Appendix A.

Substance Safety Data Sheet and Technical Guidelines for Methylene Chloride

I. Substance Identification

A. Substance: Methylene chloride (CH2Cl2).

B. Synonyms: MC, Dichloromethane (DCM); Methylene dichloride; Methylene bichloride; Methane dichloride; CAS: 75-09-2; NCI-C50102.

C. Physical data:
   1. Molecular weight: 84.9.
   2. Boiling point (760 mm Hg): 39.8 deg. C (104 deg. F).
   4. Vapor density (air = 1 at boiling point): 2.9.
   5. Vapor pressure at 20 deg. C (68 deg. F): 350 mm Hg.
   6. Solubility in water, g/100 g water at 20 deg. C (68 deg. F): 1.32.

D. Uses: MC is used as a solvent, especially where high volatility is required. It is a good solvent for oils, fats, waxes, resins, bitumen, rubber and cellulose acetate and is a useful paint stripper and degreaser. It is used in paint removers, in propellant mixtures for aerosol containers, as a solvent for plastics, as a degreasing agent, as an extracting agent in the pharmaceutical industry and as a blowing agent in polyurethane foams. Its solvent property is sometimes increased by mixing with methanol, petroleum naphtha or tetrachloroethylene.

E. Appearance and odor: MC is a clear colorless liquid with a chloroform-like odor. It is slightly soluble in water and completely miscible with most organic solvents.

F. Permissible exposure: Exposure may not exceed 25 parts MC per million parts of air (25 ppm) as an eight-hour time-weighted average (eight-hour TWA PEL) or 125 parts of MC per million parts of air (125 ppm) averaged over a fifteen-minute period (STEL).

II. Health Hazard Data

A. MC can affect the body if it is inhaled or if the liquid comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

B. Effects of overexposure:
   1. Short-term Exposure: MC is an anesthetic. Inhaling the vapor may cause mental confusion, light-headedness, nausea, vomiting, and headache. Continued exposure may cause increased light-headedness, staggering, unconsciousness, and even death. High vapor concentrations may also cause irritation of the eyes and respiratory tract. Exposure to MC may make the symptoms of angina (chest pains) worse. Skin exposure to liquid MC may cause irritation. If liquid MC remains on the skin, it may cause skin burns. Splashes of the liquid into the eyes may cause irritation.
   2. Long-term (chronic) exposure: The best evidence that MC causes cancer is from laboratory studies in which rats, mice and hamsters inhaled MC six hours per day, five days per week for two years. MC exposure produced lung and liver tumors in mice and mammary tumors in rats. No carcinogenic effects of MC were found in hamsters. There are also some human epidemiological studies which show an association between occupational exposure to MC and increases in biliary (bile duct) cancer and a type of brain cancer. Other epidemiological studies have not observed a relationship between MC exposure and cancer. WISHA interprets these results to mean that there is suggestive (but not absolute) evidence that MC is a human carcinogen.
C. Reporting signs and symptoms: You should inform your employer if you develop any signs or symptoms and suspect that they are caused by exposure to MC.

D. Warning Properties:
1. Odor Threshold: Different authors have reported varying odor thresholds for MC. Kirk-Othmer and Sax both reported 25 to 50 ppm; Summer and May both reported 150 ppm; Spector reports 320 ppm. Patty, however, states that since one can become adapted to the odor, MC should not be considered to have adequate warning properties.

2. Eye Irritation Level: Kirk-Othmer reports that "MC vapor is seriously damaging to the eyes." Sax agrees with Kirk-Othmer's statement. The ACGIH Documentation of TLVs states that irritation of the eyes has been observed in workers exposed to concentrations up to 5000 ppm.

3. Evaluation of Warning Properties: Since a wide range of MC odor thresholds are reported (25-320 ppm), and human adaptation to the odor occurs, MC is considered to be a material with poor warning properties.

III. Emergency First-Aid Procedures
In the event of emergency, institute first-aid procedures and send for first-aid or medical assistance.

A. Eye and Skin Exposures: If there is a potential for liquid MC to come in contact with eye or skin, face shields and skin protective equipment must be provided and used. If liquid MC comes in contact with the eye, get medical attention. Contact lenses should not be worn when working with this chemical.

B. Breathing: If a person breathes in large amounts of MC, move the exposed person to fresh air at once. If breathing has stopped, perform cardiopulmonary resuscitation. Keep the affected person warm and at rest. Get medical attention as soon as possible.

C. Rescue: Move the affected person from the hazardous exposure immediately. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises. Do not become a casualty yourself.

