools. While most of the focus is on styrene, it is actually acetone that is by far the more dangerous material from an explosion and fire viewpoint (see Table 3).

TABLE 3: Comparative Properties of Styrene and Acetone

	Flashpoint	Boiling Point	LEL, ppm	UEL, ppm
STYRENE	31ºC	145ºC	11,000	61,000
ACETONE	-17ºC	56ºC	29,000	128,000

At the ARMATEC factory, acetone is kept in a clean-up station with a self-closing lid. The results of acetone vapour concentrations (Gastec Detector Tube No 151L) around and within this station are given in Table 4 below.

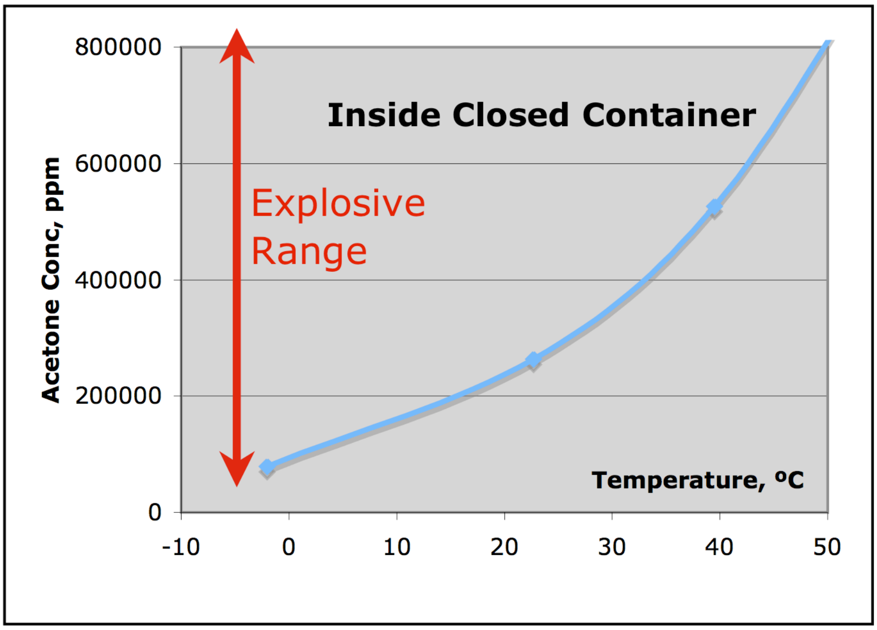
TABLE 4: Acetone Vapour Concentrations at ARMATEC Clean-Up Station

Location (factory temperature 13ºC)	Acetone Vapour Concentration
1 metre from station with lid closed	< 10 ppm (trace only)
Just above station with lid open	100 to 300 ppm
Inside station, just above acetone surface	11,200 ppm

A fire test was done with 100 ml of acetone placed in a 2 litre metal container and a flame introduced. Ignition occurred immediately. The acetone continued to burn when the flame was withdrawn, and the fire became stronger and stronger.

The place with the highest possible acetone vapour concentration is in a closed container containing acetone liquid. In this situation, with the gas in equilibrium with the liquid, the gas concentration is temperature dependent (see fig 2).

FIG 2: Acetone Vapour Concentration Inside Closed Container [5]



An explosive atmosphere is always present inside a closed container of acetone at ambient temperature. Wherever there is acetone there will be an explosive atmosphere and the risk of fire. These closed containers are generally kept within a dangerous goods store. Good work practice must always limit the amount and location of acetone at all times. Never take acetone into an enclosed space under any circumstances. Acetone should be kept away from all ignition sources such as electrical fittings and tools.

6. Toxicity Risk Due To Styrene

In New Zealand, worker exposure limits are set at 50 ppm for the 8 hour TWA (time weighted average) and 100 ppm for the STEL (short term exposure limit). Further styrene is classified as a “possible human carcinogen” by Government Department ERMA [1] based on selected international classifications.

Exposure to styrene may result in respiratory irritation even at relatively low levels. Higher concentrations (above 100 ppm) can cause symptoms such as drowsiness, headache, confusion, incoordination and in extreme cases, unconsciousness. USA organization The US Environmental Protection Agency [6] reports that there are no observed adverse effects below 34 ppm.

