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Evaluation of Workers' Exposure to Methylene Diphenyl Diisocyanate (MDI) in an Automobile Manufacturing Company, Iran

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Evaluation of personal inhalation exposure to methylene diphenyl diisocyanate (MDI) among 39 employees, working in the window fixation and window glue processes in an automobile manufacturing company was performed. This study was conducted for both case and control groups. After sampling and sample preparation processes, MDI was determined with a UV-VIS spectrophotometer at 590 nm; the lung function was assessed with a digital spirometer, too. The average concentration of MDI in the window fixation, and window glue workplaces were 34.53 and 27.37 µg/m^3, respectively, which was lower than the threshold limit value (TLV) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) (51 µg/m^3). Respiratory symptoms in the exposed group were significantly different compared to the unexposed group ($p < .05$*). Lung capacities in the case group were lower than in the control group (*$p < .05$*). Therefore, MDI can be easily measured making it possible to evaluate the adverse effects caused by occupational exposure.*

occupational exposure MDI respiratory symptoms spectrophotometer spirometer

1. INTRODUCTION

Methylene diphenyl diisocyanate (MDI) and other isocyanates are used to make urethane polymers commonly called polyurethane and polyurea [1]. Polymers of the different isocyanates have many uses, including flexible, rigid and molded foams, coating, cast elastomers, binders, fillers, sealants, and adhesives. The strong reactivity of the isocyanates also contributes to their toxicities. MDI poses an inhalation hazard primarily when aerosolized by spraying or heating due to its exceptionally low vapor pressure of 95×10^{-6} mmHg at 25 ^{o}C [1]. Information on isocyanate hazards has become more widely available through National Institute for Occupational Safety and Health (NIOSH) publications since 1973 [2, 3, 4]. During the application of car window fixation, MDI is with the necessary additives is pumped from separate containers through a proportioning and heating unit to a spray-gun, where they are mixed. In these processes, respiratory, dermal, and other mental disease have been associated with the use of MDI. Diisocyanates are now well established in industrial use. MDI can be potentially hazardous in liquid, vapor, mist (aerosol), and dust forms. If MDI in forms of vapors, mist, or dust is inhaled, it can cause respiratory symptoms similar to those caused by all other isocyanates with labored breathing in some industries [5]. About 1 million cars are discarded per year in Iran; each car has roughly 9 kg of polyurethane foam in the

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seats. There are some previous studies on MDI concentration at the workplace during spray-on truck bed lining, the process of insulating buildings with sprayed polyurethane foam, and wood product plant operations. Lofgren, Walley, Peters, et al. referred to a specific application in truck bed lining industry [1]. Crespo and Galan studied MDI exposure levels of workers in the process of insulating buildings with sprayed MDI [6]. They performed sampling processes exclusively during the spraying operation itself, using the MTA/MA-034/94 method [6]. The greatest concentrations of MDI observed around the sprayer were 4 $\mu g/m^3$ (indoor application). In outdoor applications MDI concentrations for a spraying operation reached 77 $\mu g/m^3$. The MDI time-weighted average (TWA) exposure limit for an 8-hr workday recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) [7] is 51 $\mu g/m^3$. Petsonk, Wang, Lewis, et al. also studied the asthma-like symptoms in workers exposed to MDI in wood product plants and found that 15 (out of 56) workers (27%) in areas with the highest potential exposure to liquid MDI monomer and prepolymer had asthma-like symptoms, in contrast to none of 43 workers in the lowest potential exposure areas [8].

Evaluation of workers' exposure to airborne organic isocyanides can be approached in two ways, i.e., determination of concentrations ($\mu g/m^3$) of specific isocyanide monomers as described in method 5521, recommended by NIOSH [9], and also, determination of concentrations of isocyanates, including monomers and oligomers, shown as a function of free isocyanate groups present in the sample, using methods MDHS (method for determination of hazardous substances) 25.2 and 49 recommended by HSE [10, 11]. The aim of this study was to investigate an indoor determination of MDI (Figure 1), using a sampling and analysis method of MDHS 49 and also evaluation of physiological disorders caused by occupational exposure to MDI.

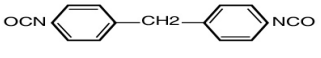

Figure 1. Chemical structure of methylene diphenyl diisocynate (MDI).

