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HK80-09
CGPC

October 19, 1976

Mr. Bryan H. Gambrill
China Gulf Plastics Corporation
P. O. Box 22144
3, Tun Hwa South Road
Taipei, Taiwan 105
Republic of China

Dear Bryan:

Enclosed are two copies of my report on the industrial hygiene survey of CGPC operations conducted in August, 1976. Because many times I have referred to the initial industrial hygiene report of 1974, an additional copy of that report is also enclosed for your convenience.

Thanks very much for the many courtesies you and others at CGPC extended to us during our visit. Please let me know if you have any questions with regard to this report, or if I can be of further assistance.

Warm regards,

Robert T. Cheng

Robert T. Cheng, Ph.D.
Senior Industrial Hygienist

RTC/ELK

Encl.

cc: Mr. R. J. Comeaux
Dr. F. D. Gassaway
Dr. R. L. Gibson
Mr. G. F. Huff
Dr. W. A. McClellan
Dr. H. T. Miller

INDUSTRIAL HYGIENE SURVEY

OF

CHINA GULF PLASTICS CORPORATION

August 1976

by

Robert T. Cheng, Ph.D., P. E.

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I. SUMMARY

An industrial hygiene survey of CGPC's manufacturing facilities at the Toufen General Plant, Taoyuan Plant, and TVCM Monomer Plant in Kaohsiung, was conducted in August, 1976. The purpose of the survey was to evaluate the progress of CGPC's Industrial Hygiene Program after it was set up in 1974, following visits by medical and industrial hygiene personnel of Gulf's Medical Department. Primary attention was given to the review and evaluation of occupational exposures to vinyl chloride and solvent vapors (MEK, Toluene, and Benzene). Other occupational hazards reviewed include workers' exposure to mercury vapors, chlorine gases, dusts from lead, barium and cadmium, chromates and cyanides in the plating room, dioctyl phthalate fumes, and heat stresses. Preliminary results of this survey have been reported to Mr. B. H. Gambrill, CGPC President. Mr. Wilbur, T. C. Shyeh and other top management personnel at the Toufen General Plant have also been appraised of the findings and recommendations during a two-hour debriefing and discussion meeting.

The CGPC Industrial Hygiene Program is the best in Taiwan. The personnel involved in managing and implementing this program are enthusiastic and well trained individuals. CGPC also has the best equipped industrial hygiene laboratory with advanced field and laboratory instruments not available elsewhere in Taiwan. Most important of all, CGPC management has given full support of the Medical and Industrial Hygiene Program. Changes in work and engineering modification have considerably reduced exposures to the above mentioned occupational hazards. However, many additional improvements are required to bring the exposures down to acceptable levels.

Following is a brief summary of the important findings, severe hazards and suggested corrective measures:

1. Employees at Toufen's Polymer Plant, Monomer Plant and R&D Pilot Plant were frequently exposed to vinyl chloride at concentrations over 2000 ppm. Two measurements inside the Polymer Plant's control room office showed VC concentrations at 24 ppm and 7 ppm. The time-weighted average VC exposure for Polymer Plant workers was estimated to have exceeded 50 ppm.

2. The most recent experimental data reported by Professor Maltoni proved carcinogenic effects of VC at 10 ppm and 25 ppm. Even 1 ppm of VC showed some indications of carcinogenic potential. We believe that, eventually, Canada and other countries in the world will lower their presently acceptable higher exposure levels to limits specified under U.S. standards.

3. So that management and workers can feel the results of improvement, and because we want to attack and eliminate the most severe exposures first, a three-step vinyl chloride control program is recommended to reduce occupational VC exposures. Step one is to reduce workplace VC below odor detectable concentrations (2000 ppm) within three months. Step two is to achieve Canada's VC exposure standards within one year. Step three is to comply with U.S. standards within two years.

4. The primary emphasis during step one will be the elimination of all large scale VCM emission sources using the sense of odor as the tool. At least a temporary engineering or procedural solution should be used to control VC emission from the reactor's top manhole during material discharge.

5. A "Search and Secure" team should be formed during step two to search with an OVA instrument for VCM leak sources and repair the leaks. Reactor cleaning frequency should be greatly reduced with one of the many available automatic cleaning techniques, including the B. F. Goodrich solvent spraying technique presently on trial at CGPC.

6. To meet U.S. standards in step three, the goal is to achieve a completely enclosed, automated and essentially leak-proof reaction system which will require minimum reactor opening and entry. The inplant industrial hygiene monitoring program should be extended to cover workers' dormitories and the nearby community.

7. Employee training should be greatly emphasized. All employees likely to be exposed to vinyl chloride, or other types of hazards, should be fully instructed of the potential health risks and protective measures necessary.

8. Solvents MEK and toluene have acquired new significance following an announcement on June 18, 1976 that eight cases of cancer had been observed in workers at Shell's Deer Park Petrochemical Complex near Houston. MEK and toluene (or benzene contaminations) are prime suspects of the agents involved.

9. Considerable improvement has been made in the Fabrication Plant since 1974 to reduce solvent vapor concentrations. Results of this survey showed, however, that workers are still over-exposed to the combinations of MEK, toluene and benzene. CGPC's toluene could contain 0.5% to 2% of benzene as an impurity. Recently, benzene was proven to cause cancer of the blood-forming organs (leukemogenic). The exposure limit for benzene will soon be reduced to 1 ppm.

10. Additional engineering control by local and general exhaust ventilation is suggested for surface treating machines and 4 and 6-color printers. Employee education and good house-keeping should also be strengthened.

11. Mercury concentrations in the Chlor-Alkali Plant have been reduced roughly 50% since 1974. However, concentrations remained high along the central and southern aisles of the mercury cell room. Workers at the basement flake-soda machines were definitely over-exposed to mercury vapors.

12. More wall fans should be installed in the cell room. The flake-soda machines should be moved out of the cell room basement. Scrupulous cleanliness and personal hygiene are of the essence wherever there is contact with mercury.

13. Chlorine emissions from the tail gas absorbing tower caused occupational hazards as well as community air pollution complaints. A caustic soda, wet scrubber system is suggested to control emissions.

14. Dusts from lead, barium and cadmium will remain a serious threat to employees' health unless the pneumatic transport system (which is due for completion soon) can drastically reduce the dust levels in the Extrusion Plant. CGPC's Industrial Hygiene Monitoring Program should be expanded to cover measurements of lead, cadmium and barium dusts.

15. Effective local exhaust ventilation should be provided wherever powdery dyes and pigments are poured, weighed and mixed. Any dyestuff that causes skin irritation, sensitization, or other health symptoms should be investigated. Replacement of unsafe dyestuffs with a safer product should be considered.

16. Great improvements have been made in the plating room since 1974. New fans should be installed for the cyanide bath local exhaustion hoods.

17. Dioctyl phthalate (DOP) fumes remained to be a nuisance for inplant workers, and present a serious air pollution problem as viewed by the local air pollution control agency. Canopy hoods at higher ventilation rates should alleviate inplant DOP fog. A system employing a high energy wet Venturi scrubber is suggested to combat community air pollution.

18. Heat stress during the summer time grossly exceeded the Chinese Government's heat exposure standards. Roof fans, spot cooling system, personal cooling fans and isolation of heat sources are suggested to alleviate the heat problems.

19. CGPC's Industrial Hygiene Laboratory should have a larger work area and, most importantly, should be maintained orderly and clean. CGPC should periodically send parallel samples to Gulf's Health Sciences Laboratory for comparative analysis.

20. The Taoyuan Plant is a much healthier workplace compared to the Toufen General Plant. A few suggestions are made to reduce hazards of noise, epoxy, and dusts of lead, barium and cadmium.

21. Four air samples collected from Kaohsiung's TVCM Plant showed workplace VC concentrations ranged from 5 to 21 ppm. This should be reduced by the same "Search and Secure" technique suggested for the Toufen General Plant.

22. Based on odor threshold of ethylene dichloride (EDC), the TVCM Plant workplace EDC concentrations are over 100 ppm at many locations. In the U.S., the exposure standard for EDC will be lowered to 5 ppm, with ceiling restriction at 15 ppm. A conscientious effort should be made at TVCM to reduce EDC emissions from various leaks and from the many intentional release sources such as pressure relief valves and steam blow-down points.

Many thanks to Messrs. W. Shyeh, K. Yü, C. C. Yang, Tsung-Lin Chow, Ed Lu and other members of the Plant management for their courtesies and cooporation. Special thanks to Ed Lu and O. H. Huang for their assistance in carrying out the survey work.

II. VINYL CHLORIDE

A. General

During the past two years, CGPC has made great strides in improving the general health and hygiene conditions at Toufen's main plant, but as far as workers' vinyl chloride exposures are concerned, the improvements are far short of the goal.

The significance of vinyl chloride odor has been repeatedly emphasized during several management debriefing sessions and during classroom discussions. The odor threshold limit for vinyl chloride is approximately 2000 ppm (i.e., a sensitive nose can detect vinyl chloride at 2000 ppm concentration). The ordinary nose or a nose which is used to or dulled by the vinyl chloride smell, may not be able to detect vinyl chloride at 2000 or 3000 ppm concentrations.

Unfortunately, after two years of vinyl chloride exposure control, the Toufen Plant remained at the stage where one can still conduct a rough vinyl chloride survey without the use of a detector instrument. To just walk through the various units of the monomer plant and the polymer plant, the nose can detect that vinyl chloride concentraitons have exceeded 2000 ppm at the reactor's top manhole opening and at the high boiling point material storage area.

B. Vinyl Chloride Survey Results

Air samples of the work place were collected by charcoal adsorption tubes with battery-operated, personal sampling pumps. The samples were taken at flow rates between 50 to 100 ml/min. The captured vinyl chloride was desorbed from the charcoal tube with carbon disulfide. An aliquot of the desorbed sample was injected into a gas chromatograph and the area of the resulting VCM peak was used to calculate the VCM concentration.

Tables 1, 2 and 3 summarize results of the vinyl chloride surveys at three plant locations (Polymer Plant, Monomer Plant, and R&D Pilot Plant). The exact sampling times were included in the tables so that one can refer to the measured vinyl chloride

Table 1 - Vinyl Chloride Concentrations at CGPC's Polymerization Plant. Sampling by Charcoal Tubes, Analysis by G.C.
(Sample Date: August 16, 1976)

Sample Number	Sampling Time	Duration (minutes)	Volume (liters)	Sample Location	Vinyl Chloride Conc. (ppm)
1	14:41 - 15:50	69	6.15	4' from #403E upper manhole	111.1
2	14:50 - 15:53	63	4.54	near #403C upper manhole	66.0
3	sample ruined because of bad pump				
4	15:00 - 15:57	57	5.34	office of Control Room	23.4
5	15:10 - 16:00	50	4.13	bottom manhole of #403A during late stage of purging	82.6
6	15:52 - 17:15	83	6.40	same as sample #1	66.0
7	15:54 - 17:17	83	6.18	same as sample #2	90.2
8	15:57 - 07:50	953	88.8	office of Control Room	7.3
9	16:03 - 17:18	75	7.20	bottom manhole of #403E	126.9

Table 2 - Vinyl Chloride Concentrations at CGPC's Toufen Monomer Plant. Sampling by Charcoal Tubes, Analysis by GC
(Sample Date: August 16, 1976)

Sample Number	Sampling Time	Duration (minutes)	Volume (liters)	Sample* Location	Vinyl Chloride Conc. (ppm)
10	17:20-18:50	90	6.48	1st column	60.2
11	17:20-18:50	90	4.78	2nd column	140.0
12	17:20-18:50	90	5.57	3rd column	86.6

*All three samples were collected near the unloading station of high boiling point materials. The sampling pumps were fixed at the steel columns along the narrow concrete walkway. Odors of vinyl chloride and/or high boiling point materials were occasionally detectable.

Table 3 - Vinyl Chloride Concentrations
at CGPC's Polymerization R&D Pilot Plant
(Sample Date: August 17, 1976)

Sample Number	Sample Time	Volume (liters)	Sample Location	Vinyl Chloride Conc. (ppm)
21	? - 12:57	10.7	Beside 100 liter Polymizer	8.1
22	? - 12:57	10	Beside 1000 liter Polymizer	12.7
23	12:58 - 13:40	9.70	Beside 100 liter Polymerizer	158.8
24	12:58 - 13:40	9.13	Beside 1000 liter Polymerizer	66.2

concentrations to the specific plant and to the Unit operational conditions during those time intervals. In general, we incline to believe that the vinyl chloride survey results represent the typical areas of vinyl chloride concentrations at those locations.

Since 1974, the Polymer Plant's control room has been modified to reduce employees' VCM exposure. The control room has been isolated from the reactor room and a sole passage way between the two rooms was created. The passage way was fitted with two spring-loaded doors in a series to prevent the air in the reactor room from contaminating the air in the control room. The control room was air-conditioned. Workers in the control room were supposedly breathing the outdoor "clean" air supplied by the window-mounted air conditioning unit. However, it turned out that VCM concentrations in the control room were still at unacceptable levels (Table I, sample #4 and #8). A 57-minute air sample collected in the office area of the control room showed 23.4 ppm of VCM, while an overnight, sixteen-hour, long-term air sample showed 7.3 ppm VCM in the same location.

Even after air purging, the VCM concentrations inside the reactors were found to be higher than expected. Sample #5 in Table I represents an air sample collected near the bottom manhole of Reactor 403A during the late stage of air purging. VCM concentration was found to be 72.6 ppm. Consequently, the reactor cleaners could be exposed to over 50 ppm VCM while they were cleaning the reactors.

