유기용제노출사업장의 역학조사를 위한 기초연구(Ⅰ)

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1. 서 론

Various organic solvents are most commonly using material in various factories, for examples, paint producting process and other industries, actually most of them are toxic materials. If many kinds of organic chemicals are concurrently exposed to workplace, toxidities can be influenced as additive effect or synergistic effect[1].

Eventhough the leading work-related diseases and injuries are originated from organic solvents, actually it's are not well recognized. Because the informations and understanding of the hygiene challenge from that are not generalized[2]. Therefore, it is necessary to investigate the potential risk to health, of course, possibility of occupational disease, and epidemiology by checking exposures in wokplace. The purpose of organic vapor monitoring is to check personal and static exposure from toxic materials, and most important one is increasing the accuracy of exposure monitoring, of which should be obtainable by worker's cooperations.

Recently paint manufacturing technique has been much more developed because of advanced polymer chemistry. The process of production is so highly complicated, therefore hundreds of chemical including organic solvent should be supplied as raw materials and many kinds of products can be produced, evenif the process is batch type. These processes are consisted of following steps like formulation, dispersion, combination, color matching, washing and package, etc.

The purposes of this study are discussing exposures of organic solvent to workers in paint manufactering industry and recognition of health hazards from it. Finally, we would like to investigate epidemiology that can provide the relation between organic chemicals and occupational disease. Therefore, reasonable countermeasures, like biological monitoring, improvement of facility and personal protective equipment, could be suggested to prevent occupational diesease from organic vapors.

2. 실험

Procedures applied for this experiment are cited from NIOSH. Sample collection,

storage, desorption, and gas chromatographic analysis have been previously published. Passive diffusional samplers were from 3M(OVM #3500) and activated charcoal tubes from SKC(tube size 6×70㎜, sorbent 50×100㎜ cat #226-97), and air sampling pump from Gilian(Air-3). Passive diffusional sampler is clipped to the worker's collar throughout the work shift, close to breathing zone. Charcoal tube sampler was determined gases and vapors by drawing air samples at 0.1~0.2 ℓ/min flow rate. Sampling hours of both methods are about 6 hours. The paint manufacturing factories, large and small-medium size around Busan were chosen to represent overall paint industry, which were 3 large with 300-400 workers and 2 small-medium size with less than 100.

Passive diffusional samplers were injected 1.5 ㎖ CS_2 as desorbent, after that 30 minitues occasional gentle agitation and decanted into virials. Activated charcoals were also injected 3.0 ㎖ CS_2 as desorbent, and with agitation, into virials. All of the samples were analyzed by Gas Chromatography (HP 6890) at columnn (HP-INNOWax 30m×0.32㎜×0.50㎛), temperature (injector: 250 ℃, detector: 300 ℃, column: 50~90 ℃).

The TWA of toxic component in PPM can be calculated by formula (1). The recovery coefficient and sampling rate are cited from 3M[7] for diffusional passive monitor.

$$C(\text{concentration : ppm}) = \frac{W(\mu g \text{ of analyte})}{r \times t(\text{minutes})} \times \frac{1000 \times 24.45}{S.R \times M.W} \quad \cdots\cdots (1)$$

3. 결과 및 토론

3.1 유기물질의 노출: Producting processes are mainly consisted of formulation, combination, dispersion and color matching, washing and package, etc. More than hundreds of chemicals like organic materials, heavy metals as vehicle and powders are supplied as raw materials, and most of the processes are operated in batch type, therefore the numbers of toxic material to be exposed could be terribly much.

Most of them are organic solvents, but it's are depended upon characteristics and specifications of product. Evenif the toxicities of the chemicals were so high like TDI (toluene 2,4-diisocyanate), HDI(hexamethylene diisocyanate), MDI(diphenyl-methane diisocyanate), IPDI(isophorone diisocyanate) and 2-Ethoxyethyl acetate, Pyrrolidine as film former, if frequencies of exposures were not so much like 1~2 times/year, it were not handled here.

The occupational environment determination results for two years, about 190 times were summarized and to put it concretely 3~4 kinds of organic materials could be recognized. Important component of them are acetone, methyl ethyl ketone, methyl isobutyl ketone as ketones, benzene, toluene, xylene, ethyl benzene as aromatics. Also methyl alcohol, butyl alcohol, isopropyl alcohol as alcohols and pentane, hexane, butyl acetate, dichloromethane, carbon tetrachloride, tetrachloroethylene, trichloroethylene, ethyl acetate, pentyl acetate, cyclohexane and styrene monomer as other chemicals.