IV. Respirators, Protective Clothing, and Eye Protection
A. Respirators: Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not feasible, when such controls are in the process of being installed, or when these controls fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the National Institute for Occupational Safety and Health (NIOSH). Supplied-air respirators are required because air-purifying respirators do not provide adequate respiratory protection against MC. In addition to respirator selection, a complete written respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation. If you can smell MC while wearing a respirator, proceed immediately to fresh air. If you experience difficulty in breathing while wearing a respirator, tell your employer.
B. Protective Clothing: Employees must be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid MC or contact with vessels containing liquid MC. Any clothing which becomes wet with liquid MC should be removed immediately and not reworn until the employer has ensured that the protective clothing is fit for reuse. Contaminated protective clothing should be placed in a regulated area designated by the employer for removal of MC before the clothing is laundered or disposed of. Clothing and equipment should remain in the regulated area until all of the MC contamination has evaporated; clothing and equipment should then be laundered or disposed of as appropriate.

C. Eye Protection: Employees should be provided with and required to use splash-proof safety goggles where liquid MC may contact the eyes.

V. Housekeeping and Hygiene Facilities
For purposes of complying with WAC 296-800-220 and 296-800-230, the following items should be emphasized:

A. The workplace should be kept clean, orderly, and in a sanitary condition. The employer should institute a leak and spill detection program for operations involving liquid MC in order to detect sources of fugitive MC emissions.

B. Emergency drench showers and eyewash facilities are recommended. These should be maintained in a sanitary condition. Suitable cleansing agents should also be provided to assure the effective removal of MC from the skin.

C. Because of the hazardous nature of MC, contaminated protective clothing should be placed in a regulated area designated by the employer for removal of MC before the clothing is laundered or disposed of.

VI. Precautions for Safe Use, Handling, and Storage
A. Fire and Explosion Hazards: MC has no flash point in a conventional closed tester, but it forms flammable vapor-air mixtures at approximately 100 deg. C (212 deg. F), or higher. It has a lower explosion limit of 12%, and an upper explosion limit of 19% in air. It has an autoignition temperature of 556.1 deg. C (1033 deg. F), and a boiling point of 39.8 deg. C (104 deg. F). It is heavier than water with a specific gravity of 1.3. It is slightly soluble in water.

B. Reactivity Hazards: Conditions contributing to the instability of MC are heat and moisture. Contact with strong oxidizers, caustics, and chemically active metals such as aluminum or magnesium powder, sodium and potassium may cause fires and explosions. Special precautions: Liquid MC will attack some forms of plastics, rubber, and coatings.

C. Toxicity: Liquid MC is painful and irritating if splashed in the eyes or if confined on the skin by gloves, clothing, or shoes. Vapors in high concentrations may cause narcosis and death. Prolonged exposure to vapors may cause cancer or exacerbate cardiac disease.

D. Storage: Protect against physical damage. Because of its corrosive properties, and its high vapor pressure, MC should be stored in plain, galvanized or lead lined, mild steel containers in a cool, dry, well ventilated area away from direct sunlight, heat source and acute fire hazards.

E. Piping Material: All piping and valves at the loading or unloading station should be of material that is resistant to MC and should be carefully inspected prior to connection to the transport vehicle and periodically during the operation.
F. Usual Shipping Containers: Glass bottles, 5- and 55-gallon steel drums, tank cars, and tank trucks.

Note: This section addresses MC exposure in marine terminal and longshore employment only where leaking or broken packages allow MC exposure that is not addressed through compliance with WAC 296-56.

G. Electrical Equipment: Electrical installations in Class I hazardous locations as defined in Article 500 of the National Electrical Code, should be installed according to Article 501 of the code; and electrical equipment should be suitable for use in atmospheres containing MC vapors. See Flammable and Combustible Liquids Code (NFPA No. 325M), Chemical Safety Data Sheet SD-86 (Manufacturing Chemists' Association, Inc.).

H. Firefighting: When involved in fire, MC emits highly toxic and irritating fumes such as phosgene, hydrogen chloride and carbon monoxide. Wear breathing apparatus and use water spray to keep fire-exposed containers cool. Water spray may be used to flush spills away from exposures. Extinguishing media are dry chemical, carbon dioxide, foam. For purposes of compliance with WAC 296-24-957, locations classified as hazardous due to the presence of MC shall be Class I.

I. Spills and Leaks: Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed. If MC has spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

J. Methods of Waste Disposal: Small spills should be absorbed onto sand and taken to a safe area for atmospheric evaporation. Incineration is the preferred method for disposal of large quantities by mixing with a combustible solvent and spraying into an incinerator equipped with acid scrubbers to remove hydrogen chloride gases formed. Complete combustion will convert carbon monoxide to carbon dioxide. Care should be taken for the presence of phosgene.