All three samples collected at the Monomer Plant were outdoor air samples. They were collected near the unloading station of high boiling point materials. Odors of vinyl chloride and/or high boiling point materials were occasionally detectable at this general area. Results of this survey, as shown in Table 2, verify the presence of high concentrations of VCM as detected by the nose.

The U. S. Vinyl Chloride Standard requires that no worker shall be exposed in excess of 1 ppm of vinyl chloride as time weighted average (TWA) concentration and 5 ppm of vinyl chloride

as short time (15 minutes) ceiling concentration. The less stringent (and less justifiable) Canada Standard calls for 10 ppm TWA and 25 ppm ceiling. As surveyed in August, 1976, CGPC's Polymer Plant workers were exposed to more than 50 ppm vinyl chloride TWA concentration, and over 2000 ppm ceiling concentration.

A number of charcoal tubes collected from the Fabrication Plant for solvent vapors showed small amounts of vinyl chloride. For example, sample #19, a personal air sample collected from the operator of No.5 surface treating machine, showed 1.0 ppm of vinyl chloride. Sample #14, 15 and 17 also showed 0.5 ppm of vinyl chloride. It is likely that the vinyl chloride gas found in the Fabrication Plant drifted from the Monomer and Polymer Complex (300 feet away). In fact, on a calm day with little or no wind, the Toufen Plant could be enveloped within a dome of vinyl chloride gas.

C. Recommendations

The U.S. vinyl chloride exposure standards are based on the best evidence available at the time the standards are published. Very recently, Professor Maltoni of Bologna, Italy reported results of the on-going VCM inhalation studies. The results indicate that VC at 50 ppm was confirmed again to cause various types of cancer. Another experiment at 25 ppm VC still shows a definite carcinogenic effect. One Zymbal gland tumor has also been observed at the 10 ppm level. This recent development tends to reinforce our belief that, eventually, Canada and other countries in the world will lower their present acceptable higher exposure limits to the permissible levels specified under U.S. standards.

The recommendations which follow consist of a three-step vinyl chloride exposure reduction program. Step one is to reduce the workplace vinyl chloride concentrations below the odor threshold within three months. Step two is to achieve the less stringent Canada standards within one year. The last step is to meet the U.S. vinyl chloride exposure standards in two years.

The step-by-step approach is suggested so that workers and management can both "see" the results of the program (by the sense of odor); can attack the major problems and eliminate the grossly excessive exposures first and achieve the detailed refinements later. It should be reemphasized here that our final goal is to comply with the U.S. standards, not the temporary Canada standards.

STEP ONE - Eliminate Gross Exposures:

1. The first priority in VCM exposure control at CGPC is to eliminate all large scale VCM emission sources. Remember that wherever odor of vinyl chloride is detected, the area VCM concentration is at least 2000 ppm. Locating and controlling the emission sources by the sense of smell will not reduce exposures to safe levels, but it should eliminate the grossly excessive occupational exposures to vinyl chloride.

2. No one should be exposed to concentrations of vinyl chloride vapor at odor threshold concentrations for even a very brief period. Therefore, all practicable steps should be taken immediately to keep concentrations of vinyl chloride in the working atmosphere below the odor threshold limit.

3. Workers should be encouraged to report vinyl chloride odor and help to identify the leak source. Unless during emergency, workers should be able to refuse working in an area where vinyl chloride odor is detectable unless proper respiratory protection equipment is available.

4. Management should put all emphasis on engineering control. Respiratory protective equipment should be used only as the "last resort" type of control, to be used only where engineering controls cannot be used or made adequate.

5. Where equipment is not totally enclosed, or where the enclosure must necessarily be breached as a routine process operation, then procedures should be adopted which ensure that vinyl chloride is not released into the working atmosphere. These procedures include local exhaust ventilation or other suitable means.

6. Largest VC release in the reactor room occurs when the reactor top manhole is opened after completion of the polymerization reaction. During the 1974 survey, a special lid was designed for the reactor hatch opening to reduce VC release. This lid is not used now because of inconvenience. The problem has to be solved one way or another, and the engineering department and the unit operators should work out a system together so that the solution will be both effective and practicable.

STEP TWO - Achieving Canada Standards

1. Modify the plant equipment and process to ensure maximum containment of vinyl chloride. Where vents and reliefs are essential they should be positioned so that their outlets do not contaminate the working atmosphere.

2. Entry into confined spaces such as the reactor, autoclave, tank, chamber, vat or pit, etc. in which vinyl chloride vapor is known to have been present or is liable to be present should be reduced to the minimum. The actual time spent inside such an area should be as short as possible.

3. CGPC is striving to reduce the formation of off-spec products (resins with fish eyes) by spraying a B.F. Goodrich patented solution on the reactor walls. This treats the reactor interior walls to prevent solid deposits and scale build-up even after a large number of charges. Adoption of this new technology will effectively reduce the frequency of manual cleaning of the reactor.

4. After all reactors have been converted to the Goodrich solvent spray operation mode, the frequency of manual cleaning of the reactor will be greatly reduced, and the overall vinyl chloride concentration around the polymerization plant will be decreased. However, it is important that whenever reactor cleaning is required, more complete evacuation of the vinyl chloride vapors in the reactors should be applied before they are opened.

5. A "Search and Secure" team comprised of Unit operators and personnel from the Industrial Hygiene and Safety Office should be formed. The main objective is to locate every VCM leak source and fix the leaks as soon as possible. Searching for leaks should be conducted with a OVA-118B inustrument at every place where VCM is formed, stored and transported. VCM and PVC manufacturers in the United States,such as Goodyear and Tenneco, have used this "Search and Secure" strategy with great success.

6. When a non-routine operation necessitates opening equipment which may release vinyl chloride to the atmosphere, e.g., the maintenance or repair of equipment and where it would be impracticable to remove vapor by local exhaust ventilation, then respiratory protective equipment must be worn. Precautions must be taken to ensure that other personnel in the vicinity of the operation are not exposed to excessive levels of vinyl chloride.

7. Please achieve Canada standards during the second phase of this three-step program by following the guidelines as specified under the Ontario Province Occupational Health Protection Branch Data Sheet No.21 for Vinyl Chloride Exposures. Refer to my comments on Canada Standards (R. T. Cheng to G. M. Hale, RTC 75:008, January 17, 1975). A copy of this memo is included in the Appendix.

8. In Canada, plant working conditions are controlled by provincial government instead of the federal government. The Ontario Standard requires 10 ppm TWA and 25 ppm ceiling, while another Canada Standard (Province of Alberta) calls for 5 ppm TWA and 10 ppm ceiling.

STEP THREE - Comply With U. S. Standards

1. The permanent U. S. OSHA Standard on vinyl chloride issued on October 5, 1974 is stringent. It calls for an exposure limit of 1 ppm over any 8-hour period (time-weighted average), and a ceiling of 5 ppm average over any period not exceeding 15 minutes.

2. Before publication of the permanent standard, the viewpoint expressed through the Society of the Plastics Industry (SPI) was that the standard could have led to a shutdown of the PVC industry. Now most PVC manufacturers in the U.S. are meeting the permanent standards.

3. To meet U.S. standards, the goal is to achieve a completely closed, automated and essentially leak-proof reaction system which will require minimal reactor opening or entry. The process control is supplemented with the use of respiratory equipment when required.

4. Since VC gas is continuously under pressure in the PVC manufacturing operations, even the smallest apertures in the valves, flanges, pipings and vessels can release the gas into the work environment. In many cases this would require the development or special procurement of new, more highly engineered pumps, flanges and gasketing materials. It may also require extensive re-engineering of piping systems to reduce the number of possible leak sources. Many PVC plants in the U.S. have used flanged pipe couplings to replace leak-prone threaded couplings. Welded joints are sometimes used to eliminate both flanged and threaded couplings.

5. During the third phase of vinyl chloride exposure reduction, the inplant vinyl chloride monitoring program should be expanded to cover areas such as workers' dormitories and the nearby community. This is important because many workers are living in the company dormitories within the factory complex. Their VC exposures, therefore, are not limited to 8 hours per day working time, but extended to 24 hours continuous experience.

6. Copies of the U.S. Vinyl Chloride Exposure Standards have been sent to CGPC previously. Please follow the provisions of the standards to assure compliance as soon as possible.

D. Employee Education

Some CGPC workers still cannot comprehend the hazards of vinyl chloride. One worker told me that the company should dispense preventative drugs to control vinyl chloride disease instead of spending money on engineering control. Another worker asked whether the company could supply free milk to neutralize the vinyl chloride poison.

All employees likely to be exposed to vinyl chloride in the course of their employment should be instructed of the potential health risks and protective measures necessary. Such instruction should include, in particular, the following subjects:

1. The nature of the health hazard from chronic exposure to vinyl chloride including specifically the carcinogenic hazard.

2. The specific nature of operations which could result in exposure to vinyl chloride in excess of the permissible limit and necessary protective steps. The purpose for proper use and limitations of respiratory protective devices.

3. The purpose for an a description of the monitoring program.

4. The purpose for and a description of the medical surveillance program.

5. Specific information to aid the employee in recognition of conditions which may result in the release of vinyl chloride.

6. The role of the employee in safe working methods and personal hygiene.

7. Procedures for reporting defects in the plant and equipment, and for making suggestions.

III. SOLVENTS

A. General

Large quantities of industrial solvents are consumed at the Flexible Products Fabrication Plant (軟質工場) and at the Catalyst Plant and the Research & Development Pilot Plant. Methyl ethyl Ketone (MEK) and toluene are by far the largest solvent consumption; other solvents include methanol, butyl acetate, methyl isobutyl ketone, cyclohexanone, ethyl acetate, trichloroethylene, dimethylformamide and tetrahydrofuran.

The solvents MEK and toluene have acquired new status following an announcement on June 18, 1976 that eight cases of cancer had been observed in workers at Shell's Deer Park Petrochemical Complex near Houston. Long-term cancer studies in animals on MEK and MEK-Toluene mixture have never been done. Chronic cancer studies have recently been initiated in the United States by the Chemical Industries Institute of Toxicology (CIIT) at Industrial Biotest (IBT) in Chicago and early results are not expected for at least one year. Many toxicologiests believe that it is not MEK or MEK-Toluene mixture that was responsible for the increase in cancer risks. They speculate that it was benzene or other impurities in MEK and Toluene that caused the cancer incidences. Just one month ago, the National Institute for Occupational Safety and Health (NIOSH) issued an update Criteria and Recommendations for a Revised Benzene Standard. Based on the accumulated evidence from clinical as well as from epidemiologic data, NIOSH found it is conclusive at this time that benzene causes progressive, malignant disease of the blood-forming organs (leukemogenic).

In view of this conclusion, NIOSH recommends that exposure to benzene be kept as low as possible. The use of benzene as a solvent or diluent in open operations should be prohibited. NIOSH recommends that occupational exposure be controlled so that no worker will be exposed to benzene in excess of 1 ppm in air as determined by charcoal tube air sample collected at one liter per minute for 2 hours.

CGPC acquires its MEK from a U.S. manufacturer and its Toluene from Chinese Petroleum Corporation. Analysis of the two bulk samples of MEK and Toluene brought back from CGPC showed that the MEK sample contained 0% by weight of benzene and the Toluene sample contained approximately 2% by weight of benzene.

Chinese Petroleum Corporation claimed that its Toluene is 99.5% pure with 0.5% impurity. Therefore, our finding of 2% by weight of benzene in the bulk toluene sample could be in error. It could be that the bulk toluene at CGPC was contaminated somewhere between Chinese Petroleum's shipping tank car to CGPC's storage tank. The contamination could also have occurred somewhere between sample collection at CGPC and sample analysis at Gulf's Health Sciences Laboratory. Anyhow, whether it is 0.5% benzene or 2% benzene, we know benzene is in the Toluene in very significant quantity.

B. Surface Treating Machines

During the 1974 survey, total solvent vapor concentrations as measured with Century Organic Vapor Analyzer around the surface treating machines varied between 200 to 1000 ppm. The plant was not in full operation at that time. Workers commented that the solvent concentrations can go much higher when the plant was in full operation.

Conditions have been greatly improved since 1974 following the installation of effective side-draft and down-draft location exhaust hoods at the surface treating machines. Total organic solvent vapor in the work area as determined by OVA-118B ranged from 50 ppm to about 300 ppm. Determination of specific solvents by chemical detector tubes showed 70 ppm toluene and 50 ppm MEK in front of the #4 surface treating machine.

Solvent vapor concentrations at the surface treating machine varied depending on the location and on the operation. The highest concentration was determined directly above the solvent trough during pouring and frequent stirring of the solvent slurry. Unfortunately, since this was a manual operation, workers usually have to stay very close to the solvent trough and received full dosage of the solvent vapors.

There was no local exhaust hood at the No.5 surface treating machine, and our survey results confirm this fact. Determination of organic vapors by chemical detector tubes at the #5 surface treating machine showed 100 ppm toluene and 120 ppm MEK. Benzene determination by chemical detector tube method show approximately 5 ppm benzene under the machine.

Workers' personal solvent vapor exposures were evaluated by drawing a measurable amount of air through a charcoal adsorption tube with a personal sampling pump. The charcoal tube was fastened to the workers' lapel close to their breathing zone. Solvent vapors were collected by the charcoal by adsorption, and the adsorbed solvents were removed from the charcoal and analyzed by gas chromatograph at Gulf's Health Sciences Laboratory. Table 4 summarizes results of the personal solvent vapor exposure survey.