Fig. 1 shows frequencies on exposure for 30 kinds of organic chemicals, actually it is described for higher than 5% frequencies. The highst exposure frequencies is 96% for toluene, second is 92% for xylene and third one is 67% for MIBK. If two or three kind of xylene are exposured simultaneously, it is counted as one material. The toxidities of these chemicals were reviewed by permissible exposure limit which were suggested by Korea and ACGIH, both of them were not so big difference. But the Korean limit of toluene is twice of ACGIH limit.

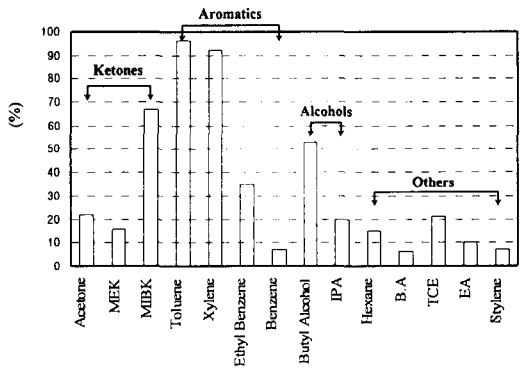

Fig. 1 Exposured frequencies of organic chemicals in paint producting process

3.2 노출지수(EI)의 평가 : According to distribution of exposure measurements, the result is lognormal distrbution, so the geometric mean is calculated and range of concentration is suggested. Most of the workplaces are exposured by mixed organic materials, therefore additive effect of the mixture is described by formula (2) as exposure index(EI).

$$EI(\text{exposure index}) = \frac{C_1}{T_1} + \frac{C_2}{T_2} + \frac{C_3}{T_3} + \cdots \frac{C_n}{T_n} \quad \cdots \quad (2)$$

If the EI value is higher than 1, the concentration of mixed organic material

shows exceeding permissible exposure limit. EI values are calculated for 3 large and 2 small-medium size companies. Higher friquencies of exposed materials in the workplaces are summarized to size of it. To calculate EI on additive effect, five of higherly exposured substances, that is, toluene, xylene, MIBK, butyl alcohol and ethyl benzene are adapted, and comparision of those are plotted in Fig. 2.

The comparisons of personal exposure between large and small-medium size company are classified in Fig. 2. The EIs of large size companies are obtained as 0.20~0.29, the values of small-medium are 0.30 and 0.36. This results can be guessed that EIs of small size companies are normally higher than large size companies. It's are depended upon management technique, facilities and maintenance, etc. To put it concretely, local exhaust system in workplace were inappropriated, for examples, flexible ventilation systems are not installed or working positions and ventilation system are not reasonable around reactor and packagement, evenif they are fixed. Therefore it is very difficult to exhaust hazardous materials or very low efficiency to remove it, of course, respiratory protective devices should be enforced to worker.

Above results are very important to investigate epidemiology from harzardous materials, especially to check occupational deseases, for examples, possibilities of acute and chronic symptom. Of course, much more additional researches are necessary to find out the relations between organic vapors and work-related deseases.

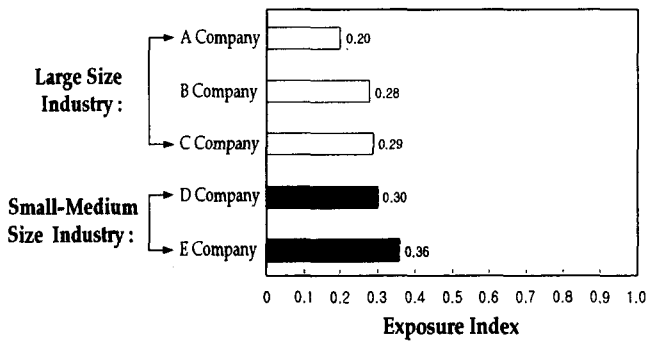

Fig. 2 Exposure indices to organic vapors by two kinds of paint manufacturing industry

3.3 활성탄관법과 수동확산형 시료채취기의 비교: To compare the differences between charcoal tube and passive diffusional sampler, Passive diffusional sampler is simultaneously clipped to the worker's collar beside charcoal tube at the breathing zone in A company. The results we have obtained are summarized in

Table 1. Both sampling methods for personal and static exposure in processes were applied. The results of those determinations were similar. Reliability and reappearance of passive diffusional sampler were very good, already this method was approved in ACGIH, but was not accepted as occupational environment determination procedure in Korea. Therefore this method, of course, should be accepted for official experimental procedure because it is very simple and useful,, if there are not problems.

