A Field Study to Determine the Effectiveness of Several Respiratory Protection Masks on the Styrene Exposure during Lamination Activities

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Abstract: Purpose of the study: The purpose of this study is to examine the effectiveness of several types of personal respiratory protection equipment at styrene exposed laminators under real workplace conditions. Subjects and method: 99 male styrene exposed workers were examined. During their lamination activities the average styrene concentrations in air ranged between 30 to 60 ppm (maximum: 205 ppm). The laminators were followed during an usual workweek from Monday to Thursday. The external styrene exposure was measured by means of passive active carbon badges. The excretion of mandelic acid (MA) and phenyl glyoxylic acid (PGA) in end-of-shift urine samples was used to quantify the internal styrene load. During the work shift some laminators did not use respiratory protection masks. The majority used either a half face mask with active carbon filter or an air purifying respirator. Results: The respiratory masks were worn during an average between 31% and 72% of the work time. The styrene concentrations of the ambient air were depending on the activity in the range of 30 to 60 ppm. The end-of-shift concentrations of MA and PGA in urine samples varied considerably, their means range from 153 to 606 mg/g creatinine. The comparison shows that workers with air purifying respirators experience the lowest internal styrene body burden in spite of high external exposures. Their effectiveness during usual working condition was around 83% whereas the use of half face masks with active carbon filters reduce styrene exposure only of 26% as an average. Conclusions: The use of styrene-containing resins in boatbuilding can be associated with increased external styrene exposure of the laminators. During the use of different types of respiratory protection masks it is shown that only the application of air purifying respirators leads to a significant reduction of the internal styrene body burden of 83% when worn during 72% of the total work time. In this way it is possible to comply with or to stay clearly below the biological limit value of 600 mg MA + PGA/g creatinine (BAT-value).

Key words: Styrene, Respiratory protection masks, Effectiveness, Biological monitoring

Introduction and purpose of the study

When using styrene-containing resins, styrene emission occurs regularly, which under unfavourable occupational hygiene conditions leads to relatively high airborne styrene concentrations. Investigations in Denmark, Germany and the United States have shown, that the styrene concentration in the air can exceed 25 ppm several times, for example1–4).

Our investigations of lamination workplaces in a shipyard have shown that in spite of having modern installations for supply fresh air and to remove contaminated air the Occupational Exposure Limit (OEL) in Germany of 20 ppm is clearly exceeded from time to time5, 6).

Workers performing lamination work without using personal protective measures show a higher styrene load measured as excreted styrene metabolites that exceeds the Biological Limit Value (BAT-Value)5, 6). In order to min-
imize the health effects caused by styrene exposure the use of respiratory masks is required. This issue has been addressed already by several studies resulting in different conclusions due to the variation in methods with which the studies were performed7–10).

From this starting point the essential purpose of this study was to examine the effectiveness of various respiratory protection systems under real workplace conditions. Therefore the internal styrene load was measured using a biomonitoring method in which the excretion of mandelic acid and phenyl glyoxylic acid at the end of the work shift was compared to the external styrene exposure measured with passive air sampling. The difference between both measurements is an indication for the effectiveness of the respiratory protection.

### Subjects and Method

**Subjects**

From the total workforce of approximately 180 laminators in a shipyard, 99 men were randomly selected. The participation to the study was voluntary. The workers were informed about the content, the purpose and the time schedule of the investigations.

In Table 1 the age, height and body-mass index (BMI) of the laminators are shown.

**Work areas and Activities**

The laminators were working in the following areas of the boat production:

1. Production of the decks N=40
2. Production of the hulls N=33
3. Interior construction N=16
4. “Top coating”, i.e. the application of resin by means of spraying N=10

**Respiratory protection masks**

Depending on the activity most workers used respiratory protection masks, either part or full time. The non-users and users were divided in the following groups with respect to the effectiveness of the respiratory protection (see Figs. 1 to 4):

1. No use of respiratory protection or use of a dust

### Table 1. Age, height, weight and body-mass index (BMI) of 99 examined laminators

<table>
<thead>
<tr>
<th></th>
<th>M ± SD</th>
<th>Median (min–max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age [Years]</td>
<td>39 ± 9</td>
<td>38 (23–66)</td>
</tr>
<tr>
<td>Height [cm]</td>
<td>174 ± 7</td>
<td>174 (162–192)</td>
</tr>
<tr>
<td>Weight [kg]</td>
<td>82 ± 13</td>
<td>81 (52–130)</td>
</tr>
<tr>
<td>BMI [kg/m²]</td>
<td>27 ± 4</td>
<td>27 (18–40)</td>
</tr>
</tbody>
</table>