The 1976 threshold limit values are 100 ppm for toluene, 200 ppm for MEK, and 10 ppm for benzene (new standard for benzene will be 1 ppm). Unless otherwise indicated, threshold limit values (TLV) are for industrial exposures of 8 hours per day, 5 days per week. However, the normal work schedule at China Gulf Plastics Company is 8 hours per day, 6 days per week. This increase in work time could result in over-exposure if the environmental concentrations of the air contaminants were not reduced accordingly. For example, the normal TLV for toluene is 100 ppm; but for 6 days per week work schedule, the permissible environmental level of toluene should be reduced to approximately 83 ppm.

When two or more types of solvents are present, their combined effect, rather than that of the individual solvents, should be given primary consideration. In the absence of information to the contrary, the effects of the different solvents should be considered as additive. For example, workers are allowed to be exposed to 100 ppm of toluene or 200 ppm of MEK per an 8 hour working day. However, if both 100 ppm of toluene and 200 ppm of MEK are present in the environment, then the duration of exposure should be limited to 4 hours per day.

Table 4 - Personal Solvent Vapor Exposures at the Survace Treating Machines (Samples collected on August 17, 1976)

Sample Number	Sample Duration	Sample Volume (liters)	Employee Number	Job Classification	Worker's Ave. Exposure: MEK (ppm)	Benzene (ppm)
13	115 min	9.34	61270	#3 Mach.Op'r	111	4.7
14	120 min	7.29	60222	#4 " "	172	2.6
15	?	7.22	58260	#5 " "	132	*
17	35 min	5.55	61270	#3 " "	76	2.8
18	30 min	3.85	60222	#4 " "	42	2.4
19	31 min	5.16	58260	#5 " "	192	*

*Not determined because of apparent toluene contamination.

Notes: The bulk toluene sample bottle leaked as result of improper packaging and shipping. Most of the charcoal tubes were contaminated by the leaked-out toluene. Therefore, determinations of toluene concentrations were not made.

In general, if the sum of the following fractions

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \ldots \frac{Cn}{Tn}$$ exceeds 1.0, then the threshold limit value for the mixture should be considered as being exceeded. C_1, C_2 ... indicates the observed atmospheric concentrations of individual compounds, and T_1, T_2 ... the corresponding threshold limit values.

Although no determination of toluene concentration was made due to contamination caused by the leak of the bulk toluene sample container, it is believed that toluene concentrations, if determined, should be somewhat less than the MEK concentrations for each charcoal tube sample (based on the difference in vapor pressure and boiling point of these two compounds).

C. Printing Shop

There are two huge printers inside the printing shop. A four-color printer (3224A) by the outside wall, and a six-color printer (3224B) by the inside wall neighboring the laminating shop.

During the 1974 Industrial Hygiene Survey, neither of the two printers were ventilated. Concentrations of solvent vapors ranged from 100 ppm to 1500 ppm at various locations under and around the four-color printer. The six-color printer was not used at that time, but solvent vapor concentrations were still 100 ppm under and around that machine. Essentially no solvent was used next door at the laminating shop, however, solvent vapors from the four-color printer entered the laminating shop through the connecting open doorways and affecting laminating machine workers.

This time, when both the four-color and the six-color printer were in operation, solvent vapor measurements with the organic vapor analyzer showed 150 ppm concentration between the two machines, 300 to 500 ppm under the six-color printer, and about 150 ppm under the four-color printer. Next door at the laminating shop, no odors of solvent vapors were detected.

The significant improvements have been achieved through installation of ventilation control system. Since 1974, six propeller blade wall fans have been installed on the outside wall near the four-color printer according to recommendations. The six fans have effectively reduced the solvent vapor concentrations around the four-color printers.

A local exhaust system has been designed and partially completed for the six-color printer. The design was similar to what was recommended in the August, 1974 letter (Robert T. Cheng to Wilbur Shyeh, RTC 74:143). However, it is noticed that small suction tubes were still used. Those 2-inch, or 3-inch branch suction tubes will restrict the exhaust air flow and increase the system pressure drop. This in turn will reduce the total exhaust volume of the blower.

Rough calculations show that when a piece of 2-inch branch suction pipe is used to connect the slotted exhaust hood to a main header, most of the pressure losses will occur at the 2-inch pipe section. The losses include the entrance, the restriction and the expansion, and the 90 degree bend. You will get no more than 50 cfm per hood if a 2-inch pipe is used. Please also remember that those small pipes will get plugged by the inks, paints, and other deposits and their effective diameter will gradually reduce.

D. Recommendations

1. Workers' solvent exposure at the No.4 surface treating machine can be further reduced if side-draft local exhaust hoods can be installed on both sides of the machine. As of now, solvent vapors can accumulate on the side adjacent to the wall.

2. Side-draft and down-draft local exhaust hoods should be installed on No.5 surface treating machine. The natural air current at the No.5 machine appeared to be from left to right (when facing the machine). Therefore, the side-draft hood should be installed on the right-hand side of the machine to take advantage of the natural wind direction

3. The huge four-color and six-color printers are like two continuous solvent vapor evaporating monsters when they are in operation. On each printer the travelling PVC fabric, which may be 10 feet wide and 100 feet in length, is evaporating solvent vapors from both sides of its surfaces. It is physically impossible to catch all the vapors before they mix up with the workplace air. Therefore, the workable ventilation control technique should consist of picking up the larger emission sources, e.g., the ink troughs, with local exhaustion hoods and continuously refreshing the room air with large quantities of fresh air from outdoors by general ventilation.

4. Because the ceiling of the building is but a few feet taller than the printers, it is feasible to install roof fans on the roof to exert effective control of the solvent vapors evaporated from the PVC fabric. It will require three (3) roof fans on top of the four-color printer and six (6) roof fans for the six-color printer. These fans should be approximately 24 to 30 inches in wheel diameter, each powered by a 1/4 to 1/3 horsepower totally-enclosed motor. Choose low fan speed to obtain longer service life. The exhaust capacity for each fan should be around 3000 to 5000 cfm at no more than 1/2 inch fan static pressure. Costs for this type of roof fan are low.

5. General housekeeping should be strengthened in the printing shop. There were close to a hundred cans of paint, ink and solvent stacked up inside the printing shop, some of them with lids opened and some of them empty. Most of them should be removed out of the printing shop to a ventilated storage area.

6. The local exhaust system for the six-color printer should be completed. Eliminate any suction tube below 4" i.d.

7. Information and training are essential for the protection of employees against solvent hazards. The management should apprise the employee of the specific hazards associated with his work environment. Further, the employee should be instructed to report promptly the development of symptoms or conditions which could be attributed to solvent over-exposure.

8. Where feasible engineering controls are not sufficient to reduce solvent vapor exposures below the permissible limits, they should be supplemented by work practice controls such as job rotation.

IV. CHLOR-ALKALI PLANT

A. Mercury Exposures

In the Chlor-Alkali Plant, chlorine is manufactured by the electrolysis of brine in the mercury cells. Sodium hydroxide and hydrogen gas are produced as by-products. Since 1974, a few engineering control measures have been adopted to reduce the workplace mercury vapor concentrations in the Brine Electrolysis Building. These include opening up all windows on both sides of the main floor to promote natural air circulation between indoor and outdoor air; removing most of the walls on all four sides of the basement to achieve the same general air circulation effect; installation of a local exhaustion ventilation system along the central aisle of the mercury cells; and installation of local exhaust system for the flake soda machines downstairs.

The chlor-alkali plant was surveyed for mercury vapors sixteen (16) times between October, 1975 and July, 1976. Mercury concentrations were measured with a J-W Mercury Vapor Detector (Model MV-2). Figure 1 shows the arrangement of the 36 mercury cells and the locations of the 29 mercury vapor sampling points. Table 5 shows one of the sixteen mercury survey data sheets. Several conclusions can be drawn from analysis of the numerous amount of data from the 16 surveys.

1. Along the northern aisle of the main floor (sampling point 19 to 25), mercury vapor concentrations were consistently low, almost always below the threshold limit value (TLV) of 0.05 mg/m^3.

2. Along the central aisle between the two rows of mercury cells (sampling point 12 to 17), mercury vapor concentrations were usually higher and exceeded the TLV about half the time. The local exhaust system was partially effective because, when compared with the estimated average concentration of 0.25 mg/m^3 in the 1974 survey, the central aisle mercury vapor concentrations have been reduced to about 0.05 mg/m^3 average.

Figure 1 - Mercury Vapor Monitoring Points at Chlor-Alkali Plant

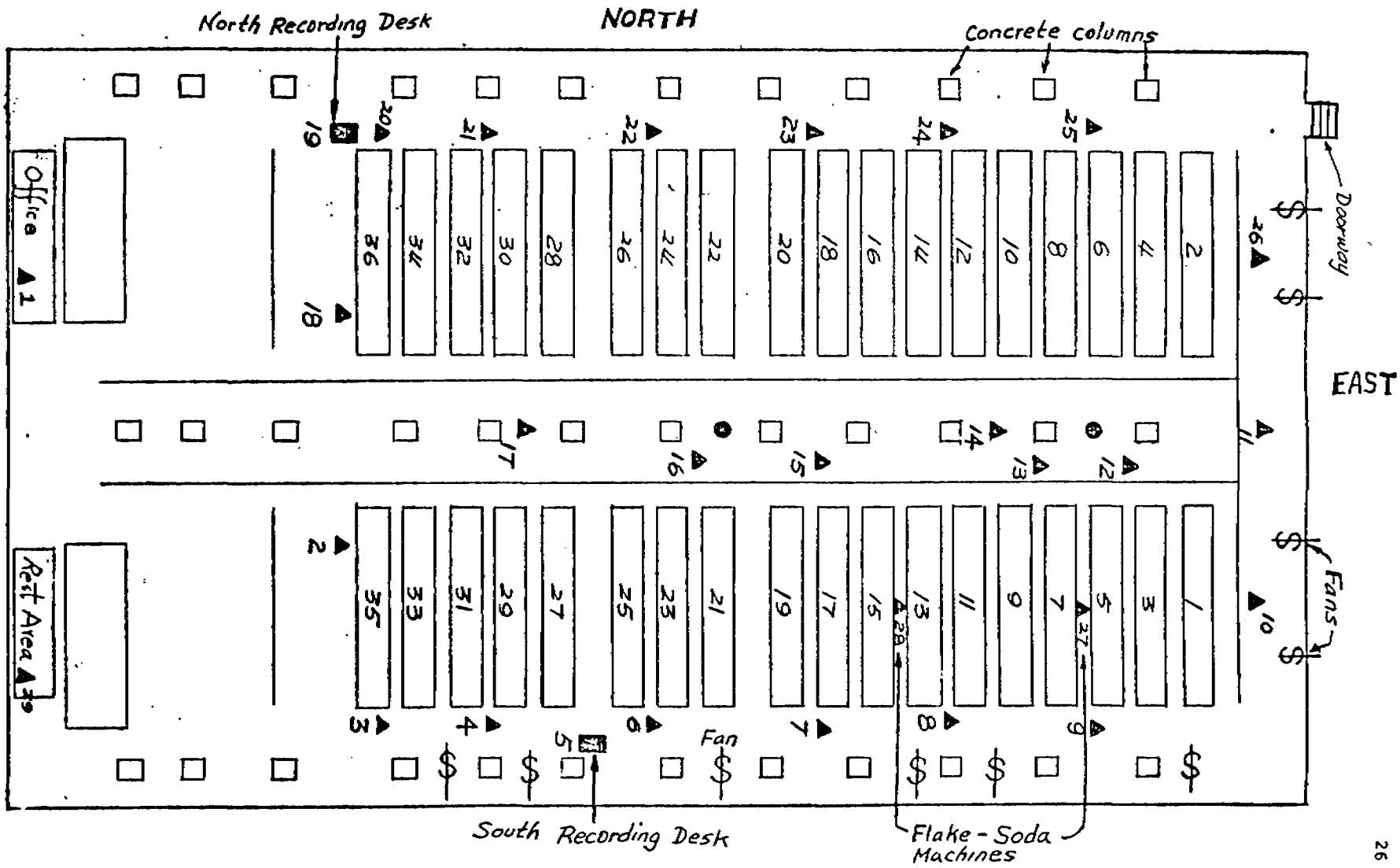

Table 5 - Chlor-Alkali Plant Mercury Survey Results

華夏海灣塑膠公司工業衛生第(51)次測量記錄

CGPC Industrial Hygiene Mercury Surveying Report

1. 使用儀器 Instrument Used	MV-2 Mercury Sniffer		
2. 天候 Weather	Sunny	3. 氣溫 Temperature	28 °C
4. 濕度 Humidity	RH 85 %	5. 風向 Wind	NE-SW 0.8-2.4 m/s
6. 測定地點 Monitoring Area	Alkali-Chloro Plant	7. 測定日期 Monitoring Date	65.5.8 PM 14:00-16:00
8. 測定結果 Surveying Data			

Location		Concentration (PPM)	Location		Concentration (PPM)
1		0.02	21		0
2		0.04	22		0.02
3		0.025	23		0
4	*	0.05-0.06	24		0.01
5		-	25		0.02
6	*	0.12-0.19	26		0.01
7	*	0.08	27	*	0.15
8	*	0.07-0.08	28	*	0.10
9	*	0.23-0.25	29		0.01
10	(?)	0.3-0.4 ← Should this be 0.03 - 0.04			
11		0.02			
12	*	0.15			
13	*	0.25-0.3			
14	*	0.3-0.35			
15		0.02			
16		0.04			
17	*	0.07-0.08			
18		0.01-0.015			
19		0.01			
20		0.02-0.03			

9. 備註 Remarks

1. Operating condition was 46,000 AMP 34 cells.
2. Two flake caustic soda machines were not in operation.
3. The blower has been demolished for a long time.
4. * mark notes conc. exceeds TLV of 0.05 mg/m³

主管: Approved By

審查: Checked By

測量員: Surveyed By

工業安全衛生室 Industrial Safety & Hygiene Office

CUSAROSS 00505

3. Along the southern aisle (sampling point 3 to 9), mercury vapor concentrations were usually higher than the TLV of 0.05 mg/m^3. This is not surprising when one takes the wind direction into consideration. The predominant wind direction was either from north to south, or from northeast to southwest. Therefore, mercury vapors were swept away from the northern aisle and accumulated along the southern aisle where the wind died down and essentially lost all its effectiveness.