The toxicity and health effects of styrene have been and continue to be widely researched. Many studies [7] have been made on more than 100,000 Composites Industry workers and have all concluded that there is no overall increase in risk for lymphatic and haematopoietic cancer due to exposure to styrene. Studies on rodents by oral administration of styrene have found a small increase in tumours in some mice but not in rats. Mice uptake more styrene than rats or humans for a given exposure level. It is reported [8] that humans are more efficient at metabolising styrene than rodents, and as a result less styrene oxide and other DNA damaging intermediates are found in humans. Further research [9] has shown that DNA damage does occur in workers exposed to low concentrations of styrene which could lead to work related cancers, but is influenced by genetics, smoking habits and length of exposure. Here the prediction is that over a 40 year working life with continuous work-time exposure to 10ppm styrene vapour there could be one additional case of lympho-haematopoietic cancer in ten thousand workers. In practice there has been no identified increase in these cancers in workers using styrene even though exposure levels have been considerably higher.

The response of regulatory agencies around the world has been varied [10]. In the USA, OSHA and NIOSH currently assess that styrene does not pose any risk of cancer. The Canadian authorities assess that styrene is non toxic for regulatory purposes. The UK and EU authorities assess that styrene should not be treated as a carcinogen. The IARC and France assess that styrene is a possible human carcinogen. The New Zealand regulatory authority ERMA [1] has followed the IARC even though the IARC state that their classification should not be used for regulatory purposes.

7. Application to a Workplace

Styrene vapour concentrations in the workplace at times of up to 300 ppm exceed the worker exposure standards of 100 ppm STEL and 50 ppm TWA. Measures need to be taken to reduce worker exposure to styrene.

A typical solution is ventilation with sufficient air changes to reduce the ambient styrene concentration, and to stop high concentrations migrating to where other workers are. Other opportunities include lower styrene resins, and different manufacturing systems. Closed moulding techniques such as vacuum infusion dramatically lower the amount of styrene vapour evolved into the workplace.

There are still situations where this is not sufficient and personal protective equipment is required for the workers. An air fed breathing system or a facemask with a carbon filter unit can eliminate all styrene in air being inhaled by a worker. With the latter it is important that the mask is maintained and the carbon filter replaced regularly for effective protection to be maintained.

In the reality of the workplace in the Composites Industry, with individual habits of workers, and with work done at a variety of project sites, no one solution can be used. A ventilation system used in conjunction with personal protective equipment is usually required to give workers the protection needed.

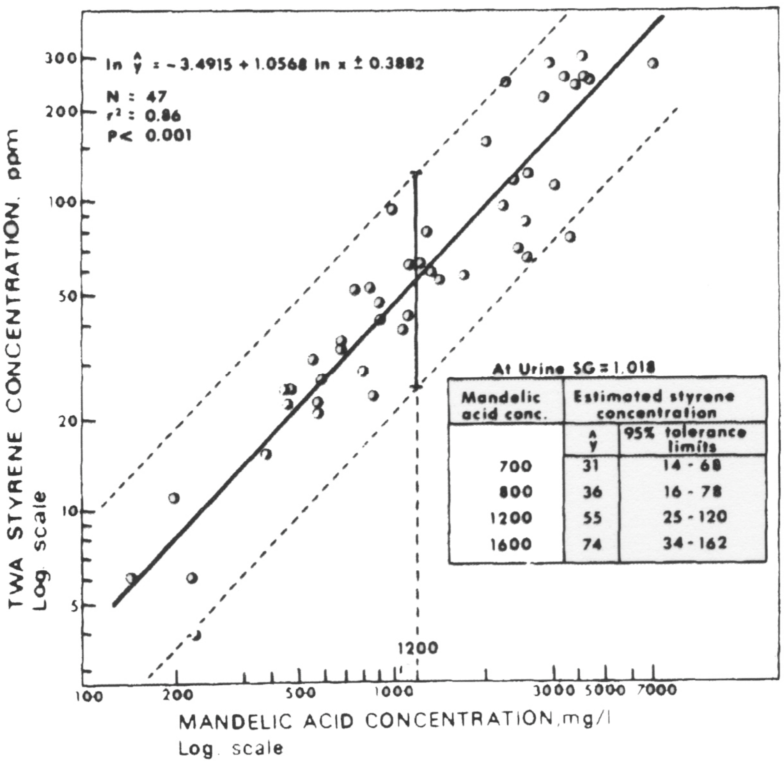
8. Monitoring the Workers – A Test Case

The styrene uptake by workers and thus the effectiveness of the ventilation system, personal protection equipment and their work habits can be monitored. Styrene exposure meters are available that can be worn on the lapel or on the belt, and these give a good indication of exposure levels. These are not without limitations as they are not directly in the air stream the worker is breathing. They cannot for example take account of the time when a worker is wearing personal protective equipment such as a mask.