**Fig. 1.** View of a typical lamination workplace. The workers do not use respiratory protective equipment.

**Fig. 2.** Lamination activity in a small room. The workers are using half face masks with active carbon filter cartridge.
2. Wearing half face masks with an active carbon filter cartridge (Filter type A2)

The filter type A2 was used for organic vapours with a boiling point of > 65°C. According to the supplier of the filters they are suitable to clean the surrounding air to such a degree that even at a concentration exceeding the occupational exposure limit (OEL) by a factor of 30 the concentration in the air breathed will be below the OEL.

The active carbon filters were renewed before every shift.

3. Wearing an air purifying respirator with active carbon filter cartridge (Filter type A2).

According to the supplier this respirator is effective even under circumstances where the exposure limit (e.g. OEL or MAK-value) is exceeded by a factor of 200 (Fa. Moldex, Walldorf, Germany).

**Study day**

<table>
<thead>
<tr>
<th>Monday</th>
<th>Tuesday</th>
<th>Wednesday</th>
<th>Thursday</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taking urine sample</td>
<td>Attach active carbon air sampler</td>
<td>Attach active carbon air sampler</td>
<td>Attach active carbon air sampler</td>
</tr>
<tr>
<td>At start of work shift</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>During work shift</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At end of work shift</td>
<td>Stop and conservation of active carbon air sampler</td>
<td>Stop and conservation of active carbon air sampler</td>
<td>Stop and conservation of active carbon air sampler</td>
</tr>
<tr>
<td></td>
<td>Taking urine sample</td>
<td>Taking urine sample</td>
<td>Taking urine sample</td>
</tr>
<tr>
<td></td>
<td>Taking blood sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filling out questionnaire</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Observations at the workplace</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 4. Chronological sequence of the study and individual steps of examinations.**
sample is taken from the participants at the end of the work shift at the 1st and 4th workday.

In order to document the conditions under which the exposure has been taken place, the participants are requested to fill out a standardized questionnaire.

The following details regarding the styrene exposure are documented:
1. The duration of the exposure before the blood sample is taken
2. The use of protective clothing, use of respiratory protection masks and duration of the use
3. Dermal contact with styrene and/or resin.

Examinations
Before starting the study, the workers are examined according to the guidelines for Occupational Medical Examinations G 45 (styrene) and G 26 (Respiratory protective equipment)\(^{11}\).

The examinations include:
- Medical and occupational history
- Physical examination (skin, lung, heart, nervous system)
- Delivery of an urine sample
- Sampling of a blood specimen by venipuncture at the end of shift to measure styrene in blood

Procedure of the analysis
Styrene that has been absorbed on the active carbon cartridges is desorbed and dissolved with carbon disulphide. Styrene is separated by means of gas chromatography and analysed with FID. As internal standard p-xylene is used. The analytical limit of determination is approx. 0.5 ppm.

From the venous blood sample 2 ml is transferred into a gastight gas container (headspace container) and till the analysis stored at –20°C.

The determination of styrene is done by means of gas space gas chromatography according to a recommended method of the German Research Society (DFG 1996 and 1997). The analytical limit of determination is approx. 5 \(\mu\)g/l.

In urine the main metabolites of styrene, i.e. mandelic acid (MA) and phenyl glyoxylic acid (PGA) are determined by means of high-pressure liquid chromatography (HPLC) and UV detection\(^{12,13}\). The analytical limit of determination is 10 mg/l (MA) and 20 mg/l (PGA). In order to compensate for diuresis-caused fluctuations, the concentrations of the metabolites are related on the excretion of creatinine.

Statistics
For the data analysis SPSS Version 11.0 is used. The results are displayed as mean values with SD, resp. medians and ranges. The differences are checked by means of a \(t\)-test. As limit of significance \(p<0.05\) is accepted.

To calculate the relationship between the external and internal styrene exposure knowledge of the styrene concentration in the breathed air is necessary. This concentration cannot be measured at workers, wearing respiratory masks; it has to be calculated from the correlation between the styrene concentration in the inhaled air and the excretion of the styrene metabolites in the urine samples. For this reason the derived correlation by Benignus \textit{et al.}\(^{14}\) is used. This correlation is based on a comprehensive regression analysis of data from five studies with approx. 300 styrene exposed workers.