4. The highest mercury vapor concentrations were downstairs in the basement near the two flake-caustic soda machines (sampling point 27 and 28). There the concentrations were found to be consistently higher than the TLV, and usually several times higher.

The working conditions in the basement have not been improved appreciably since 1974. A second flake-soda machine has been added in the basement since that time, and this would mean more workers were exposed to excessive mercury concentrations. The excessive mercury concentrations were due to leaks and spills of mercury from the cell room above; and due to the fact that mercury vapor is much heavier than air and tends to sink and accumulate in the basement.

Drops of mercury metal were observed to scatter everywhere on the basement floor and in the drainage ditch. The floor mat was worn out at several places, and no doubt mercury drops can be found beneath the mat. The air in the basement was hot, humid and stuffy due to poor air circulation, water dripping from cell room above, wet floor, and steam and heat generation from the flake-soda machines. Furthermore, fine dusts of caustic soda were floating in the basement air and caused irritations of the eye, nose and throat.

B. Recommendations

1. Remove most of the wall on the east side of the chlor-alkali building to promote air circulation. All windows along the north and south sides should be kept open or simply have them removed. Taiwan is not particularly cold in the winter time, and

I sincerely believe that it is better to feel a little chill than suffer from mercury poisoning. (Incidently, while at Koahsiung TVCM Plant, we noticed that Taiwan Chlor-Alkali Work has no walls on their cell room building.)

2. Workers commented that the existing axial fans make extremely loud noises. How about replacing these fans with lower speed wall fans. The wall fans should be installed along the south side of the building and exhaust to outdoors to take advantage of the predominant wind direction. The replaced axial fans can be used elsewhere such as on the tall roof of the leather plant to exhaust DOP fumes and relieve heat stress.

3. For those employees working at the flake-soda machines, the ideal solution is to move the two flake soda machines out of the basement. The mercury vapor concentration is simply too high in the basement; and the heat, humidity and caustic soda dusts aggravate the unhealthy working condition.

4. If it becomes infeasible to move the flake soda machines out of the basement, you may consider the installation of a system of fan and ductwork to supply outdoor fresh air to the work stations. There are drawbacks in this solution, e.g., workers may turn off the fresh air supply in the winter time because of coldness.

5. Scrupulous cleanliness and personal hygiene are of the essence wherever there is contact with mercury. Work areas should be regularly cleaned to remove mercury deposits that might vaporize and contaminate the air. Workers should wash thoroughly, or preferably shower at the end of each work shift. Adequate washing facilities should be provided.

6. In view of the importance of the skin as a route of absorption for all mercury compounds, workers must wear shoes in the basement of the Brine Electrolysis Building. It also makes good sense to have separate lockers for street and work clothes to prevent contamination of the former and also to prevent the introduction of the mercury compound into the workers' residence.

7. Food and beverages should be consumed only in an area away from mercury contamination. Workers should be educated to thoroughly wash their hands before eating. Smoking shall be prohibited in mercury work areas.

8. Where attempts to reduce atmospheric concentrations of mercury to less dangerous levels have not been successful, workers' total mercury exposure can be reduced by limiting working hours in dangerous mercury concentration areas through administrative methods such as job rotation.

C. Chlorine

Chlorine manufactured from the Chlor-Alkali plant is subsequently dried, cooled, purified and liquified at a plant north of the Extrusion Plant. Further to the north is the tail gas (chlorine) absorbing tower which recovers all unreacted chlorine. This tail gas unit was apparently not working as evidenced by the large quantities of chlorine gas emitted to the atmosphere and caused air pollution problems. Workers at the Extrusion Plant, which is usually directly downwind from the tail gas absorbing tower complained about severe eye, nose and throat irritations from chlorine. At times, the chlorine concentrations were so strong that workers have to either leave the Extrusion Plant or wear acid gas masks. Also affected were residences in the nearby community. The plant management have received many complaints about chlorine odor from neighbors.

A concentration of about 1 to 3 ppm chlorine produces a detectable odor. Five to ten ppm causes irritation of the eyes and respiratory tract. Because of its intensely irritating properties, severe industrial exposure seldom occurs, as the workman is forced to leave exposure before he can be seriously affected. Repeated inhalation of chlorine at low concentrations might lead to disease of the bronchi and inflammation or ulceration of the mucous membrane of the nose. The current threshold limit value for chlorine is 1 ppm (or 3 mg/m^3).

As an air pollutant, chlorine causes vegetation damage at 0.3 to 3 ppm. Serious health hazard could also occur to the general public when chlorine is released under unfavorable climatic conditions. In the community, the aged citizens and people with chronical pulmonary illness could cause special problems. Aggravation of the existing illness or even death could occur under an unfortunate air pollution incident involving chlorine. As CGPC management likes to refer to Canada Standard, the Air Pollution Standard in Ontario, Canada calls for 0.1 ppm as the maximum average chlorine concentration for a period of 30 minutes interval.

D. Chlorine Emission Control

The liquefaction of chlorine by compression and cooling recovers about 85-95% of the chlorine. The remaining chlorine is present in the residual vent gases by virtue of its vapor pressure at liquefaction temperatures. The residual tail gas or "sniff gas" (also called "blow gas") contains carbon dioxide, hydrogen, air and chlorine.

Recent improvements in chlorine liquefaction techniques have yielded liquefaction efficiencies as high as 99%. One such technique, for instance, involves second-stage liquifaction at lower temperatures with air dilution to prevent buildup of hydrogen beyond the 4-5% explosive limit. Such improvements not only add to overall process efficiencies and economics but also decrease the chlorine content in the sniff gas.

There are several chlorine sniff-gas recovery or treatment systems reported in literature and in patents. Some of these are water scrubber and desorber, caustic and/or lime scrubber, silica gel adsorber and desorber, and brine absorber.

A simple system, one that involves treatment of the sniff gas only, employs a caustic scrubber to react chlorine with sodium hydroxide. The reaction products are bleach, salt and water. The reaction can be carried out in packed tower, plate or

tray tower, or spray tower. A dilute NaOH solution (less than 5% by weight) should be used to prevent sludge formation.

$$Cl_2 + 2NaOH \longrightarrow NaOCl + NaCl + H_2O$$

Since caustic is often found in excess near chlorine plants, it represents an inexpensive approach to the tail gas problem. The main disadvantage of the caustic scrubber arises from the disposal of bleach-salt solutions. Some plants dispose of this waste in nearby rivers or streams if damage to fish and aquatic lives present no problem. Chlorine emissions from the caustic scrubber are virtually nil, provided that caustic flow rates and concentrations are maintained. Caustic mist eliminators should be employed on the gas outlets.

V. COMPOUNDING MATERIALS

A. Dusts of Lead, Cadmium and Barium

The compounding processes start in the Compounding Ingredients Mixing Room which is located on the second floor of the Extrusion Plant. The compounding ingredients include plasticizers, stabilizers, lubricants, fillers, pigments, etc. The stabilizers are added to avoid the disintegration of the PVC resin and to prevent discoloration. At CGPC, powders of lead, cadmium and barium stearates are used as stabilizers.

There have been improvements in the working conditions since 1974 at the Compounding Ingredient Mixing Room. The old, ineffective canopy hoods have been removed. New, side-draft slotted hoods have been installed for control of lead, cadmium and barium dusts. These side-draft slotted hoods were mounted on top of all the mixers, and they provided effective control of the toxic dusts.

After the compounding ingredients were thoroughly mixed in the mixers, they flowed in pipelines to a package station below on the first floor of the Extrusion Plant. The material dropped out from a filling spout which was controlled with a sliding gate. Bags and barrels were filled at this packaging station. Large clouds of dust were generated during the filling process. This is one of the major sources of emission of dusts from lead, cadmium and barium to the working environment.

Another release source of toxic dusts observed during 1974 and again during this recent trip was the mixing and transfer station on the main floor of the Extrusion Plant. Manual transfer of mixer compounding ingredients from a storage bin to barrels created huge clouds of dust.

No air samples for lead, barium and cadmium dusts were collected during this recent survey. However, if conditions were not much different from that of 1974, the permissible occupational exposure limits for these toxic dusts are most likely exceeded.

CGPC was about to complete the installation of a pneumatic transport system whereby transfer of powdery material from one location to another will be confined within pipelines. Hopefully, once this pneumatic transport system is completed, occupational exposure to dusts of lead, barium and cadmium will be greatly reduced.

The hazards of lead, cadmium and barium have been discussed in the 1974 Industrial Hygiene Survey Report. Recently, the U. S. Department of Labor's Occupational Safety and Health Administration (OSHA) published a Guideline for Controlling Occupational Exposure to Lead. It gives detailed recommendations on industrial hygiene air monitoring, medical surveillance, medical examination, employee education, personal protection, and housekeeping and hygiene practices. A copy of this guideline is enclosed as Appendix 2.

Unless the pneumatic transport system (which is due for completion soon) drastically reduces the dust level in the Extrusion Plant, it is believed that most of the original recommendations in the 1974 report with regard to lead, cadmium and barium dusts are still applicable. Please refer to page 25 through 31 of the 1974 Industrial Hygiene Survey Report for specifics.

B. Dyes and Pigments

Many types of dyes and pigments were mixed with PVC resins to impart color to products. Dyestuffs were also used extensively in the printing shop. A worker claimed that contacts with a dye caused his skin to itch, and a red colored dye reduced his appetite.

It is not unusual to find very toxic compounds in dyes and pigments. A few synthetic organic dyes and pigments such as azo dyes were found to be potent experimental carcinogens. A group of "fast salts" azoic dyestuffs are highly reactive compounds, and inhalation of the dust may lead to respiratory sensitization and asthma. Inorganic pigments are salts and oxides of lead (particularly lead chromate), cadmium, selenium, iron,

chromium, antimony, and titanium. The potential hazards of these compounds are all related to the biological properties of the parent metal.

It is recommended that we handle all dyestuffs with care. Effective local exhaust ventilation should be provided whenever powdery dyestuffs are poured, weighed and mixed. Any dyestuff that causes skin irritation, sensitization, or other hazards should be investigated. Replacement of unsafe dyestuffs with a safer product should be considered.

VI. PLATING ROOM

Great improvements have been made since February, 1974 at the plating room. The chrome plating tank and the dipping tank have been equipped with effective side-draft local exhaust hoods. The effective control zone of the local exhaust hoods were tested with smoke tubes, and results showed that these hoods created plenty of capture velocity to catch any gas or mist evolving from the open tanks.

The cyanide bath at one corner of the plating room was also fitted with a side-draft local exhaust hood. However, the hood was not functioning because the exhaust fan was too old and too corroded to work properly. A new fan should be installed because there have been cases of accidental poisoning by hydrogen cyanide gas in plating industries.

It is of great importance that the sodium and copper cyanide solutions in the cyanide bath be maintained well on the alkaline side and protected from accidental addition or accumulation of acids. Overflow or drippings from the cyanide bath should not be permitted to mix with overflow and drippings from the adjoining acid tanks.

There are several well designed health and safety caution and warning signs posted on the walls of the plating room. These were the creations of an amateur artist who works at the plating room. Possibly the same idea can be expanded to other plant areas.

The locally designed and manufactured emergency shower and eyewash fountain at the entrance of the plating room was rusted and awkward to operate. Location of the control valves should be rearranged to make operation simple. The fountain and shower should be frequently tested to make sure they are in order.

VII. DOP FUMES

A. DOP Fumes, Inplant Problems

Large quantities of dioctyl phthalate (DOP) are consumed as plasticizer in the manufacturing of PVC products. DOP is a light colored oily liquid and has a mild oily odor. Its toxicity has been widely investigated, and it appears that this material is rather inert and presents a very little health hazard.

Unfortunately, DOP has a tendency to fume under heat treatment. High concentrations of DOP fumes, although low in toxicity, can be obnoxious and sometimes even nauseating. At the leather shop the DOP fume was as dense as fog. Situations at the #7 and #8 calendering machines were especially bad. The canopy hoods over these two calenders did not have adequate exhaust capacity. Canopy hoods are a correct choice of hood for the exhaustion of DOP fumes because the fumes are generated from heating processes. DOP fumes will arise with the hot air and easily captured by the canopy hood. Please refer to page 57 through 59 of the 1974 Industrial Hygiene Report for hood design and the required hood face velocities.

B. DOP Fumes, Air Pollution Control

DOP fumes present a real air pollution problem. CGPC has been cited by the Government's Air Pollution Control Agency for failure to provide effective control of the emission of DOP fumes from the fabrication plant. During the management debriefing session I was asked to assist in the investigation of the DOP control know-how, i.e., what other U.S. PVC manufacturers are using for DOP fumes control, what are the readily available, economical and effective air pollution control hardwares for DOP fumes control.

One U.S. rubber manufacturer I contacted used a self-designed cooling and condensation technique. Plant exhaust air carrying DOP fumes is conveyed in a long duct which is cooled from the outside with very cold water. The DOP fumes are

coalesced or condensed into larger drops due to the cooling. At a 90° turn and a vertical rise the air is impinged on a coarse, metal screen or on the duct wall; and the droplets of DOP are caught on the screen or on the duct wall. The DOP droplets flow down to a catcher and are drained out for reclamation. The collection efficiency for this system is not great. They have to further dilute the stack gas with fresh air to meet the Ringelmann Opacity Standard.