K. You should not keep food, beverage, or smoking materials, or eat or smoke in regulated areas where MC concentrations are above the permissible exposure limits.

L. Portable heating units should not be used in confined areas where MC is used.

M. Ask your supervisor where MC is used in your work area and for any additional plant safety and health rules.

VII. Medical Requirements

Your employer is required to offer you the opportunity to participate in a medical surveillance program if you are exposed to MC at concentrations at or above the action level (12.5 ppm eight-hour TWA) for more than thirty days a year or at concentrations exceeding the PELs (25 ppm eight-hour TWA or 125 ppm fifteen-minute STEL) for more than ten days a year. If you are exposed to MC at concentrations over either of the PELs, your employer will also be required to have a physician or other licensed health care professional ensure that you are able to wear the respirator that you are assigned. Your employer must provide all medical examinations relating to your MC exposure at a reasonable time and place and at no cost to you.

VIII. Monitoring and Measurement Procedures

A. Exposure above the Permissible Exposure Limit:

1. Eight-hour exposure evaluation: Measurements taken for the purpose of determining employee exposure under this section are best
taken with consecutive samples covering the full shift. Air samples must be taken in the employee's breathing zone.

2. Monitoring techniques: The sampling and analysis under this section may be performed by collection of the MC vapor on two charcoal adsorption tubes in series or other composition adsorption tubes, with subsequent chemical analysis. Sampling and analysis may also be performed by instruments such as real-time continuous monitoring systems, portable direct reading instruments, or passive dosimeters as long as measurements taken using these methods accurately evaluate the concentration of MC in employees' breathing zones. OSHA method 80 is an example of a validated method of sampling and analysis of MC. Copies of this method are available from OSHA or can be downloaded from the internet at http://www.osha.gov. The employer has the obligation of selecting a monitoring method which meets the accuracy and precision requirements of the standard under his or her unique field conditions. The standard requires that the method of monitoring must be accurate, to a ninety-five percent confidence level, to plus or minus twenty-five percent for concentrations of MC at or above 25 ppm, and to plus or minus thirty-five percent for concentrations at or below 25 ppm. In addition to OSHA method 80, there are numerous other methods available for monitoring for MC in the workplace.

B. Since many of the duties relating to employee exposure are dependent on the results of measurement procedures, employers must assure that the evaluation of employee exposure is performed by a technically qualified person.

IX. Observation of Monitoring

Your employer is required to perform measurements that are representative of your exposure to MC and you or your designated representative are entitled to observe the monitoring procedure. You are entitled to observe the steps taken in the measurement procedure, and to record the results obtained. When the monitoring procedure is taking place in an area where respirators or personal protective clothing and equipment are required to be worn, you or your representative must also be provided with, and must wear, protective clothing and equipment.

Access To Information

A. Your employer is required to inform you of the information contained in this Appendix. In addition, your employer must instruct you in the proper work practices for using MC, emergency procedures, and the correct use of protective equipment.

B. Your employer is required to determine whether you are being exposed to MC. You or your representative has the right to observe employee measurements and to record the results obtained. Your employer is required to inform you of your exposure. If your employer determines that you are being over exposed, he or she is required to inform you of the actions which are being taken to reduce your exposure to within permissible exposure limits.

C. Your employer is required to keep records of your exposures and medical examinations. These records must be kept by the employer for at least thirty years.

D. Your employer is required to release your exposure and medical records to you or your representative upon your request.

E. Your employer is required to provide labels and safety data sheets (SDS) for all materials, mixtures or solutions composed of greater than 0.1 percent MC. These materials, mixtures or solutions would be classified and labeled in accordance with WAC 296-901-140.
X. Common Operations and Controls

The following list includes some common operations in which exposure to MC may occur and control methods which may be effective in each case:

<table>
<thead>
<tr>
<th>Operations</th>
<th>Controls</th>
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<tr>
<td>Use as solvent in paint and varnish removers cold cleaning and ultrasonic cleaning, and as a solvent in furniture stripping.</td>
<td>General dilution ventilation; local; manufacture of aerosols; cold cleaning exhaust ventilation; personal protective equipment; substitution.</td>
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<tr>
<td>Use as solvent in vapor degreasing.</td>
<td>Process enclosure; local exhaust ventilation; chilling coils; substitution.</td>
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<tr>
<td>Use as a secondary refrigerant in air scientific testing.</td>
<td>General dilution ventilation; local conditioning and exhaust ventilation; personal protective equipment.</td>
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