The correlation is given in the following equation:

\[
\text{Styrene in inhaled air (ppm)} = 0.289 + 0.0793 \times \text{mandelic acid concentration (in mg/g creatinine)}.
\]

The effectiveness of respiratory protection masks is then calculated from the difference between real measured styrene concentrations in the air and the extrapolated styrene concentrations by equation.

Results

Occupational history
The examined laminators have been working since 5 yr as laminators. The daily shift length is on average 8.7 h, the lunch break of half an hour is not taken into account. None of the workers has facial hair.

During production related breaks in the work activities, the participants stay in the work area. During these periods no respiratory masks are worn. This results in an additional exposure to styrene originating from the concentration of styrene present in the ambient air of the workplace.

Protective clothing and dermal contact
The mentioned details concerning the use of protective clothing and dermal contact with resin are given in Tables 2 and 3.

The majority of laminators wear protective clothing and nitrile gloves. In spite of these personal protective measures around half of the workers indicate dermal contact with the styrene containing resins.

Respiratory protection masks
Table 4 contains the duration of wearing respiratory protection as a percentage of the total shift working time, as indicated by the participants.

The average duration of the use of respiratory protection varies between 31% and maximum 72% of the total shift working time. Ventilation assisted full face masks are used more often, compared to half face masks.
Styrene exposure

Table 5 demonstrates the styrene airborne vapour concentrations in the different work areas.

The highest styrene concentration of 205 ppm is measured in the top coating area. However, top coating is only a temporary activity and therefore the average styrene exposure in this area is lower in comparison to the deck construction, which is a continuous activity.

Figure 5 shows the average styrene concentrations in the ambient air for the days 1 until 4 in relation to the type of respiratory protection device used.

It can be seen that the styrene air concentrations are clearly lower for those workers that use no respiratory protection device. Workers which are not exposed over the full shift to styrene or just having a limited exposure to styrene, are not obliged to wear respiratory protection.

Styrene in blood

Table 6 shows the styrene concentrations in the end-of-shift blood samples. The styrene concentrations in the blood samples vary in a wide range of minimum 46 µg/l to 749 µg/l. When comparing the average blood concentrations as well as the SD and the maximum values of day 1 and day 4, it turns out that the values at day 4 are not higher. This indicates that there is no accumulation of the styrene blood level during the four days of exposure.

Mandelic acid and phenylglyoxilic acid in urine

Table 7 shows the concentrations of MA and PGA for day 1 to day 4, in relation to the use of respiratory protection masks. It should be taken into consideration that workers without respiratory protection and laminators using fine dust masks (no protection for vapours) are shown together.

It is shown that workers using air purifying respirators show the lowest styrene body burden. On the contrary there is no major difference between the urine secretion.
of workers without respiratory protection and those wearing a half face masks with active carbon cartridge.

The increase in metabolite concentrations for day 1 is statistically significant, independent from the protective measure. It is as could be expected the least pronounced for those laminators using air purifying respirators.

The metabolite concentrations from day 1 to day 4 at end-of-shift also show an increase for those participants without adequate respiratory protection; it is however not statistically significant ($p>0.05$).

**Effectiveness of respiratory protection masks**

Table 8 shows the average styrene vapour concentrations in the ambient air and in the breathed air as well as the differences, in relation to the used respiratory protection masks.

The styrene concentration in the breathed air is calculated from the mandelic acid secretion in urine according to the equation (see Statistics in Subjects and Method).

The small difference of approx. 3 ppm at those workers without respiratory protection masks confirms the used calculation method.

The use of half face masks with active carbon cartridges reduces the styrene concentration only by about 26%. The use of ventilation assisted full face masks on

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**Fig. 5. Styrene concentrations in ambient air of workers using different respiratory protective equipment.**

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### Table 6. Concentration of styrene in venous blood samples

<table>
<thead>
<tr>
<th>Styrene in blood [µg/l]</th>
<th>M ± SD</th>
<th>Median (min–max)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>243 ± 165</td>
<td>198 (49–749)</td>
<td>85</td>
</tr>
<tr>
<td>Day 4</td>
<td>228 ± 145</td>
<td>198 (46–712)</td>
<td>87</td>
</tr>
<tr>
<td>Total</td>
<td>235 ± 155</td>
<td>199 (46–749)</td>
<td>172</td>
</tr>
</tbody>
</table>

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### Table 7. Concentration of Mandelic acid (MA) and Phenyl glyoxylic acid (PGA) in urine of workers with different respiratory protective equipment during the days of examination. Given are mean and medium values with standard deviation and range.