Removal of DOP fumes by filtration was not very successful at another plant. The problem is that the DOP fumes tend to plug up the filter and become a consistent headache for maintenance workers.

DOP fumes are very fine-sized particles (sub-micron to a few microns). Since DOP is insoluble in water, a high energy wet scrubber should remove the DOP fumes without difficulty. Tenneco Chemical installed a flooded disc scrubber for DOP fumes control and achieved satisfactory results. Briefly, liquid is introduced at the hub of a disc through a pipe from below, thus flooding it. The velocity of the gas stream as it passes through the liquid on the disc creates a collection action. The amount of gas handled may be varied by raising or lowering the position of the disc in the scrubbing region.

I believe the most effective system for the removal of sub-micron-sized, oily particles would be the venturi scrubber. A high energy venturi scrubber system is virtually maintenance-free, and provides efficiencies better than 99% for 1 micron-sized particle. The venturi design relies on high gas velocities on the order of 100 to 500 ft/sec at the venturi throat where water is added. The impact breaks the water into droplets which impinge on the particulate matter in the gas.

Once the DOP is collected by the scrubbing water, separation of DOP from water can be accomplished because DOP is insoluble in water. Although the density of DOP is very close to that of water, gravity separation is still possible. The separated DOP can be reclaimed or disposed of.

Please contact me again if you need further assistance in the system design, unit sizing, equipment selection, specification writing, manufacturer contact and/or DOP reclamation or disposal.

VIII. HEAT STRESS

A. Heat Problems

Inplant heat generation sources, plus the hot summer climate in Taiwan, created significant heat stress problems at several job locations. The worst of these are the leather shop, the upstairs polyurethane plant, the tile shop, the PVC drying plant and the chlor-alkali plant.

The Chinese Government uses the same WBGT system to express heat stress:

$$WBGT = 0.7\ WB + 0.3\ GT$$

Where WB = wet bulb temperature
GT = globe bulb temperature

The permissible heat exposure threshold limit value set by Chinese Government is 30.6°C (87°F) WBGT for 8 hours of light load work. Table 6 gives an example of heat stress survey conducted by Mr. O. H. Huang, Industrial Hygiene Technician on May 26, 1976. Survey data shows that when the ambient temperature was at 32°C (~90°F), the WBGT index ranged from 38°C to 40.4°C at the mixing rolls in the fabrication plant. The Government's Heat Stress Standard was exceeded.

On August 9, 1976 when the outdoor ambient temperature was a cool and windy 26°C (79°F), the dry bulb temperature at the second floor polyurethane plant read 33.5°C (92°F).

The physical reaction to prolonged exposure to excessive heat includes heat cramps, heat exhaustion, and heat stroke. Psychologic reaction to prolonged exposure to excessive heat includes decrease in morale, inability to concentrate, increased irritability and anxiety. The results are mirrored by a general decrease in the efficiency of production and in the quality of the finished product.

B. Recommendations

1. For general reduction of inplant temperature, please consider the installation of additional roof fans at many of the hot places. Hot air tends to rise, and the roof fans can effectively remove the indoor hot air and replace it with cooler outdoor air.

Table 6 - CGPC Heat Stress Survey

華夏海灣塑膠公司工業衛生第(67)次測量記錄

CGPC Industrial Hygiene Heat Surveying Report

1. 使用儀器 Instrument Used	Heat Radiation Measuring Apparatus		
2. 天候 Weather	Sunny	3. 氣溫 Temperature	32 °C
4. 濕度 Humidity	RH 80 %	5. 風向 Wind	S-N 2.7-4.3 m/sec
6. 測定地點 Monitoring Area	Film Plant	7. 測定日期 Monitoring Date	65.5.26 AM 10:00-11:00

8. 測定結果 Surveying Data	Location	Temperature (°C) WBGT
1.	# 7 Mixing roll	* 38.5
2.	# 1 Mixing roll	* 38.0
3.	#3 Mixing roll	* 40.4

9. 備註 Remarks

1. #5 Calender was not in operation.
2. Permissible Heat Exposure Threshold Limit value given in °C WBGT is 30.6 °C for 8 hours light load work.
3. WBGT = 0.7 WB + 0.3 GT
   While WBGT = Wet Bulb - Globe Temp. Index
   WB = Natural Wet - Bulb Temp.
   GT = Globe Thermometer Temp.

主管： Approved By

審查： Checked By

測量員： Surveyed By

工業安全衛生室 Industrial Safety & Hygiene Office

Heat stress and DOP fumes usually go hand-in-hand at CGPC. Solve one problem with roof fans and you usually solve the other problem too.

2. At many places spot cooling is the preferred way to achieve heat stress relief. Here no attempt is made to control the general plant temperature. The main purpose is to provide the worker or a small localized work area with a more acceptable environment with respect to temperature or air motion. Supply air may be provided from a general ventilation system or from an individual unit. The outlets are located as close as practical to the workers.

3. The simplest way for spot cooling can be provided by local personal cooling fans. The personal cooling system at Taoyuan Plant is excellent in principal. We should make sure, however, that the blowing air current would not increase the existing dust inhalation.

4. When certain radiant heat generating sources do not require constant monitoring, then consider the installation of shields, partitions, screens, heat reflecting glass, etc. to separate the heat source from the workers and the general work area.

IX. MISCELLANEOUS OBSERVATIONS AND COMMENTS

1. Laminating Shop

No more solvent vapor contamination from next door printing shop. Open one or two extra windows may solve heat stress problem during summer season.

2. Master Batch Shop

The existing two exhausters worked effectively in controlling dusts.

3. Tile Plant

The 1000 ton and the 300 ton Hot Press Machines for tile making were equipped with canopy hoods which provided fairly good control for heat ventilation. Personnel cooling fans may be added at a few spots to relieve heat stress in the summertime.

4. Boiler House

Isolation of the boiler house workers from noise by building a simple work booth was a success.

5. Brine Pit (or waste water pit?) needed fencing for safety reason.

X. CGPC INDUSTRIAL HYGIENE LABORATORY

CGPC has the best trained industrial hygienist in Taiwan. Mr. Ed Lu is very capable and very bright. He has been able to bring problems and recommendations to the direct attention of Mr. Wilbur Shyeh, the General Plant Manager.

Ed is very fortunate to have Mr. O. H. Huang as his industrial hygiene technician. Mr. Huang is a conscientious and methodic worker. He had basic education in chemistry and instrument operations from a vocational junior college, and received industrial hygiene training from Ed.

We are quite certain that, at this moment, CGPC has by far the best equipped industrial hygiene laboratory in Taiwan. The organic vapor analyzer OVA-118B, the charcoal tube personal sampling pumps, the mercury vapor detector, and the Alnor velometer can all be claimed as the most advanced instrument in their respective field. The Hewlett Packard Gas Chromatograph is an expensive and ultrasensitive instrument. Many experts in instrumental analysis have said that operating a GC is both an art and a skill. Almost anybody can read the manual and operate the instrument, but it takes years of experience to master all those little tricks to become a competent GC operator.

Therefore, to help Mr. Huang strengthen his operating skills, it is recommended that CGPC should periodically send parallel charcoal tube samples of vinyl chloride and solvent vapors to Gulf's Health Sciences Laboratory for comparative analysis.

CGPC's OVA-118B instrument appeared to show irrational and insensitive responses to vinyl chloride and other organic gases. If the instrument can not be repaired locally, please ship it to its U.S. manufacturer or Gulf's Health Sciences Lab for repair.

Although CGPC has the best equipped industrial hygiene laboratory in Taiwan, those expensive instruments were not operated inside an ideal laboratory environment. The Hygiene Laboratory's work space consisted of a narrow counter and a small

desk. The counter was fully occupied with chemical reagents, bottles and flasks, and instruments. The little desk was equally crowded. There were too many persons in the laboratory (a regular staff of four, plus many extraneous visitors who dropped in to cool off and to chatter over a cigarette). The laboratory floor and the work counter was dusty. Cigarette butts were littered on the floor while cigarette smoke filled the air.

It is suggested that the laboratory space should be enlarged and preferably separated from the office space. The laboratory area should be maintained meticulously clean, free from dust and smoke. At least one ventilated laboratory hood should be installed in the laboratory. The storage and use of chemicals and solvents in the laboratory should be conducted in such a way so that they would not cause contamination of the instruments or the samples.

XI. TAOYUAN PLANT

China Gulf Plastic Corporation's Taoyuan Plant is a fabrication plant which manufactures PVC films and fabrics from PVC resins and compounding ingredients supplied by Toufen Main Plant. There are at present two large calendering machines for sheeting. Upstairs there is the compounding material weighing and mixing facilities.

It was the second day after a typooon when we visited the Taoyuan Plant. The plant was shut down for roof repair. We were able to talk to Messrs. P.S. Wang, S.F. Chen, and C. C. Tsung, three supervisors at Taoyuan Plant, about health, sanitation and hygiene practices at the plant.

We were told that the plastic leather curtains installed on the overhead canopy hoods for the two calendering machines achieved effective containment of the DOP fume spillage. For the third calender to be installed in the near future, please consider the use of a plain canopy hood instead of the existing double canopy hood. Please refer to pages 57 to 59 of the 1974 Industrial Hygiene Survey Report for the required hood face velocity and exhaust capacity.

Compounding materials including plasticizers, stabilizers, lubricants, fillers and pigments are weighed, added, and mixed in the upstairs area. Powders of lead stearate, cadmium stearate, and barium stearate are used in addition to pre-mixed solutions of cadmium and barium compound. It is suggested that the handling (pouring and weighing) of lead, cadmium and barium dry powders be confined within an isolated spot such as one corner of the upstairs room with partition walls built around it. Local exhaust ventilation should be applied to this isolated area. Once the dry lead, cadmium and barium powders are wetted with DOP or epoxy liquids, the dust hazards are automatically solved.

The hazards of lead, cadmium and barium have been discussed elsewhere in this report and in Chapter IV, pages 23 through 25 of the 1974 Industrial Hygiene Survey Report. It is felt that all workers should be required to wear dust masks wherever lead, cadmium and barium powders are handled.

Liquid epoxy (brand name JPO manufactured by Union Carbide) was also used in the upstairs area. The degree of toxicity of uncured epoxy resins varies, some of these materials are highly hazardous. Prolonged or repeated contact of liquid, or breathing of vapors or mists of uncured epoxy usually causes delayed and serious injury. Therefore, it is advised that skin exposure should be avoided and accidental spillage must be thoroughly removed by washing with soap and water. In case of an eye spill, eyes should be irrigated with large quantities of water and a physician consulted. An emergency eye wash fountain (or at least a wash basin) should be available in the upstairs workplace.

Through Medical Department's Toxicology Group, we will contact Union Carbide Company to find out the specific hazards of JPO epoxy. A Product Safety and Health Data Sheet for JPO epoxy will be mailed to CGPC at a later date.

There are a few noisy areas at Taoyuan Plant. Noise from the strainers for each calender can not be controlled at the source because of operational inconvenience. Therefore, Mr. K. L. Lu suggested the installation of noise insulating partition wood panels around the noise source. We were told the noise reduction was satisfactory.

Upstairs at the mezzanine level there are two work locations where noise levels exceeded 90 dBA. This noise problem can be controlled by building a wood box around the overhead mixer. A layer of PVC leather lining inside the wood box would achieve even better noise reduction. Try to build the box with slanted bottom

so that oil drippings from the mixer can be drained away. Please also wrap the material discharge metal tube with PVC leather to reduce transmission of noise and vibration.

Finally, for the boiler watchers' hearing protection, it is suggested that a simple wood-frame room be built at the boiler watchers' small work area. Heat-tempered glass should be installed on one wall so that they can read the meters and gauges without leaving the room.

XII. KAOHSIUNG TVCM PLANT

TVCM produces VCM at its Kaohsiung Plant by reacting ethylene and chlorine to form ethylene dichloride (EDC) and subsequent dehydrochloronation of EDC to form vinyl chloride and HCl. The processing is normally confined within vessels and pipings. It could escape to the workplace air through minor leaks from compressor packings and piping flanges.

Although no vinyl chloride odor was detected at the Kaohsiung TVCM Plant (odor threshold ~ 2000 ppm), four air samples collected from various locations of the plant with charcoal adsorption tubes showed the following results:

TABLE 7

Vinyl Chloride Concentrations At Kaohsiung TVCM Plant

Sampling Date - August 12, 1976

SAMPLE NUMBER	SAMPLE LOCATION	VINYL CHLORIDE CONC. (PPM)
2	Chloronation Unit	21.3
3	T-402, EDC Light End Column	12.3
4	T-1505, Residue VCM Recovery Tower	9.5
6	T-503, VCM Column, Second Floor	5.1

Unfortunately, Mr. Ed Lu's OVA-118 organic vapor analyzer was not functioning properly on the day of the survey, otherwise one might be able to double prove those concentrations listed in Table 7 above. No explanation can be given as to why samples No.2 and 3 showed more vinyl chloride concentrations than samples No.4 and 6. One might think that samples No.4 and 6 should show more vinyl chloride because monomer was processed at those two sampling locations.

Another of our major concerns for TVCM Kaohsiung Plant is the occupational exposure to EDC. Recently, the U.S. National Institute for Occupational Safety and Health (NIOSH) published a Criteria Document Recommendations for an EDC standard. It recommended that occupational exposure to EDC shall be controlled so that no worker will be exposed to EDC in excess of 5 ppm determined as a time-weighted average exposure for up to a 10-hour workday, 40-hour workweek, or to peak concentrations above 15 ppm as determined by a 15-minute air sample. This is calling for a reduction from the present 50 ppm standard to a 5 ppm standard, plus an added ceiling restriction of 15 ppm. A copy of this NIOSH Recommended Standard is attached to this report as Appendix 3.