2. MATERIAL AND METHODS

2.1. Reagents and chemicals

Hydrochloric acid (37%), 1,6-diaminohexane, and dimethylformamide were used for perpetrating the absorption solution. N-2-aminoethyl-1-naphtylamine, sodium nitrate, sodium bromide, and solphamic acid were used as reagents for spectrophotomeric determination of MDI. MDI, toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI) were used as references. All reagents were purchased from Merck (Germany).

2.2. Apparatus

A glass impinger obtained from SKC (UK) was used for personal sampling. A PTI-15 digital pH meter with a glass electrode from EDT (UK) was used for pH adjustment. A high-resolution diagnostic spirometer from Mir (Italy) was used to measure pulmonary functions. A UV-VIS spectrophotometer from Beckman (USA) was used for determination of MDI.

2.3. Procedure

A cross-sectional evaluation of exposure to MDI among 39 employees, working in the window fixation and window glue processes in an automobile manufacturing company was undertaken. Workers were interviewed with a health work practice questionnaire, and worksite inspections. A control group of 117 unexposed employees at other workstations was also interviewed. Inhalation exposure, while MDI was used, was determined with MDHS 49 [11], as well as through an assessment of lung function with a diagnostic spirometer (Mir, Italy). In this method, breathing zone air was pumped at a flow-rate of 60 ml/min for 8 hrs and the total air sampled was 30 L. However, according to MDHS 49, the total volume of air sampled by the pump over sampling periods should be within ±0.05 of the calculated volume. As an aromatic primary amine is suspected to be the most likely interference, on the basis of the MDHS 49, two impingers (called A and B) were used in parallel, each with a sampling pump; they were

operated at a defined flow rate. Impinger A contained 3 ml of dimethylformamide having 7 mg 1,6-diaminohexane without HCl, and impinger B contained 3 ml of dimethylformamide and 1,6-diaminohexane with 2 ml of HCl, so, the isocyanate present in the working area was determined by the difference. This allowed an exact evaluation of MDI present in the working environment and removal of the possible interference compound. After adding sodium bromide, sodium nitrate, and N-2-aminoethyl-1-naphtylamine, the final solution was used for spectrophotometery, adjusting at 590 nm. A calibration curve was also constructed, using a different amount of standard MDI, ranging from 0 to 5 μg, in which linearity was .997. This calibration curve was then used for determining MDI present in the absorbent solution. Through this study, workers' health symptoms, including respiratory, mental, eye, and skin disorders caused by MDI were also investigated. Information on personal characteristics, medical history, and symptoms caused by MDI exposure as well as work practice were collected with a questionnaire. Exposed and unexposed (control) workers were interviewed privately prior to inspection and air monitoring. An information sheet describing the background, aims of the project, and procedures was given the subjects before the interview. For each subject, forced vital capacity (FVC), forced expiratory volume in 1 s (FEV_1), forced expiratory volume after 1 s of FVC (FEV_1/FVC), and peak expiratory flow (PEF), were obtained using a spirometer (Mir, Italy). The statistical analyses were performed using SPSS/PC version 11.5. Therefore, data obtained from this study were analyzed using statistical tests including Fisher test, *t* test, and chi-square. Comparisons were considered to be statistically significant when $p \leq .05$.

3. RESULTS

This study was conducted in window fixation and window glue processes departments of an automobile manufacturing company located in Tehran, the capital of Iran. The personal characteristic data present in exposed (39 workers) and unexposed workers (117 persons) are illustrated in Table 1; there were no significant differences between the exposed and unexposed groups in age, height, and duration of service ($P < .05$). However, the duration service of the study group was shorter than that of the unexposed subjects. The results obtained from 39 workers exposed to MDI are shown in Table 2. With regards to the findings, in the window fixation process, workers showed the highest exposure to MDI in site 5 (47.28 ± 2.61 μg/m^3), while in the window glue process, in site 6, exposure was lowest (12.57 ± 3.07 μg/m^3). However, the average concentration of MDI in both window fixation and window glue processes were 33.36 and 26.43 μg/m^3, respectively, which was lower than the amount recommended by ACGIH, in which, the threshold limit value (TLV) is 51 μg/m^3 [7].