<table>
<thead>
<tr>
<th>MA &amp; PGA [mg/g Creatinine]</th>
<th>no protection</th>
<th>half face mask</th>
<th>air purifying respirator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M ± SD</td>
<td>Median (min–max)</td>
<td>N</td>
</tr>
<tr>
<td>Day 1 before start of shift</td>
<td>50 ± 29 (9–160)</td>
<td>29</td>
<td>16</td>
</tr>
<tr>
<td>Day 1 at end-of-shift</td>
<td>359 ± 223 (19–1,333)</td>
<td>223</td>
<td>14</td>
</tr>
<tr>
<td>Day 2 at end-of-shift</td>
<td>416 ± 234 (24–2,033)</td>
<td>234</td>
<td>16</td>
</tr>
<tr>
<td>Day 3 at end-of-shift</td>
<td>450 ± 248 (6–1,750)</td>
<td>248</td>
<td>14</td>
</tr>
<tr>
<td>Day 4 at end-of-shift</td>
<td>412 ± 241 (28–1,666)</td>
<td>241</td>
<td>15</td>
</tr>
</tbody>
</table>
the contrary leads to a decrease in styrene exposure of about 83%. In both cases the differences are significant.

Figure 6 shows that there is hardly any difference between the measured and the calculated styrene concentrations at workers not using respiratory protection during the test period. The differences are statistically not significant.

On the contrary—as shown in Figs. 7 and 8—the styrene concentration in breathed air for workers wearing respiratory protection masks is lowered with an average 12 ppm or 26% compared to ambient air concentrations when used during an average of 54% of the total time.

The differences are more pronounced for workers using air purifying respirators (Fig. 8). Whereas the measured styrene concentration is between 50 and 60 ppm, the extrapolated styrene concentration in the breathed air is below 10 ppm.

Using air purifying respirators at an average duration

<table>
<thead>
<tr>
<th>respiratory protection</th>
<th>ambient air (measured)</th>
<th>inhaled air (calculated)</th>
<th>Δ</th>
<th>%</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>no protection</td>
<td>23 ± 33</td>
<td>21 ± 31</td>
<td>3 ± 15</td>
<td>9</td>
<td>0.19</td>
</tr>
<tr>
<td>half face mask</td>
<td>38 ± 16</td>
<td>28 ± 21</td>
<td>12 ± 33</td>
<td>26</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>air purifying respirator</td>
<td>52 ± 33</td>
<td>9 ± 7</td>
<td>45 ± 36</td>
<td>83</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Fig. 6. Styrene concentrations in ambient and breathed air of workers without respiratory protective equipment.

Fig. 7. Styrene concentrations in ambient air and breathed air of workers using half face masks.
of 72% of the total work time results in a reduction of the styrene concentration of average 45 ppm or 83% of the ambient air concentration.

Discussion

Main result of this study is that under real workplace circumstances, e.g. laminating large surface areas the internal styrene body burden can be lowered significantly by using personal respiratory protective masks. Laminators with high styrene exposures use mostly air purifying respirators with active carbon filters. This leads to a reduction in the internal styrene load of 83% of the ambient air concentrations as an average.

In comparison to this the use of half face masks with active carbon cartridges decreases the styrene exposure of only 26% as an average. It should be considered that the duration of wearing the half face masks is lower compared to the time full face masks are used (on average 54% compared to 72% of the shift). Based on the partly high external styrene concentrations, that exceed the occupational exposure limit of 20 ppm clearly, using ventilation assisted full face masks is required for all workers under these exposure circumstances. After having exercised all possible measures at the workplace from an occupational health point-of-view, an acceptable level of styrene exposure can only be achieved by using proper respiratory protection.

In practice it is observed that for a variety of reasons the respiratory protection masks are not worn during the full working period. This is caused by discomfort in wearing, poor fit, limitation on body movement and an increase in physical strain caused by using the mask. Additionally, communication is hampered when wearing the air purifying respirators. This has already been indicated by Löf et al.9).

Masks are not worn in the immediate vicinity of the workplace for an average of 44% of the shift. This relatively large time span can cause styrene body burden above current biological limit value (BAT-Value) of 600 mg MA + PGA/g creatinine15).