Assessment of the permissible exposure to workers was done by Regulations on determination of occupational environment and accuracy control[6]. Analysis and sampling errors of materials(RSt) including mixed organic vapors were calculated by formula (3), control limit of mixture was calculated by following formula 1 + RSt.

According to the results which we have obtained from both sampling methods, Exposure concentrations of each organic vapor were not exceeded permissible exposure limit. The exposure indices (EI) of formulation and despersion process are 0.5172, 0.5672, and both of them are below the control limit(CL) 1.0830, 1.0726. But these values are a little bit higher than action value, actually the maximum values of toluene and xylene were detected as 22.775, 28.243 ppm.

$$RSt = [(R_1 \times SAE_1) + (R_1 \times SAE_2) + \cdots + (R_n \times SAE_n)]^{1/2} \cdots (3)$$

here $Rn = Yn / EI$, $Yn = Xn / TLVn$

SAE : sampling and analytical error

4. 결론

1) Toluene is the highst exposure frequencies as 96% in paint producting process, the second is xylene as 92% and the third is MIBK as 67%. That means aromatics and ketones are main organic solvent in the company.

2) According to exposure indices for mixed organic vapors between large size and small-medium size company, the values of large size are generally smaller than the others. These could be guessed that it is depended on mangement of technique, operation and maintenance of facilities, etc.

3) To investigate the epidemiology of work-related disease, biological monitorings including organic vapor exposure are also necessary. Of course, further research is required to evalate significant clinical abnormalities and epidemiology between occupational disease and organics vapors.

Table 1. Comparision between charcoal tube and passive diffusional organic vapor sampler in A company

Process	Sampling Method	Exposed chemicals					Assessment	
		Toluene	Xylene	MIBK	B A	E B	Rst	CL
Formulation	Charcoal Tube	6.652~ 9.048	3.431~ 6.048	0.156~ 0.204	0.001~ 2.073	1.155~ 1.534	0.0792	1.0792
	Passive diffusional	6.148~ 22.775	4.326~ 22.114	0.252~ 3.097	0.084~ 2.852	1.696~ 4.213	0.0726	1.0726
Dispersion	Charcoal Tube	3.265~ 19.814	2.954~ 28.243	0.186~ 0.419	0.047~ 2.305	0.896~ 1.671	0.0930	1.0830
	Passive diffusional	1.819~ 15.649	3.748~ 6.916	0.333~ 1.329	0.000~ 1.819	1.250~ 1.553	0.0919	1.0818
Color matching	Charcoal Tube	5.225~ 5.614	3.890~ 4.134	0.327~ 0.407	4.362~ 5.338	1.514~ 1.643	0.0712	1.0712
	Passive diffusional	6.447	5.074	0.664	5.979	1.800	0.0699	1.0699

참고문헌

1. American Conference of Governmental Industrial Hygienists(ACGIH) : 1997 Threshold Limit Values for Chemical Substance and Physical Agents, ACGIH, Ohio, 1997.

2. Nam Won Paik, Young Hwan Lee and Chung Sik Yoon, A Study on Worker Exposure to Organic Solvents in Korea, Korean Ind. Hyg. Assoc. J, Vol. 8, No. 1, May, 1998.

3. NIOSH : NIOSH manual of analytical methods(3rd edition) : Vol. 1, 1501-1(1984), 1300(1989).

4. Nam Won Paik, Mi Jin Park and Chang Sik Yoon, Evaluation of Commercially Available Passive Samplers and Development of New Passive Samplers, Part 1 : Evaluation of Commercially Available Passive Samplers, Korean Ind. Hyg. Assoc. J, Vol. 6, No. 1, April, 1996.

5. OSHA : Occupational Safety and Health Administration Subscription Service Volume VI-OSHA Technical Manual, 1990.

6. Labor of ministry: Regulations on determination of occupational environment and accuracy control (notice of labor ministry No. 2001-39), Korea, 2001.

7. 3M : 3M Organic Vapor Monitor Samplig and Analysis Guide, Organic Vapor Monitors 3500/3510 and Organic Vapor Monitors 3520/3530, September, 1996

8. Labor of ministry: Permissible exposure limit of chemical substances and physical agents (notice of labor ministry No. 97-65), Korea, 1998.