According to D. D. Irish's article on "Industrial Hygiene and Toxicology" Volume II, page 1284, EDC is described as having a sweet, not particularly disagreeable odor. The odor is barely detectable but not unpleasant at 100 ppm. At 300 ppm, EDC is very obvious but still would not be considered disagreeable. While walking through the Kaohsiung TVCM Plant, we noticed the odor of EDC at many places. At a few locations the EDC odor can only be described as disagreeably or nauseatingly strong. Even the waste water inside the drainage ditch around the process unit gave out a definitely detectable EDC odor.

Based on the subjective odor evaluation (many times the nose is as good, or even better than a fancy instrument), it is believed that EDC exposures at the Kaohsiung TVCM Plant were extremely high. A conscientious effort should be made in this plant to reduce EDC emissions from various intentional release sources such as pressure release valves and steam blow-down points. A good maintenance program should greatly reduce the loss of EDC from leaks in vessels, pipings and compressors.

Please forward copies of this Chapter and Appendix 3 to Mr. Tsung-Lin Chow, Manager, Kaohsiung TVCM Plant.

APPENDIX

A. Letter from R. T. Cheng to G. M. Hale, January 17, 1975 proposing VCM Standard to the Government of the Republic of China.

B. Guidelines for Controlling Occupational Exposure to Lead.

C. Criteria Document Recommendations for an Ethylene Dichloride Standard.

INTERNAL CORRESPONDENCE
GA 1076

FROM R. T. Cheng

IN REPLY REFER TO RTC 75:008

TO G. M. Hale

DATE 1/17/75

SUBJECT Proposing VCM Standard to the Government of the Republic of China

In reference to your letter of December 20, 1974 to Mr. S. E. Beadle, Jr., wherein you requested comments from Gulf Medical Department on whether CGPC personnel should propose a VCM Standard somewhat similar to that issued by the Province of Ontario, I have the following comments:

First of all, I would like to point out that the publication by the Province of Ontario's Department of Health and Labor is not really a health standard, but a sort of health guideline. They call it "Data Sheet No. 21", and on Page 2, Threshold Limit Value, they stated that "For the present, the Occupational Health Protection Branch, Ontario Ministry of Health, is using a time-weighted average of 10 ppm....." Therefore, it appears to me that the document is really an interim guideline, not a permanent health standard.

The Ontario publication was dated October 1974, just at or around the time when the U. S. Department of Labor published its Permanent Standard on Vinyl Chloride (October 4, 1974). I understand that Ontario was under heavy pressure from plastics industries to adopt that Data Sheet No. 21. Had the Ontario's Ministry of Health, Occupational Health Protection Branch, waited another month, they may not have issued their Data Sheet No. 21.

I have contacted OSHA Office at Washington, D. C., with regard to VCM health standards in other countries. I was told that as of November 1, 1974, Britain used 25 ppm time-weighted average (TWA), and 50 ppm ceiling; Holland used 50 ppm ceiling; Italy used 50 ppm ceiling; West Germany also used 50 ppm ceiling (all of above are temporary standards), but Sweden, like the U. S., has adopted the new standard of 1 ppm TWA and 5 ppm ceiling. This means that most of these western countries have taken a "wait and see" approach to observe what will come out of the U. S. Standards and how the U. S. Standard will fare. Only Sweden has chosen to adopt a Standard similar to the U. S. Standard. I also understand that Japan at this time is using a temporary standard of 50 ppm ceiling.

Although the enforcement of the U. S. permanent standard is temporarily delayed because of the Society of the Plastics Industry (SPI) lawsuit, it should be pointed out that nowhere in the SPI petition was it argued that the 1 ppm TWA and 5 ppm Ceiling Standard was set too stringent, or that SPI has proposed an alternate standard setting the workplace VCM concentrations at higher levels. Essentially, the entire SPI argument was that the effective date of the Standard should be delayed because at this time there are not enough commercially available respirators for the VC industries to use.

I feel this is not a good time for CGPC to propose to the Taiwan Government

a vinyl chloride standard somewhat similar to that of Ontario. I feel that the OSHA Standard will be enforced in the U. S. with minor modifications on respirator requirements and others, but the 1 ppm TWA, 5 ppm Ceiling Standard will stand. I feel that other countries will later adopt VCM Standards similar to the OSHA Standard, and even the Province of Ontario will nullify their Data Sheet No. 21 and adopt the OSHA Standard.

If CGPC would prefer to propose a permanent standard to the Chinese Government at this time, I would suggest that you propose something similar to the U. S. OSHA Standard, not to that of the Province of Ontario. However, if CGPC is proposing a temporary, interim standard to the Government with a statement specifying the rules and regulations therein are temporary guidelines for industries, subject to change, pending investigation under way, then I would agree that a standard somewhat similar to that of the Province of Ontario is appropriate.

In reviewing Ontario's Data Sheet No. 21, I find that it is loosely written, very vague, and not fully substantiated by recent research findings, medical or epidemiological. Above all, it lacks strength in the sections on monitoring and respiratory protection, and it has no mention of signs and labels and record keeping. My specific comments on the points listed under Engineering are as follows:

General: If CGPC wishes to propose 10 ppm TWA and 25 ppm Ceiling as temporary standard, then an "action level" concentration of say 3 to 5 ppm should be specified.

Pt. 1,2,3,4.: Good, but whether adequate ventilation has been provided should be based on monitoring data showing VCM concentrations are normally below the action level concentration.

Pt. 14 (a): Lockers are not required for all workers. Only those employees engaged in reactor cleaning or other operations involving vessel entry, and those packaging and transporting PVC powder are required to have a locker.

A double locker system is not essential if there are other ways and means to separate those severely contaminated work clothes from the clean work clothes and the street clothes. I would prefer that the protective garments be provided clean and dry for each use, and severely contaminated work clothes be taken off and decontaminated. However, if we cannot provide clean and dry clothes for each reactor entry, then it is better to hang the used clothes in an open area with plenty of air circulation, instead of hanging them in an unventilated locker where the trapped vinyl chloride monomer cannot escape.

It is not essential to provide a "clean" locker room and a "dirty" locker room. However, it is a good practice to connect the shower room to the "clean" locker room.

Pt. 5: Written reactor and vessel entry procedure should be developed. Employees shall be trained and rehearsed in the technique provided for in the procedure. Supplied air respirator and protective clothing shall be worn unless air monitoring prior to entry indicates VCM concentration in the reactor below action level.

Pt. 5: Ontario's rule on monitoring is too vague. The monitoring rules specified under U. S. Permanent Standard are preferred. We can set the action level at a much higher level, say at 3 to 5 ppm instead of the 0.5 ppm in OSHA Standard.

Pts. 7,8, and 9: Good.

Pt. 10: Emergency plan should include ways and means of eliminating leaks and spills of VCM, the availability of emergency equipment such as respiratory protection device and special clothing, and emergency medical procedures.

Pts. 11 and 12: Good.

Pt. 13: Emergency shower rule should be adopted. Eye wash rule is good not because VCM presents any eye damage hazard, but because eye wash fountains are something useful in a chemical plant.

Pt. 14(b): It is felt that this type of personal hygiene practice should not be made the law unless the major route of entry of the toxic agent is by ingestion and/or skin contact. In the case of vinyl chloride, the major hazard is through inhalation of the gas. Therefore, frequent washing of hands and face should be encouraged, but the enforcement of frequent wash by law is not desirable. It is felt that eating, drinking and smoking regulations similar to that covered by No. 11 and No. 12 of the Ontario Data Sheet is adequate.

Pt. 14(c): It is felt that the employer should at least provide laundry service at frequent intervals for reactor cleaners and others whose work requires them to be exposed to exceptionally high VCM concentrations.

R. T. Cheng

R. T. Cheng

RTC:mm
cc: S. E. Beadle, Jr.
R. L. Gibson, M. D.
G. E. Ivory
H. E. Runion

LEAD

Guidelines for Controlling Occupational Exposure to Lead

In accordance with the Occupational Safety and Health Administration's standard for air contaminants (29 CFR 1910.1000), employee exposure to lead shall not exceed an 8-hour time weighted average limit of $0.2mg/m^3$. In addition to those legal requirements currently in OSHA Section 1910.1000 and 1910.134, the following recommendations are made to ensure that employee exposure does not exceed the permissible exposure limit.

1. Monitoring

a. Each employer who has a place of employment in which lead is occupationally produced, reacted, released, packaged, repackaged, transported, stored, handled, or used should inspect each workplace and work operation to determine if any employee may be exposed to lead. Indicators that an evaluation of employee exposure should be undertaken would include:

(i) Any information, observations, or calculations which would indicate employee exposure to lead;

(ii) Any measurements of airborne lead; and

(iii) Any employee complaints of symptoms which may be attributable to exposure to lead.

(iv) Whenever there has been a production, process, or control change which may result in an increase in the airborne concentration of lead, or whenever the employer has any other reason to suspect an increase in the airborne concentrations of lead.

b. Air Monitoring

(i) Employee exposure measurements should represent the actual exposure conditions for each employee. Any appropriate combination of long-term or short-term samples would be acceptable, but all exposures should be calculated on an 8-hour time-weighted average (TWA) based on a 40-hour workweek.

(ii) Accuracy of measurement. The method of monitoring and analysis should have an accuracy (to a confidence level of 95%) of not less than plus or minus 20% for concentrations of airborne lead equal to or greater than the TWA. (Some methods meeting

this accuracy requirement are available in the "NIOSH Manual of Analytical Methods").

(iii) Frequency of Monitoring. Where the employer has determined that employees are exposed to lead in excess of the TWA, monitoring should be repeated monthly.

2. Medical Surveillance

a. Each employer should institute a medical surveillance program for all employees who are or will be exposed to airborne concentrations of lead above the TWA. The program should provide each employee with an opportunity for biological monitoring and medical examination performed by or under the supervision of a licensed physician and should be provided during the employee's normal working hours without cost to the employee.

b. Biological monitoring should include blood or urine sampling and analysis every two months for each employee exposed to lead above the TWA and should continue at least four months after the last exposure above the permissible limit. Biological monitoring shall have an accuracy (to a confidence level of 95%) within plus or minus 0.01 milligrams of lead per 100 grams of whole blood or liter of urine.

(i) Blood sample

(a) Where such blood sampling and analysis indicates that the blood lead level of an employee is at or above 60 ug/100g of whole blood, a second blood sampling test should be performed within two weeks after the results of the first blood sampling test are received by the employer.

(b) Where the results of the second blood sampling test indicate that the blood lead level of the employee is at or above 60 ug/100g of whole blood the employee should:

(1) Make available, within one week after the results of the second blood sampling test are received, a medical examination to determine whether the employee has symptoms of lead intoxication.

(2) Take immediate steps to reduce the employee's blood lead level to below 60 ug/100g of whole blood. (Chelating agents should not be routinely administered to employees, and should not be administered at all except by, and at the discretion of a licensed physician.

(3) Conduct blood sampling and analysis on the employee at least monthly thereafter. This sampling and analysis should be continued for at least two months after the employees' blood level has dropped below 60 ug/100g of whole blood.

(ii) Urine Sample

(a) Where urine sampling and analysis is the biological monitoring method chosen by the employer, at least 100 milliters of urine should be collected during the workday, and any urine sample with a specific gravity of less than 1.010 should be discarded and another sample obtained.

(b) Where the employee's urine lead level is at or above 100 ug/L, or urine delta-aminolevulinic acid (ALA) is at or above 500 ug/100ml, calculated to a specific gravity of 1.024, another urine sample or blood sample should be taken and analyzed within two weeks after the results of the first sampling are received by the employer.

(c) Where the second urine sample indicates that the urine delta-aminolevulinic acid (ALA) is at or above 500ug/100ml, blood sampling should be performed within two weeks.

C. Medical examination.

(i) Each employer should provide a medical examination which includes a complete medical history and physical examination, complete blood count, and routine urinalysis (specific gravity, sugar, protein determinations, and microscopic examination), and pregnancy test where appropriate, to each employee exposed to lead in excess of the TWA.

(ii) Medical examinations should also be made available:

(a) To employees prior to their assignment to areas in which airborne concentrations of lead are above the TWA;

(b) At least annually for each employee exposed to airborne concentrations of lead above the TWA at any time during the preceding 12 months;

(c) For each employee whose second blood sampling indicates blood lead levels at or above 60 ug/100g of whole blood and at least every two months thereafter until the employee's blood lead level is below 60 ug/100g of whole blood; and

(d) Immediately, upon notification by the employee that the employee has developed signs or symptoms commonly associated with toxic exposure to lead.

(iii) Where medical examinations are performed, the employer should provide the examining physician with the following information:

(a) A description of the affected employee's duties as they relate to the employee's exposure.

(b) A description of any personal protective equipment used or to be used;

(c) The results of the employee's exposure measurements, if available;

(d) The employee's anticipated or estimated exposure level;

(e) The results of the employee's biological monitoring; and

(f) Upon request of the physician, information concerning previous medical examination of the affected employee.

d. Physician's written opinion

(i) The employer should obtain and furnish the employee with a written opinion from the examining physician containing the following:

(a) The signs or symptoms of lead intoxication manifested by the employee, if any;

(b) A laboratory report of the lead content in blood or urine or delta-aminolevulinic acid (ALA) content in urine if such analysis is performed by or under the supervision of the physician, or reported to the physician by a laboratory to which such samples have been submitted for analysis;

(c) The physician's opinion as to whether the employee has any detected medical condition which would place the employee at increased risk of material impairment to the employee's health from exposure to lead or would directly or indirectly aggravate any detected medical condition;

(d) Any recommended limitation upon the employee's exposure to lead or upon the use of personal protective equipment and respirators; and

(e) A statement that the employee has been informed by the physician of any medical condition which requires further examination or treatment.

