Introduction

Organic solvents benzene, toluene and xylenes (BTX) are present in a range of commercial products because of their wide industrial use in the production of plastic, paints, glues, solvents, and also as intermediates in the production of other chemical substances. Exposure to solvents occurs in a variety of workplace and community settings, including oil refining and petrochemical facilities, plastics manufacturing, painting, paint manufacturing processes and building maintenance. At low or moderate concentrations, organic solvents may cause transient symptoms in the central nervous system, such as euphoria, headaches, and dizziness. At high concentrations, however, disturbance in consciousness and the failure of respiratory and circulatory control centers may result in death.

Solvents are the most important components of paints. The major purpose of their application is to dilute paints to a suitable handling consistency or viscosity for easier manufacturing and application. After the application of paint, the solvents evaporate leaving the dry paint film on the painted surface.

In paint and ink facilities, solvents vapors are generated throughout the manufacturing process. If the process is left uncontrolled, high concentrations of organic solvents can be built up at the work place, threatening workers’ health and safety. Release of volatile organics solvents to atmosphere can increase level of Ozone and photochemical pollutants leading to adverse effects in public health.
Paints are usually a mixture of 45% low solvent-based, 45% high solvent-based paints and 10% thinners. The primary factors affecting emissions from paint manufacturing process are the types of solvents used and mixing temperature. About 1 to 3% of the solvent is lost under well-controlled conditions. The emission rate for the uncontrolled manufacturing of paints and varnishes is 15 g/kg of consumed solvent.

Equipment and process modification, improved operating practices and recycling can lead to lower emission rates of organic solvents. The application of ventilation systems equipped with well designed capturing (hoods) and removing (aircleaning) devices can remove the organic solvents from indoor and outdoor atmosphere. However proper execution of ventilation design work will also be necessary for better controlling results.

The purposes of present study were to: a) determine the capabilities of implementing well known ventilation standards in controlling indoor air pollutions due to solvents used in a paint manufacturing factory, b) Highlight the existing challenges with current threshold limit values and c) Identify residual risks after applying such an engineering controls.

Subjects and Methods

Ventilation system design and test

The paint manufacturing process in the factory, where the study was performed consists of mixing, milling and shearing (canning) stages. Different types of mixers and mills were used. All equipments were located in one hall. Figure 1 shows the machinery layout. Natural ventilation was the only means of diluting air pollutants in the absence of ventilation systems. Partitioning of the process was impossible because of transportation and technical problems. The lids of paint tanks which influence the ventilation capacity were not usable in all situations.

Thus, workers were expected to experience high concentrations of evaporated solvents in their breathing zone. However the application of personal protective equipment was limited for many reasons including their price, effectiveness and application assurance.

When the mixing tanks are equipped with lids, ACGIH (American Conference of Governmental Industrial Hygienists) recommends dilution ventilation for paint mixing halls. According to its ventilation standard VS-75-30, ACGIH suggests to exhaust polluted air from hall sides (close to mixing tanks) and supply fresh air from top center of the hall. Based on this Ventilation Standard, the pressure should be slightly negative in paint mixing hall. For this purpose, the exhausted air flow rate must be 5% more than supplied air flow rates. According to the same standard, supply and exhausted air flow rates are recommended to be 10 to 12 air changes per hour.

When the paint tanks are without lids, ACGIH has no special suggestion, but its ventilation standard number VS-70-20 is considered for solvent degreasing tanks that is the most similar process to the paint tanks and mixers without lids.

ASHREA (American Society of Heating, Refrigeration and Air-conditioning Engineers) and EPA (U.S Environmental Protection Agency) emphasize on the most possible enclosure of paint manufacturing equipments. According to their literatures, local exhaust ventilation accompanying with dilution ventilation systems would act the best in controlling of pollutants in paint manufacturing processes. An atmosphere of flammable liquid safeguarded against fire and explosion usually will be kept below 25% of the lower explosive level (e.g. with a safety factor of 4). This will fulfill NFPA (U.S National Fire Protection Agency) and ACGIH recommendations on fire prevention of organic solvents in these areas as well.

In present study, recommendations of several knowledgeable institutes were taken into consideration. Since most of them were similar to each other, ACGIH recommendations were finally applied. For this purpose, a combination of local exhaust ventilation based on VS-70-20 and general dilution ventilation based on VS-75-30 both recommended by ACGIH were implemented.

Exhausted air was designed for 20% more than recommended values. As mentioned previously, 10 to 12 air changes per hour (VS-75-30) and 50 cfm/ft² of tank open area (VS-70-20) were considered as main design criteria.