There are several studies published in literature which reported the effectiveness of respiratory protection masks. Brooks et al.16) performed serial measurements of expired breath and blood styrene and urinary excretion of mandelic and phenylglyoxylic acid in eight female workers during 4 consecutive days with or without respirator. The authors reported a significant reduction of around 70 to 80% in the post shift concentrations of styrene in breath and blood when disposable organic respirators were used. Löf et al.9) examined laminators in the boat building industry using either a half face mask or a full face mask with external supply of air. The use of respiratory protection masks led to a reduction in styrene exposure of approx.76% compared to activities without protective measures. This result is of the same order of magnitude as our observations. Contrary to other authors Löf et al.9) have determined the styrene concentrations in the air outside and inside the mask, but not the internal exposure by using the styrene metabolites in urine.

We have considered this procedure at the start of this study in order to take the inter-individual variability in excretion of the metabolites into account.

In the study of Gobba et al.7) seven workers were examined who processed styrene containing materials by means of rollers, brushes and spray guns. The authors determined the concentrations of metabolites in urine and compared the activities during one week with and without using a half face mask. The mask could be worn however only during the morning. This resulted in an average reduction of styrene exposure of 60% with a variation between 30% and 90%. The authors concluded that...
using the masks resulted in a large intra-individual variability and in several cases it was insufficient to achieve a tolerable exposure.

Inaoka et al. examined around 100 men and women in ten smaller companies by means of analysis of urine samples. They compared the airborne styrene concentrations with the excretion of mandelic acid in the urine. Based on the different correlations between the external and internal styrene exposure the authors came to the conclusion that respiratory protection masks with an active carbon cartridge absorbed 45 to 49% of the inhalable styrene quantity. They concluded that this relatively limited protective effect is caused by the fact that masks are used too long without a change of the filter cartridge.

In a field study Nakayama et al. have examined the effectiveness of three respiratory protection masks. To determine the effectiveness they compared the inhaled styrene concentration with excretion of mandelic acid in urine samples in 39 workers. Taking the wearing time and the exchange rate of the filters into consideration, the authors found that the effectiveness was maximal when the half face masks with active carbon filters were changed twice per day. In comparison, the effectiveness of active carbon impregnated gauze-masks as well as dust masks proved to be minute or absent.

The fact that most laminators take off their masks several times during the work shift does not comply with the instructions of the management of the company. All laminators are obliged to use adequate masks. The foremen are instructed to supervise the correct use of respiratory protection equipment. Therefore it is to expect that the efficiency could be above 90% if the masks are used without break.

Considering the dermal contact to styrene-containing resin it is to conclude, that this exposure did not significantly contribute to the internal body burden. There was no statistically significant correlation between the frequency of dermal contact and the body burden as indicated by styrene level in blood as well as the excretion of metabolites in urine (results not shown).

This result can be explained by the fact that percutaneous resorption of styrene under this working condition is of minor importance compared to the inhalation of styrene vapours. According to Limasset et al., who performed a field study in a real situation in the fibre-glass-reinforced polyester industry, percutaneous absorption is not a particularly important pathway for styrene exposure. The urinary excretion level of the group with total protection did not significantly differ from that of the group with respiratory protection only.

Brooks et al. monitored eight workers in the reinforced plastics industry for levels of styrene in blood and for urinary metabolites of styrene after lamination work. There was no significant difference in levels of styrene in blood or metabolites in urine between the shift when gloves were worn and the shift when no dermal protection was worn. Therefore it was concluded, that cutaneous absorption of styrene is not a significant exposure source and does not significantly contribute to the body burden of styrene of workers in the reinforced plastic industry engaged in hand lay-up operations.

Conclusions

When considering the results of this study and comparing them with the literature references, it becomes clear that the effectiveness of respiratory protection masks depends on several circumstances.

The construction of the mask (i.e. basically with or without active carbon filter) and the time period the mask is worn during the work shift are of particular importance. Both determinants have a strong relation to each other; respiratory masks that are uncomfortable or restrict the freedom of movement will or cannot be used during a full working period.

The results of this study show that the use of air purifying respirators during the lamination of large surface areas is indispensable during longer periods of exposure in order to stay below the occupational exposure limits. In contrary to this, the use of half face masks with active carbon cartridges is not sufficient to reach this target at styrene concentrations in the ambient air of more than 50 ppm.

Acknowledgement

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