(ii) The written opinion obtained by the employer should not reveal specific findings or diagnoses unrelated to occupational exposure to lead.

(iii) If the employer determines, on the basis of the physician's written opinion, that any employee's health would be materially impaired by maintaining the existing exposure to lead the employer should place specific limitations, based on the physician's written opinion, on the employee's continued exposure to lead.

3. Training

a. Each employer who has a workplace in which lead dust, fume, mist or solution is produced, reacted, released, packaged, repackaged, stored, handled, or used should

(i) Inform employees who work or will be assigned to work in the presence of lead dust, fume, mist, or solutions of the quantity, location, and manner of use, release, or storage of lead at the workplace and the specific nature of operations which could result in lead exposure at or above the TWA;

(ii) Each employer whose employees are exposed to lead dust, fume, mist, or solutions above the TWA or whose employees have skin contact with lead dust, fume, mist, or solutions should provide prior to initial placement of new employees and at least annually for all affected employees, a training program which should:

(a) Advise affected employees of the signs and symptoms of overexposure to lead.

(b) Instruct affected employees to advise the employer of the development of the signs and symptoms of overexposure to lead.

(c) Inform employees of the specific nature of operations which could result in exposure to lead above the permissible exposure limit, as well as any necessary protective measures.

(d) Instruct employees that chelating agents should not be routinely used to remove lead from their bodies and should not be used at all except under the direction of a licensed physician.

(e) Inform employees of measures necessary to protect them from exposures in excess of the permissible exposure limit.

(f) Instruct employees as to the purpose, proper use, and limitations of respirators.

(g) Provide employees with a description of, and explain the purposes for, the medical surveillance program.

4. Personal Protective Equipment

Where respirators are required under 1910.1000(e) and

1910.134, the employer should select and provide an appropriate respirator from the table below

Table I

RESPIRATORY PROTECTION FOR LEAD

Airborne Concentration of Lead	Recommended Respirator
(i) Fume, dust, or mist in excess of 200 mg/m^3 (1 mg=1000 ug).	(A) Self contained breathing apparatus with a full face-piece operated in pressure-demand or other positive pressure mode; or (B) a combination respirator which includes a type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
(ii) Fume, dust or mist not in excess of 200 mg/m^3.	(A) A type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode; or with a full facepiece, hood, or helmet operated in continuous flow mode.
(iii) Fume, dust, or mist not in excess of 100 mg/m^3.	(A) A powered air purifying respirator with a full face-piece and high efficiency particulate filter.*
(iv) fume, dust, or mist not in excess of 5.0 mg/m^3.	(A) A high efficiency particulate filter* respirator with a full facepiece; or (B) A supplied-air respirator with a full facepiece, helmet, or hood; or (C) A self-contained breathing apparatus with a full facepiece.
(v) Fume or combined fume dust and mist not in excess of 1.0 mg/m^3.	(A) An air purifying respirator (except single use types), with fume or high efficiency particulate filter*; or (B) A supplied-air breathing apparatus.

(vi) Dust or mist not in excess of 1.0 mg/m^3.	(A) An air purifying respirator (except single use types), with dust or mist filter; or (B) A supplied-air respirator; or (C) a self-contained breathing apparatus.

*NOTE--High efficiency particulate filter means 99.97% efficient against 0.3 micron size particles.

5. Protective Clothing

a. Where protective clothing is required under 1910.132, the employer should provide and ensure that employees wear appropriate, clean, protective clothing, such as, but not limited to, coveralls, smocks, aprons, gloves, shoes, or hats, in the following situations:

(i) Where employees may be exposed to concentrations of lead above the permissible exposure limit; or

(ii) Where the skin or clothing of employees may have repeated contact with accumulations of lead fume, dust, mist or solutions.

b. The employer should launder and maintain protective clothing and dispose of all nonreusable clothing.

c. The removal of lead fume or dust from protective clothing by blowing or shaking should be prohibited.

d. The employer should ensure that all protective clothing is removed in change rooms.

e. The employer should inform any person who launders or cleans lead protective clothing of the potentially harmful effects of exposure to lead and of precautions to take, such as not blowing or shaking the clothing to remove lead fume or dust.

6. Housekeeping

a. All exposed surfaces should be maintained free of accumulations of lead which, if dispersed, would result in airborne concentrations in excess of the permissible exposure limit.

b. Dry sweeping and the use of compressed air for the cleaning of floors and other surfaces should be prohibited.

c. Persons not wearing protective equipment should be excluded from areas where spills or leaks of lead have occurred until cleanup has been completed.

7. Hygiene facilities and practices

a. All food, beverages, tobacco products, nonfood chewing products, and unapplied cosmetics should be prohibited in areas where there is a likelihood that skin or clothing may come in contact with fume, dust, mist, or solutions of lead or where the airborne concentrations of lead are above the TWA.

b. The employer should ensure that employees who work in areas specified in paragraph 9(a) wash their hands, forearms, face and neck before eating, drinking, smoking or applying cosmetics, and at the end of each work shift.

c. Employers should provide an adequate number of lavatories.

d. Where employees wear protective clothing or equipment, or both, change rooms should be provided in accordance with §1910.141(e).

West Farms Express, Inc., Bronx, N.Y., is contesting a $425 penalty for a nonserious citation for 1903.4(a) for failure to post a citation (No. 76-1362)

Western Bowl, Inc., Omaha, Neb., is contesting two serious citations and a total penalty of $1,200 for 1910.212 (a))4) for failure to guard pin wheels and 1910.219 (e) (3) (i) for failure to guard a belt.

The company also is contesting a six-item nonserious citation and a $540 penalty, including 1904.5 (d) (1) for failure to post annual summaries of occupational injuries and illnesses, 1910.309(a) for failure to ground electrical equipment, and 1910.176(c) for failure to keep storage areas free from accumulations of materials (No. 76-1043)

Williams and Lintel Painting, Inc., Poughkeepsie, N.Y., is contesting a nonserious citation and a $50 penalty for 1903.2(a) for failure to post an OSHA poster, 1926.50 (d) (2) for failure to provide a first aid kit and for 1926.451 (e) (8) for failure to lock casters on a mobile scaffold (76-1353)

Wooster Sheet Metal and Roofing Company, Akron, Ohio, is contesting a nonserious citation and a $60 penalty for 1926.450 (a) (9) for failure to provide suitable side rails for a ladder (No. 76-1045)

Full Text

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH CRITERIA DOCUMENT RECOMMENDATIONS FOR AN ETHYLENE DICHLORIDE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to ethylene dichloride (1,2-dichloroethane) in the workplace be controlled by adherence to the following sections. Based on present information available to NIOSH the standard is designed to protect the health and safety of workers for up to a 10-hour workday, 40-hour workweek over a working lifetime; compliance with the standard should therefore prevent adverse effects of ethylene dichloride on the health and safety of workers. The standard is measurable by techniques that are valid, reproducible, and available to industry and governmental agencies. Sufficient technology exists to permit compliance with the recommended standard. The standard will be subject to review and revision as necessary.

"Occupational exposure to ethylene dichloride" is defined as exposure above half the time-weighted average (TWA) environmental limit.

Occupational exposure to ethylene dichloride requires adherence to all the following sections. Exposure at lower environmental concentrations will not require adherence to Sections, 1, 2, 7(b), (c), and (d), and 4(a) except 4 (a) (4).

Section 1 — *Environmental (Workplace Air)*

(a) Concentration

Occupational exposure shall be controlled so that no worker will be exposed to ethylene dichloride in excess of 5 ppm (20 mg/cu m) determined as a TWA exposure for up to a 10-hour workday, 40-hour workweek, or to peak concentrations above 15 ppm (60 mg/cu m) as determined by a 15-minute sample. Unless future research shows it to be unnecessary, nurisings mothers shall not work with ethylene dichloride.

(b) Sampling and Analysis

Procedures for sampling and analysis of workroom air for compliance with the standard shall be as provided in Appendices I and II or by any equivalent methods.

Section 2 — *Medical*

(a) Comprehensive preplacement and annual medical examinations shall be made available to all workers exposed to ethylene dichloride unless a different frequency is indicated by professional medical judgment based on such factors as emergencies, variations in work periods, and preexisting health status of individual workers.

(b) These examinations shall include, but shall not be limited to:

(1) A comprehensive or interim medical and work history.

(2) A comprehensive medical examination giving particular attention to cardiovascular, pulmonary, neurological, liver, and kidney functions.

(3) An evaluation of the worker's physical ability to safely wear a respirator.

(c) Proper medical management shall be provided for workers exposed to ethylene dichloride.

(d) Medical records shall be maintained for all persons employed in work involving exposure to ethylene dichloride. All pertinent medical records with supporting documents shall be maintained for 20 years after the individual's employment is terminated. The designated medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee shall have access to these records.

Section 3 — *Labeling (Posting)*

The following warning sign shall be affixed in a readily visible location on processing or other equipment, on ethylene dichloride storage tanks or containers, and at or near entrances to areas in which there is occupational exposure to ethylene dichloride:

ETHYLENE DICHLORIDE
DANGER: FLAMMABLE
May generate toxic gases on contact
with open flame, hot surfaces, or
other heat-producing conditions
BREATHING VAPOR MAY BE
HAZARDOUS TO HEALTH.
Keep containers closed when not in use
Use only with adequate ventilation
Avoid breathing of vapor.
Avoid contact with skin.

This sign shall also be printed in the predominant language of non-English-speaking workers. All employees shall be trained and informed of the hazardous areas with special instructions given to illiterate workers.

Section 6 — *Work Practices*

(a) Handling and Storage

(1) Storage containers, piping, and valves shall be periodically inspected for leakage

(2) Storage facilities shall be designed to contain spills and prevent contamination of workroom air.

(3) Processes and storage facilities shall not be located near open flames or high-temperature operations, unless precautions are taken to prevent fire and explosion hazards and exposure to pyrolysis products.

(4) Where ethylene dichloride is transferred from one metal container to another, the 2 vessels shall be grounded or electrically interconnected by bonding. The use of mechanical equipment likely to give off sparks should be avoided.

(5) Where ethylene dichloride is used as a fumigant, strict adherence to labor requirements for application and personal protection shall be followed. In addition, standards for pesticide use by agricultural workers can be found in 40 CFR 170.

(b) Contaminant Controls

(1) Suitable engineering controls designed to limit exposure to ethylene dichloride to that prescribed in subsection (a) of Section 1 shall be utilized. Ventilation systems shall be designed to prevent the accumulation or recirculation of ethylene dichloride in the workroom and to effectively remove ethylene dichloride from the breathing zones of workers. Ventilation systems shall be subjected to regular preventive maintenance and cleaning to ensure maximum effectiveness, which shall be verified by periodic airflow measurements.

(2) Portable exhaust ventilation or suitable general ventilation shall be provided for operations that require the spray application of ethylene dichloride such as in fumigation operations.

(3) Buildings in which ethylene dichloride is used where it could form an explosive air mixture shall be explosion-proof. Explosion vents are available and effective on windows, roof and wall panels, and skylights as a safeguard against destruction of buildings and equipment in which flammable vapors may accumulate. Stair enclosures shall also be fire-resistant and shall have self-closing fire doors.

(4) Forced draft ventilation systems shall be equipped with remote manual controls and designed to turn off automatically in the event of a fire in the building.

(c) Equipment Maintenance and Emergency Procedures

(1) Ethylene dichloride hazard areas

A hazard area that workers may enter shall be considered as any space with physical characteristics and sources of ethylene dichloride that could result in concentrations of ethylene dichloride in excess of the environmental limit. Exits shall be plainly mark. Emergency exit doors shall be conveniently located and shall open into areas which will remain free of contamination in an emergency. At least 2 separate means of exit shall be provided from each room or building in which ethylene dichloride is stored or handled in quantities that could create a hazard.

(2) Confined spaces

(A) Entry into confined spaces or into other areas where there may be limited egress shall be controlled by a permit system. Permits shall be signed by an authorized representative of the employer certifying that preparation of the confined space, precautionary measures, personal protective equipment, and procedures to be used are all adequate.

(B) Tanks, pits, tank cars, process vessels, tunnels, sewers, grain storage bins, or other confined spaces which have contained ethylene dichloride shall be thoroughly ventilated to assure an adequate supply of oxygen, tested for ethylene dichloride and other contaminants and inspected prior to each entry. Ventilation shall be maintained while workers are in the space.

(C) Inadvertent infiltration of ethylene dichloride into the confined space while work is in progress inside shall be prevented by disconnecting and blanking off ethylene dichloride supply lines.

(D) Personnel entering confined spaces shall be furnished with appropriate personal protective equipment and protected by a lifeline tended by another worker outside the space, who shall also be equipped for entry with approved respiratory, eye, and skin protection, lifeline, and have contact with a third party.

(E) Written operating instructions and emergency medical procedures shall be formulated and posted in conspicuous locations where accidental exposure to concentrations of ethylene dichloride which exceed the environmental limit may occur. These instructions and procedures shall be printed both in English and in the predominant language of non-English-speaking workers if any. Special instructions shall be given to illiterate workers.