The effectiveness of worker protection measures can be monitored by analysis of the workers' urine. The NIOSH publication [11] gives evidence that a worker's time weighted average exposure to styrene vapour can be effectively monitored by doing a urine analysis for mandelic acid at the end of a working week. The doted lines in fig 3 are the 95% confidence limits. Thus a mandelic acid level in the urine of 1200 mg/l is indicative of an exposure to 55 ppm of styrene (TWA for 8 hours per day and a forty hour week), with the 95% confidence range being 25 ppm to 120 ppm (fig 3).

Another way of using fig 3 is that to have more than 95% confidence that a worker has been exposed to a TWA of styrene of less than 50 ppm of styrene over the previous 40 hour shift, the mandelic acid concentration in the worker's urine needs to be less than 500 mg/l.

FIG 3: Mandelic Acid in Urine versus Styrene TWA Concentration [11]



During a project to line four pulp chests at a Pulp and Paper Mill during a 9 day shut down, ARMATEC workers worked in an atmosphere of styrene concentrations of up to 250 ppm. Ventilation systems changed the air more than 15 times per hour, and workers wore personal protective full mask respirators at times of high styrene vapour concentrations. At the end of the 9 days the workers gave urine samples and these were analysed for mandelic acid by Canterbury Health Laboratories (Table 5).

TABLE 5: ARMATEC Worker Mandelic Acid in Urine

Worker No.	Mandelic Acid In Urine	Hours worked over 9 days
1	74 mg/l	104
2	65 mg/l	99
3	53 mg/l	111
4	22 mg/l	132
5	64 mg/l	104
6	15 mg/l	132
7	13 mg/l	99
8	73 mg/l	94
9	105 mg/l	116

From Table 5 and Fig 3, the maximum mandelic acid concentration of 105 mg/l for worker 9 would have indicated a TWA exposure to styrene of less than 5 ppm, with the 95% confidence range being 1 ppm to 9 ppm. These numbers are for if the worker had done 40 hours work over 5 days, whereas the worker did 116 hours over 9 days. The wide range of results for mandelic acid in the urine of 13 mg/l to 105 mg/l is probably due to the differing individual's internal organ processing systems, plus the different degrees of diligence that workers practice in the use of their personal protective systems.

As the mandelic acid concentrations in the worker's urine are all substantially less than 500 mg/l, the ventilation and worker personal protective measures used were effective in assuring that the workers were not exposed to styrene vapour concentrations in excess of the WES-TWA.

9. Conclusion

Styrene vapour concentrations in the Composites Industry workplace vary from 20 to 300 ppm. At these concentrations there is no danger of a vapour based explosion as the LEL for styrene is 11,000 ppm, and standard electrical systems can be used.

On the other hand acetone used for clean-up is far more dangerous and there is an explosive vapour atmosphere wherever acetone is present. Workplace practice needs to strictly control the amount of acetone and where it is used.

There are known adverse health effects for workers exposed to styrene vapour at high concentrations. There is continuing debate over whether styrene is a carcinogen or not. There continues to be no evidence that styrene is carcinogenic. It is important to reduce the exposure levels of styrene vapour in the work environment to less than the TWA of 50 ppm to avoid adverse worker health effects. Where styrene vapour concentrations below 50ppm cannot be achieved, workers need to use personal protective equipment.

The effectiveness of worker protection measures can be monitored by analysis of the workers' urine. The urine mandelic acid concentration should be below 500 mg/l for 95% confidence they have been exposed to less than a styrene TWA of 50 ppm.

10. References

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[4] March, 2006. Communication between John Schweitzer of ACMA (American Composites Manufacturers Association) and Mark Hildesley of Materials Optimisation
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