TABLE 1. Comparison of Age, Height, and Duration of Service Among Exposed (Case) and Unexposed (Control) Subjects

Group	No. of Subjects	Age (years) (*M* ± *SD*)	Height (cm) (*M* ± *SD*)	Duration of Service (years) (*M* ± *SD*)
Case	39	31.871 ± 8.547	174.871 ± .074	5.807 ± 6.613
Control	117	30.068 ± 8.189	172.179 ± 5.833	6.305 ± 6.920

TABLE 2. Methylene Diphenyl Diisocyanate (MDI) Concentration (μg/m^3) in Workers' Breathing Zone in Window Fixation and Window Glue Processes (*M* ± *SD*, *N* = 3)

Site	Window Fixation Process	Window Glue Process
1	12.98 ± 2.02	39.28 ± 1.98
2	16.43 ± 2.11	31.01 ± 7.43
3	40.98 ± 4.00	39.97 ± 1.38
4	43.97 ± 2.90	21.78 ± 5.44
5	47.28 ± 2.61	14.00 ± 1.06
6	38.57 ± 5.03	12.57 ± 3.07
7	41.50 ± 3.43	—

Table 3 provides symptoms of prevalence for exposed and unexposed subjects. Results showed that skin, respiratory, eye, and mental symptoms in the exposed group were significantly different compared to the unexposed group ($P < .001$ in all symptoms). There was also a significant difference in the prevalence of respiratory, eye, and mental disorders in workers who were exposed to higher and lower concentrations than the mean value of MDI (31.22 μg/m^3).

TABLE 3. Symptom Prevalence Data for Exposed (Case) and Unexposed (Control) Workers

	Prevalence (%)	
Symptoms	**Case**	**Control**
Skin		
Itching	20.51	5.13
Eruption	7.69	0
Burning	10.26	0.85
Respiratory		
Sputum	33.33	2.56
Cough with sputum	15.38	1.71
Dry cough	5.13	0
Cough more than 3 months	12.82	0
Shortness of breath at work	2.56	0
Wheezing	2.56	0
Eye		
Irritation	2.56	0.85
Itching	15.38	0
Burning	12.82	0.85
Lacrimation	12.82	2.56
Problem in vision	2.56	0
Mental		
Fatigue	28.21	7.97
Nervousness	17.95	5.69
Anxiety	25.64	5.69
Amnesia	15.38	6.84
Vertigo	20.51	1.70
Impatience	5.13	17.09
Hardness of recalling	10.26	3.42
Lost of concentration	10.26	0

As Table 4 shows, the mean value of the flow rate of pulmonary function parameters showed that FEV_1/FVC, and PEF were lesser in the exposed group (case) than in the unexposed (control) one ($P < .001$ for both factors).

TABLE 4. Spiratory Test in Exposed (Case) and Unexposed (Control) Workers

Spirometery Factors	Case (*M* ± *SD*)	Control (*M* ± *SD*)	*p*-Value
%FVC	91.28 ± 14.36	88.33 ± 11.90	.195
%FEV1	92.10 ± 18.78	91.68 ± 13.15	.736
% FEV1/FVC	83.25 ± 9.51	88.91 ± 10.30	.001
%PEF	68.07 ± 9.51	90.69 ± 25.92	.000

Notes. FVC—forced vital capacity, FEV1—forced expiratory volume in 1 s, PEF—peak expiratory flow.

4. DISCUSSION

This study was performed in an automobile manufacturing company with typical occupational health and hygiene problems that may exist in some industries in Iran. In these industries, the technology and the machinery are generally imported from developed countries without the application of adequate engineering controls and proper safe work practice. These conditions and situations can cause great exposure to more air pollutants in the relevant workplaces and also there can be more occupational health problems than in the developed countries. This study was performed during the summer when the side windows were left fully open to facilitate natural ventilation. Many workers employed in window fixation and window glue processes departments said that the level of airborne MDI seemed to be much higher in the winter when the side windows in the polluted area were kept partially or fully closed. Through this study, the case inspection and air sampling results showed that a high percentage of workers in both window fixation and glue processes department were probably exposed to MDI (Table 2). All inhalation exposure was below the existing occupational ACGIH exposure standards of 51 μg/m^3. Low exposure was also observed by other researchers [6, 12, 13]. There are various sampling methods, all of which have some limitations in assessing air concentration of MDI [14]. Sampling of isocyanates also poses many challenges due to their reactivity and varying physical states in air [13, 14, 15]. It has been suggested that impingers should be favored for sampling [15]; therefore, in

the present study this method was selected to be used for measuring MDI, followed by evaluating its adverse effects on exposed workers.