Seven local exhaust ventilation systems were designed and implemented according to ACGIH industrial ventila-
tion standard handbook\textsuperscript{5}). All parameters in ACGIH data sheet were formulated in Microsoft Excel program for detail design. Velocity Pressure method was used to calculate the pressure of each system\textsuperscript{5}). “Balanced by Design” method was applied to balance the static pressure of each branch with its main duct. However, several dampers (gates) were employed in some critical locations for balancing purposes\textsuperscript{5}). The total supply air flow and consequently the total exhaust air flow were designed based on 10 to 12 air changes per hour according to ACGIH VS-75-30. Ducting was made of galvanized sheets with different thicknesses for ducts, elbows and hoods. Fiber dust collectors with 98% capture efficiency were selected for a few dry mixing processes. Fans were selected based on the calculation results. Figures 2 to 6 shows 3D configuration of different ventilation systems applied to different processes.

**Personal air sampling and analytical methods**

Toluene and Xylene are the most common organic solvents in paint manufacturing factory under study. Thus, the vapors of these two substances were measured and analyzed with and without the application of implemented ventilation systems. For this purpose, 32 personal air samples were collected from breathing zone of workers using OSHA (Occupational Safety and Health Administration) analytical method No: 12 before the application of ventilation systems. Then 19 similar sam-
amples were collected after the application of the ventilation system using the same method. Few samples were shown invalid during their analysis so the post control samples decreased to 19.

All samples were collected by adsorption using charcoal tubes (coconut charcoal 20/40 mesh, 50/100 mg, SKC, USA), with a 100 mg sampling section and 50 mg back-up section according to OSHA No.12 analytical method.

Manufacturing lots were used, with desorption efficiencies determined for each lot. SKC model 224-44EX pumps operated at approximately 50 ml/min were used for air sampling. All pumps were calibrated before each use by a calibrated rotameter (a flow measuring device to determine real air flow). Sampled air and contaminant vapor volumes were corrected for density variation due to ambient temperatures and pressures changes from 760 mm Hg and 25˚C.

The occurrence of breakthrough in samples taken for duration of 4 h and flow rate of 50 ml/min were examined. Then samples with breakthrough of more than 10% on the rear charcoal section were excluded from the study.

The initial desorbing solvent for all samples was carbon disulfide. Both parts of samples (front and rear) were desorbed separately with carbon disulfide, taking 30 min for desorption, and analyzed by gas chromatography. Approximately 63 charcoal tube samples were analyzed in the study, including 9 blanks (one per day per tube lot). In this study Cumene (C₉H₁₂) was used as internal standard (IS) in order to remove the errors of sample preparation lost. Thus, 0.2 µl of Cumene (1-methylethyl benzene) was added to all vials during sample preparation. All chromatography was conducted on a SHIMADZU 175A series gas chromatograph with a flame ionization detector. The Resulted chromatograms were logged, using, GC Real Time Analysis software. Standard Curves were created to quantify the samples (Figs. 7 to 10).

**Results**

Efficiency of the implemented ventilation systems was tested, so exhaust flow rates, total pressure, static pressure and velocity pressure at different parts of each ventilation system were measured based on ACGIH and BS (British Standard) recommendations. Pitot tubes, monometers and anemometers from Air Flow Company (UK) were used for measurement of aerodynamic parameters. Air density was corrected for barometric pressure, temperature, and static pressure where it was essential. Measuring equipments were calibrated by their manufacturer's local representative prior to their use in the study.

In Fig. 11, the design flow rates are compared with measured flow rates. This figure shows that apparently the installed system is not working as designed system. In fact the designed parameters have not been completely established according to ventilation detail design. These results show that 60 to 70 percent of the designed
flow rates were achieved in this project. Unfortunately in Iran the fan manufacturers are not able to deliver the exact required fans. However the difference between design flow rate and measured flow rate may be due to this fact, measuring discrepancy and probable air leakage in some duct connections. However 20 percent over design was considered during system design, so this difference between designed parameters and real achievements have little impact on final results.

Benzene, Toluene, Para-, Meta- and Ortho-Xylene were detected from personal air samples chromatograms. In Table 1 the concentrations of detected pollutants before and after application of ventilation system are listed. In this table the concentrations of Para- and Meta-Xylene are mentioned in a single value, because their analytical peak in GC set were simultaneously appeared. However there need only total Xylene value for assessment as well.