(d) Showers and Eye Wash Fountains

Showers and eye wash facilities shall be provided and so located as to be readily accessible to workers in all areas where skin or eye splash with ethylene dichloride is likely. If ethylene dichloride is splashed on the skin, contaminated clothing shall be promptly removed and the skin washed with soap and water. If liquid ethylene dichloride contacts the eyes, they shall be thoroughly irrigated with clean water following which medical assistance shall be promptly provided. Such incidents shall be reported to the immediate supervisor by the affected employee or by a fellow worker.

Section 7 — *Monitoring and Recordkeeping*

(a) Where it has been determined that the environmental concentrations do not result in TWA workday exposures above one-half the TWA environmental limit, environmental monitoring shall not be required. However, records which form the basis for concluding that the exposures are at or below one-half the limit shall be maintained and exposure surveys shall be made when any process change indicates the need for reevaluation or at the discretion of the compliance officer.

(b) Where exposure concentrations have not been determined, they shall be determined within 6 months of the promulgation of a standard incorporating these recommendations.

(c) Where it has been determined that environmental concentrations result in TWA workday exposures above one-half the limit, employers shall maintain records of environmental exposures to ethylene dichloride based upon the following sampling and recording schedules:

(1) Samples shall be collected at least quarterly in accordance with Appendix I for the evaluation of the work environment with respect to the recommended limit.

(2) Environmental samples shall be taken when a new process is installed or when process changes are made which may cause an increase in environmental concentrations. Increased production, relocation of existing operations, or other functions which can increase concentrations shall require resampling.

(3) In all monitoring, samples shall be collected which are representative of breathing-zone exposures characteristics of each job or specific operation in each work area. Sufficient numbers of samples shall be collected to express the variability of exposure for the work situation and to estimate TWA workday exposures for every employee.

(4) The minimum number of representative TWA exposure determinations for an operation or process shall be

based on variation in exposures and production schedules considering the number of workers exposed as suggested in Table I-2, or as otherwise indicated by a professional industrial hygienist

TABLE I-2

SAMPLING SCHEDULE

Number of Employees Exposed	Number of TWA Determinations
1 - 20	50% of the number of workers
21 - 100	10 plus 25% of the excess over 20 workers
More than 100	30 plus 5% of the excess over 100 workers

(d) When exposure levels are found to be greater than those prescribed in Section 1(a), environmental concentrations shall be reduced by suitable engineering controls. Exposures shall be monitored at least weekly until the effectiveness of the controls is established.

(e) All records of sampling and of pertinent medical examinations shall be maintained for at least 20 years after the individual's employment is terminated. Records shall indicate the type of personal protective devices, if any, in use at the time of sampling. Each employee shall have access to information on his own environmental exposure.

APPENDIX I

SAMPLING PROCEDURE FOR COLLECTION OF ETHYLENE DICHLORIDE

General Requirements

(a) Air samples representative of the breathing zone of workers shall be collected to characterize the exposure from each job or specific operation in each work area.

(b) Samples collected shall be representative of exposure of individual workers.

(c) A record shall be made of:

(1) The date and time of sample collection.

(2) Sampling duration.

(3) Total sample volume.

(4) Location of sampling.

(5) Temperature, pressure, and relative humidity at time of sampling

(6) Other pertinent information

Sampling

(a) Samples shall be collected as near as practicable to the face of workers without interfering with freedom of movement

(b) Samples shall be collected to permit determination of TWA workday and ceiling exposures for every job involving exposure to ethylene dichloride in sufficient numbers to express the variability of the exposures for the work situation. The minimum numbers of TWA's to be determined are listed in Section 7 of the recommended standard, according to the number of employees involved.

(c) Apparatus for Charcoal Tube Sampling

(1) Pump, battery-operated, complete with clip for attachment to the worker. Airflow through the pump shall be within +5% of the desired rate

(2) Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with a 6-mm O.D., and a 4-mm I.D., containing 2 sections of 20-40 mesh activated coconut-shell charcoal separated by a 2-mm portion of urethane foam. The first is the adsorbing section and contains 100 mg of charcoal from coconut shells. The second, or reserve section, contains 50 mg. A 3-mm portion of urethane foam is placed between the outlet of the tube and the reserve section. A plug of glass wool is placed in front of the adsorbing section. The pressure drop across the tube when in use must be less than 1 inch of mercury at a flowrate of 1 liter/min.

(d) Calibration of Sampling Instruments

(1) Air sampling instruments shall be calibrated with a representative charcoal tube in line, over a normal range of flowrates (50-1000 ml/min). Calibration curves shall be established for each sampling pump and shall be used in adjusting the pump prior to and during each field use. New calibration curves shall be established for each sampling pump after making repairs on modifications to the sampling system.

(2) The volumetric flowrate through the sampling system shall be spot-checked and the proper adjustments made before and during each study to ensure obtaining accurate airflow data.

(e) Collection and Handling of samples

(1) Immediately before sampling, break both ends of the tube to provide openings at least one-half the internal diameter of the tube (2mm).

(2) The smaller section of charcoal is used as a reserve and should be positioned nearest the sampling pump

(3) The charcoal tube should be placed in a vertical position during sampling

(4) Tubing may be used to connect the back of the tube to the pump, but air being sampled should not be passed through any hose or tubing before entering the charcoal tube

(5) The sample can be taken at flowrates of 25-200 ml/min, depending on the pump. Total sample volumes of 3-40 liters are recommended, eg, a sample could be collected at 200 ml/min for 15 minutes to give a total sample of 3 liters, or at 25 ml/min for 24 hours to give a total sample

volume of 36 liters. However, it is also recommended that each sample be collected in less than 4 hours.

(6) The charcoal tubes should be capped with inert plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

(7) One charcoal tube, to serve as an analytical blank, should be handled in the same manner as the sample tube (break, seal, and transport) except that no air is sampled through this tube.

APPENDIX II

ANALYTICAL PROCEDURE FOR DETERMINATION OF ETHYLENE DICHLORIDE

Principle of the Method

(a) A known volume of air is drawn through a charcoal tube to trap the ethylene dichloride vapor.

(b) The ethylene dichloride is desorbed from the charcoal with carbon disulfide.

(c) An aliquot of the desorbed sample is injected into a gas chromatograph.

(d) The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

Range and Sensitivity

(a) The lower limit for detection of ethylene dichloride on a gas chromatograph with a flame ionization detector is 13 ng/sample.

(b) The upper limit value for ethylene dichloride is 2.0 mg/sample. This is the estimated amount of ethylene dichloride which the front section will hold before this compound breaks through to the reserve section of charcoal. If a particular atmosphere is suspected of containing a large amount of ethylene dichloride, it is recommended that a smaller volume of air be sampled.

Interferences

(a) Ethylene dichloride will not be trapped when the amount of water in the air is so great that condensation occurs in the charcoal sampling tube.

(b) Any compound which has the same retention time as ethylene dichloride with the chromatographic conditions described in this method could interfere. These may be eliminated by altering operating conditions of the gas chromatograph using a different column packing or using a selective detector, ie. electron capture.

Advantages of the Method

(a) This method is advantageous in that it provides one basic method for determining many different organic compounds.

(b) The sampling device is small, portable, and involves no liquids.

(c) The analysis of the tubes can be accomplished rapidly.

Disadvantages of the Method

(a) The amount of sample which can be taken is limited by the weight of ethylene dichloride which the tube will hold before overloading.

(b) When the sample value obtained for the reserve section of charcoal exceeds 25% of that found on the front section, the possibility of appreciable sample loss exists.

(c) Other organic compounds in high concentrations may displace ethylene dichloride from the charcoal.

Apparatus

(a) Gas chromatograph equipped with a flame ionization detector.

(b) Stainless steel column (20 ft x 1/8 in) with 10% free fatty acid polymer (FFAP) stationary phase on 80/100 mesh chromosorb w (or equivalent), acid washed and treated with dimethyldichlorosilane.

(c) A recorder and some method for determining peak area.

(d) Glass stoppered microtubes of 2.5 ml capacity of 2 ml vials that can be sealed with inert caps.

(e) Microsyringe of 10-ul capacity, and convenient sizes for making standards.

(f) Pipets, 0.5-ml delivery pipets or 1.0-ml pipets graduated in 0.1-ml increments.

(g) Volumetric flasks of 10-ml capacity or convenient sizes for making standard solutions.

Reagents

(a) Spectroquality carbon disulfide.

(b) Ethylene dichloride, preferably chromatoquality grade.

(c) Bureau of Mines Grade A helium.

(d) Prepurified hydrogen.

(e) Filtered compressed air.

Analysis of Samples

(a) All equipment used in the analysis should be washed in detergent following by appropriate tap and distilled water rinses.

(b) Preparation. Each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating foam is removed and discarded, the second section is transferred to another similar test tube. These 2 sections are analyzed separately. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each test tube to desorb ethylene dichloride from the charcoal.

EXTREME CAUTION MUST BE EXERCISED AT ALL TIMES WHEN USING CARBON DISFULIDE BECAUSE OF ITS HIGH TOXICITY AND FIRE AND EXPLOSION HAZARDS. IT CAN BE IGNITED BY HOT STEAM PIPES. ALL WORK WITH CARBON DISULFIDE MUST BE PERFORMED UNDER AN EXHAUST HOOD.

(d) Typical chromatographic operating conditions:

(1) 50 ml/min (70 psig) helium carrier gas flow.

(2) 65 ml/min (24 psig) hydrogen gas flow to detector.

(3) 500 ml/min (50 psig) airflow to detector.

(4) 200 C injector temperature.

(5) 200 C manifold temperature (dector).

(6) 60 C isothermal oven or column temperature.

(e) Injection: The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, the solvent flush injection technique is employed. The 10-ul syringe is first flushed with carbon disulfide several times to wet the barrel and plunger. Three ul of carbon disulfide are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the carbon disulfide solvent, and the plunger is pulled back about 0.2 ul to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-ul aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample

and standard should be made. No more than a 3% difference in area is to be expected.

(f) Measurement of area. The area of the sample peak is determined and preliminary sample results are read from a standard curve prepared as discussed below.

Determination of Desorption Efficiency

It is necessary to determine the percentage of ethylene dichloride on the charcoal that is removed in the desorption process. This desorption efficiency is determined once for a given compound provided the same batch of charcoal is always used.

Activated charcoal, equivalent to the amount in the first section of the sampling tube (100 mg), is measured into a 2-inch long tube, with an inside diameter of 4 mm, flame-sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with inert plastic. A known amount of the compound is injected directly into the activated charcoal with microliter syringe, and the tube is capped with inert plastic.

At least 5 tubes are prepared in this manner and allowed to stand at least overnight to ensure complete adsorption of ethylene dichloride onto the charcoal. These 5 tubes will be referred to as the "desorption samples." A parallel blank tube should be treated in the same manner except that no ethylene dichloride is added to it. The desorption samples and blanks are desorbed and analyzed in exactly the same manner as previously described.

Two or 3 desorption standards are prepared for analysis by injecting the same volume of ethylene dichloride into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the desorption samples. These are analyzed with the desorption samples.

The desorption efficiency equals the difference between the average peak area of the desorption samples and the peak area of the blank divided by the average peak area of the desorption standards, or

$$\text{desorption efficiency} = \frac{\text{area of sample} - \text{area of blank}}{\text{area of standard}}$$

Calibration and Standards

It is convenient to prepare standards in terms of mg ethylene dichloride/0.5 ml of carbon disulfide because samples are desorbed in this amount of carbon disulfide. To minimize error due to the volatility of carbon disulfide, 20 times the weight can be injected into 10 ml of carbon disulfide. For example, to prepare a 0.3 mg/0.5 standard, 6.0 mg of ethylene dichloride is injected into exactly 10 ml of carbon disulfide in a glass-stoppered flask. The density of ethylene dichloride (1.2528 g/ml) is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards is prepared, varying in concentration over the range of interest and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration versus average peak area.

Calculations

(a) The weight in mg corresponding to the peak area is read from the standard curve. No volume corrections are needed, because the standard curve is based on mg ethylene dichloride/10.5 ml carbon disulfide, and the volume of sample injected is identical to the volume of the standards injected.

(b) Separately determine the weights of ethylene dichloride on the front and reserve sections of the charcoal tube.

(c) Corrections must be made to the ethylene dichloride weights determined on both the front and reserve sections for the weights of the respective sections of the blank charcoal tube.

(1) Subtract the weight of ethylene dichloride found on the front section of the blank charcoal tube from the weight of ethylene dichloride found on the front section of the sample charcoal tube to give a corrected front section weight.

(2) Subtract the weight of ethylene dichloride found on the reserve section of the blank charcoal tube from the weight of ethylene dichloride found on the reserve section of the sample charcoal tube to give a corrected reserve section weight.

(3) Add the corrected amounts of ethylene dichloride present on the front and reserve sections of the sample tube to determine the total measured ethylene dichloride in the sample.

(4) Divide this total weight by the determined desorption efficiency to obtain M, the total mg per sample.

(d) Convert the liters of air sampled (V) to volume (V') at standard conditions of 25 C and 760 mm Hg, as follows.

$$V' = \frac{298VP}{760(T+273)} = \frac{0.392VP}{(T+273)}$$

Where:

V' = volume of sampled air in liters at 25 C and 760 mm Hg

V = measured volume of sampled air in liters

P = barometric pressure in mm Hg, measured at time of sampling

T = temperature of air in degree celsius, measured at time of sampling

(e) The concentration of ethylene dichloride in the sampled air can be expressed in various ways using M, the weight of ethylene dichloride obtained in (c)(4), and V', the standardized sample volume, obtained in (d), as follows:

(1) mg/liter = M/V'
(2) mg/1 cu m = gu/liter = 1,000 M/V'
(3) ppm = 247 M/V'