In agreement with many studies [9, 16, 17, 18], this study confirmed that workers exposed to MDI had a higher prevalence of respiratory symptoms than unexposed control subjects. However, the prevalence of respiratory symptoms was generally higher than those in other studies [9, 18, 19]. The prevalence of respiratory symptoms such as sputum, and cough with sputum was 33.33 and 15.38% among the exposed workers, whilst in unexposed workers the prevalence was 2.56 and 1.71%, respectively. Also, the prevalence of skin symptoms including itching, eruption, and burning were 20.51, 7.69, and 10.26% among the exposed workers, whereas in unexposed workers, the prevalence was 5.13, 0, and 0.85%, respectively. This difference was statistically significant in conformity with other reports [16, 18]. Respiratory symptoms generally increased with the duration of service; however, these symptoms were not significantly correlated to years or the intensity of exposure. In this study, there were significant differences between the respiratory function test results of the exposed and unexposed subjects. The results revealed that the percentage of the mean flow rate of the pulmonary function of FEV_1/ FVC and PEF was lower in the study group than in the controls, showing an indicator of an obstructive pulmonary disease and warning that asthma was starting to appear (Table 4). This is in contrast to the results obtained by Musk, Peters, DiBerardinis, et al. [9] and Pham, Teculescu, Meyer-Bisch, et al. [16], who claimed that exposure to MDI did not have a significantly lower mean FVC and FEV than the controls. However, in agreement with this study, Johnson, Chan-Yeung, MacLean, et al. [18] showed that workers exposed to MDI, in an iron and steel foundry in Vancouver, Canada, had more respiratory symptoms and a significantly lower mean FEV_1 and FVC. Similar results were also obtained in smokers and non-smokers for both case and control groups, in which there were significant differences in the flow rate of pulmonary functions of FEV_1/FVC and PEF ($P < .001$). It has been well established that inhalation of sufficient concentration of MDI can decrease the arithmetic means of FVC and FEV_1. In this investigation, statistical analysis (chi-square) also showed that exposed workers who were in higher and lower values than the average concentration of MDI (31.22 $\mu g/m^3$) had statistically significant difference in both FVC and FEV_1 ($P < .05$). There were also significant differences between factors such as FEV_1/FVC, PEF, age, and work histories ($P < .05$), while this significance was not seen in the window glue process. The results of this study also showed a decrease in the arithmetic means of FVC, FEV_1, and FEV_1/FVC of the exposed subjects during the work shift. This study confirmed that workers exposed to MDI had a higher prevalence of respiratory symptoms than unexposed control subjects. However, the prevalence of respiratory symptoms was generally higher than that in other studies. The respiratory symptoms generally increased with the duration of service, but these symptoms were not significantly correlated to years or the intensity of exposure.

It is worth mentioning that in recent years most studies in developed countries have been focused on MDI asthma and additional respiratory symptoms such as cough, wheeze, chest tightness, or breathlessness [19]. Petsonk et al., however, estimated that the incidence of wood product plant asthma is only 27% in areas with the highest potential for exposure to liquid MDI monomers [8]. Furthermore, there are many occupational health symptoms among workers exposed to MDI in developing countries due to the numerous uncontrolled health hazards present in the working environment [20, 21, 22]; therefore, more investigations should be performed on MDI and other isocyanates as well as on their control in the working environment.

5. CONCLUSIONS

After sampling and a simple sample preparation processes, MDI can be easily measured, making it possible to evaluate the adverse effects of occupational exposure. From the results obtained in this study, it can be concluded that, although MDI is an important compound used

in different industries, occupational exposure to this organic compound is an important factor in producing some chronic and some acute respiratory symptoms and it can adversely affect lung functions. Therefore, improving personal protection equipment and encouraging workers to use it appropriately can substantially reduce occupational exposure to this hazardous compound. However, efficient general and local exhaust ventilation can be considered as another important facility and should be structurally designed in the workplace.

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