The mean values of Benzene, Toluene and total Xylene concentrations before applying engineering controls were 31.98, 105.82 and 145.16 ppm respectively. The results showed that these values were reduced respectively to 4.5, 44.5 and 97.73 ppm after the application of ventilation systems. The Independent t-test before and after the ventilation was done for Benzene, Toluene and total Xylene.

Table 1. Result of independent t-test (all values in ppm)

<table>
<thead>
<tr>
<th>Pollutant (ppm)</th>
<th>Before control</th>
<th></th>
<th></th>
<th>After control</th>
<th></th>
<th></th>
<th>MD</th>
<th>t</th>
<th>Sig. (2-tailed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Mean</td>
<td>SD</td>
<td>n</td>
<td>Mean</td>
<td>SD</td>
<td>MD</td>
<td>t</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>32</td>
<td>31.98</td>
<td>26.08</td>
<td>19</td>
<td>4.50</td>
<td>3.64</td>
<td>27.50</td>
<td>5.84</td>
<td>0.001</td>
</tr>
<tr>
<td>Toluene</td>
<td>32</td>
<td>105.82</td>
<td>74.88</td>
<td>19</td>
<td>44.50</td>
<td>24.39</td>
<td>61.33</td>
<td>4.27</td>
<td>0.001</td>
</tr>
<tr>
<td>P&amp;M-Xylenes</td>
<td>32</td>
<td>145.16</td>
<td>39.70</td>
<td>19</td>
<td>56.16</td>
<td>30.52</td>
<td>89</td>
<td>8.40</td>
<td>0.001</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>32</td>
<td>76.60</td>
<td>28.83</td>
<td>19</td>
<td>41.57</td>
<td>26.56</td>
<td>35.03</td>
<td>4.32</td>
<td>0.001</td>
</tr>
</tbody>
</table>

MD: Mean Difference, SD: Standard Deviation.

These results showed that the reduction of these pollutants were statistically significant ($p<0.001$ Table 1).

Discussion

Benzene was usually contained as impurity in paint, thinner or solvent until early 1990s, even in low values of less than 1%\(^7\). Existence of Benzene in Benzene free solvents used in paint producing factories can be considered as a warning sign. Bang et al. reported in 1996 that ambient Benzene levels in painters and printing work places were 0.31 (0.02 to 3.26) ppm and 0.25 (0.02 to 3.95) ppm, respectively\(^8\). The amount of Benzene as impurity in thinners has decreased since 1980s. Paik et al. analyzed 108 different thinners in 1998. Most of the thinners were Benzene free, but eight still contained Benzene as impurity\(^9\). Lee et al. has analyzed 70 different thinners used in automobile manufacturing factory in 2002. They found that seven thinners contained Benzene, but the concentration of Benzene was less than 0.1%\(^10\).

Early Benzene application as a solvent in uncontrolled workplaces with high exposure levels was found to be a potent of bone marrow toxicant. However, it was not until 1970s that epidemiological studies conducted in the USA discovered excesses of acute and chronic leukemia.
This was essentially the starting point of many more detailed epidemiological investigations that examined leukemia in well-defined cohorts with estimated exposure profiles. These investigations enabled quantitative risk assessments to be developed.

The common type of leukemia caused by Benzene was acute non-lymphatic leukemia. However, any type of hematopoietic disease can be developed because Benzene toxicity affects the proliferating process of the stem cell.

According to a cohort study by Rinsky et al. (1981) on 1165 white men employed in the rubber hydrochloride department for at least 1 d through 1965 till 1981, the relative risks of employees were found to increase with cumulative exposure as shown in Table 2.

Supposing work-life time of workers in present study to be 30 yr, then the cumulative exposure to Benzene before and after applying ventilation systems would be 959.4 ppm-year and 135 ppm-year respectively. Comparing cumulative exposure of workers before and after application of ventilation systems, the relative risk of leukemia decreases from 66.4 to 3.2 cases per work-life time in this factory. So the relative risk of leukemia is decreased noticeably and the role of implemented engineering controls is appreciable. The complete removal of Benzene from workplace is ideal, but it is difficult to achieve using present ACGIH ventilation standards. Benzene was not intended to be produced as a raw material or an additive in this factory, so it may be leaked from purification processes of refineries. Therefore, the ventilation standards recommended by ACGIH would be significant if basic solvents for paint manufacturing could be Benzene free.

The guidelines to assess Toluene carcinogenic risk include inadequate information. Studies of humans who were chronically exposed to Toluene are inconclusive. Toluene was not carcinogenic in inhalation cancer bioassays of rats and mice exposed for life. Increased incidences of mammary cancer and leukemia were reported in a lifetime rat oral bioassay at a dose level of 500 mg/kg/d but not at 800 mg/kg/d. Toluene has generally not been found to be genotoxic in short-term testing. A number of studies examined the toxicity of Toluene following inhalation exposure in humans. The available data indicate that neurological effects are the most sensitive effect of chronic inhalation exposure to Toluene. A subset of studies was chosen from which to derive a point of departure for the derivation of the RFC (Reference Concentration). A value of 34 ppm (128 mg/m³) was chosen as the point of departure. This value is the arithmetic mean of the available NOAELs (No Observable Adverse Effect Level). This value is lower than the LOAELs (Low Observable Adverse Effect Level) identified under human exposure conditions. Confidence in the database is high. Multiple chronic studies in humans that examined neurotoxic effects are available. Numerous animal reproductive and developmental studies, as well as a two-generation reproductive toxicity study, were also performed. The results from all studies show a high confidence in the resulting RFC.

According to Draft Revised Guidelines for Carcinogen Risk Assessment, data for an assessment of the carcinogenic potential of Xylenes in human are inadequate. The available data on the ability of Xylenes to cause a carcinogenic response from animal tests are inconclusive. Evaluations of the genotoxic effects of Xylenes have consistently given negative results.

Associations between occupational exposure to Xylenes and increased risk of leukemia, non-Hodgkin's lymphoma, and cancer of the rectum, colon and nervous system have been reported. However, a number of limitations preclude the usefulness of these data, including small sample sizes, no quantified exposure concentrations, and/or concurrent exposures to other solvents.

Xylene refers to a mixture of all three Xylene isomers. The inhalation RFC for Xylenes presented herein is based on a principal study in which rats were exposed by inhalation to Meta-Xylene. There is some uncertainty associated with selecting a principal study for Xylenes that involved exposure to Meta-Xylene alone, but this isomer is generally predominant in commercial mixtures. In addition, although there are no studies comparing Xylene isomers in affecting critical neurological endpoints following sub-chronic or chronic inhalation exposure, the potencies of individual Xylene isomers were similar in affecting neuro-behavior, as shown in a study of rats following acute exposures.

The sub-chronic rat study by Korsak et al. (1994) was selected as the principal study to derive the RFC. A NOAEL of 50 ppm and a LOAEL of 100 ppm were identified for decreased rotarod performance (impaired motor coordination). This neurological test was administered 24 h after termination of the exposure period, when Xylenes would be expected to have been eliminated from the body. Other sub-chronic rat studies provide support for the finding that 100 ppm exposure produces statistically-

---

Table 2. Relative risk as a function of exposure to benzene

<table>
<thead>
<tr>
<th>Cumulative Exposure (ppm–year)</th>
<th>Relative Risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–40</td>
<td>1.1</td>
</tr>
<tr>
<td>40–200</td>
<td>3.2</td>
</tr>
<tr>
<td>200–400</td>
<td>11.9</td>
</tr>
<tr>
<td>more than 400</td>
<td>66.4</td>
</tr>
</tbody>
</table>
cally significant changes in a number of neurological endpoints: decreased rotator performance, decreased spontaneous motor activity and impaired radical maze performance indicative of a learning deficit\textsuperscript{15, 19, 16}.

According ACGIH recommendations and considering different isomers of Xylene having additive effects on human, the occupational exposure of workers in present study was lower than cumulative exposure limit after applying ventilation systems.

Based on EPA’s dose-response risk assessment, in present factory with average Toluene and Xylene concentration of 105.82 and 221.76 ppm respectively, the neurological harmful effect of Toluene and Xylenes were investigable before the application of ventilation system. However, after applying engineering controls, the concentrations of Toluene and mixed Xylenes reduced to 44.5 and 97.73 ppm respectively. The adverse effects are not expected at these levels since they are lower than LOAELs. So the engineering controls in this project were successful to an appreciable level for Toluene and Xylenes compounds. However, in regard to afore-mentioned Benzene exposure, mere conventional ventilation standard systems could not safeguard workers’ health. Therefore better quality solvents with lower content of Benzene are recommended. For time-being suitable personal protective equipment and routine health surveillance such as biological monitoring of Benzene should be considered for exposed workers\textsuperscript{21, 21}.

\section*{References}

21) ACGIH (2005) Recommended Threshold Limit Values for Work Environment, American Conference of Governmental Industrial Hygienist \textbf{16}, 57.