VI. WORK PRACTICES

The principal method for the manufacture of methylene chloride is the chlorination of methane, [1] and suitable controls for safe use of methane and chlorine should be used. Engineering controls required for the safe handling of chlorine are discussed in the Manufacturing Chemists Association's Safety Data Sheet SD-80. The major hazards from methane are its flammability and explosive characteristics. Caution must be taken to avoid exposure to other chloromethanes that may be co-products of methylene chloride manufacture and caustion must bb.

Further information concerning specific work practices for methylene chloride can be found in the Manufacturing Chemists Association's Safety Data Sheet SD-86. [137]

(a) Transport, Handling, and Use

Containers for storage or transportation of methylene chloride should be made of plain, galvanized, or lead lined, mild steel because it may be corrosive to iron, some stainless steels, copper, nickel, and other metals, especially at elevated temperatures and when in contact with water. [1,138,139] It also reacts with alkali metals (alloys of sodium are potentially explosive), aluminum, and magnesium. Aluminum, rubber, and polyvinyl chloride also are not resistant to methylene chloride.

All piping and valves at the loading or unloading station should be of material that is resistant to methylene chloride and should be carefully inspected prior to connection to the transport vehicle and periodically during the operation. Personal protection must be provided during both inspection and connection. Eye wash and safety shower installations should be readily available in the immediate area. Unloading areas must be posted "Caution: loading or unloading methylene chloride."

Broken drums or other storage or transporting containers should not be welded until thoroughly purged. [140] Although methylene chloride is oxidized only under rigorous conditions, it forms explosive mixture when combined with oxygen under pressure and phosgene, hydrochloric acid, and carbon dixoide in the presence of open flames or high intensity ultraviolet light (Table XII-21). [34,53,140]

Processes in which methylene chloride is used in large quantities should be carried out in closed systems. Well designed hoods and ventilation systems should be used to maintain exposures at or below concentrations specified by this standard. Further protective measures include the use of personal protective equipment and clothing and purging of equipment prior to and during servicing and maintenance.

Methylene chloride is a common solvent in paints and paint strippers and is therefore used in confined spaces or areas in which there are no hoods or specially constructed ventilation systems. For these uses, care must be taken to assure sufficient general room air ventilation to maintain exposures below the standard. This may require engineering controls, such as installation of fans, as well as leaving all doors and windows open. Portable heating units should not be used in confined areas where methylene chloride is used.

Safety showers and eye wash facilities are necessary in areas where methylene chloride is handled. In temporary locations where such facilities are not available, such as in painting or paint stripping operations, a container of water for emergency use must be kept with the first-aid supplies.

Special handling and disposal procedures are required because of the ability of methylene chloride to chemically react with other materials. Reactions of methylene chloride with alloys of sodium are potentially explosive. Mixtures of methylene chloride with acetone may become flammable upon evaporation in air. Cleaning rags should not be burned.

Because of its corrosive properties and its high vapor pressure, methylene chloride should be stored in cool, dry, well-ventilated areas, away from direct sunlight.

(b) Equipment Maintenance

All equipment used for handling methylene chloride must be emptied and purged prior to entry or disassembly. Pipe lines should be disconnected and capped. Under conditions where it is necessary to enter or otherwise work with methylene chloride contaminated equipment, maintenance personnel must use either a self-contained breathing apparatus, pressure demand type, with an impervious protective suit, or a combination supplied air suit with auxiliary self-contained air supply. Ventilation should still be continued during this time by blowing or drawing fresh air through the system. Safety precautions for emergency rescue require that all maintenance personnel be informed of the toxic properties of methylene chloride and be instructed on the necessity of wearing personal protective equipment. [137] Constant observation of anyone entering a tank should be maintained in case rescue work is necessary.

(c) Emergencies

Spills must be anticipated. Storage tanks should be diked to contain the contents of the tank. Drum storage areas must also be diked to contain the volume of methylene chloride present in the drums to prevent release to other areas. Areas where major spills are likely to occur should be constructed so that they may be closed until properly protected personnel can enter, clear, and ventilate the area. Normal work should not be continued until the concentration of methylene chloride has been reduced to that prescribed by this standard. Any combustion operations must be stopped until the spill is cleared. Sewering of methylene chloride should be done in compliance with local, state, and federal waste disposal regulations. Consideration should be given to pumping the diked spill to another tank. In addition, it is advisable to have facilities for transfer of the contents of a leaking tank to another suitable tank.

Areas in which small spills have occurred must be evacuated and well ventilated. Small portable fans may be used in confined areas where local exhaust ventilation is not feasible. Workers should not return to any work area until the odor of methylene chloride is no longer perceptible.

(d) Respiratory Protection

For adequate respiratory protection against the multiplicity of conditions which may be encountered in individual operations, many types of respirators have been developed and approved. Each has a particular field of application and limitations from the viewpoint of protection, as well as advantages and disadvantages from the viewpoint of operational procedures and maintenance. Detailed information on the selection and use of respirators can be obtained from the Respiratory Protective Devices Manual [141] published by the AIHA and the ACGIH in 1963. The American National Standard: Practices for Respiratory Protection, ANSI Z88.2-1969, [142] also classifies, describes, and gives the limitations of respirators.

There are 3 categories of respirators: atmosphere-supplying respirators, air-purifying respirators, and combination atmosphere-supplying and air-purifying respirators.

One factor that affects the overall performance of demand type (negative pressure) respirators is the variability of the face seal. Facepiece leakage is the major limitation of half-mask and quarter-mask facepieces operated with a negative pressure.

For purposes of uniform regulations covering the many face sizes and shapes of the US population, NIOSH recommends that the half-mask or quarter-mask facepieces operated with a negative pressure be used only for protection at or below 10 times the TWA limit, although the majority of wearers can obtain protection in atmospheres of higher methylene chloride concentrations. On the same basis, NIOSH recommends that the full facepiece, operated with negative pressure, may be used up to 50 times the TWA limit.

These maximum use concentration guides do not take into account the service life of the filters and absorbent canisters which also affect the performance of air-purifying respirators. The approval tests (under 30 CFR 11) for these 2 devices specify only carbon tetrachloride for the service life test. Based on recent tests by Nelson and Harder [143] who tested standard respirator cartridges against many types of industrial organic solvents, it is now possible to estimate the service life of approved organic vapor canisters or cartridges against methylene chloride. With a test concentration of 1,000 ppm of methylene chloride, they reported that the standard organic vapor cartridge has a service life of 15.8 minutes before a breakthrough of 100 ppm of methylene chloride. Under the same test conditions, a service life of 90 minutes for carbon tetrachloride was obtained. The standard industrial size gas mask canister is tested against 20,000 ppm of carbon tetrachloride and it must have a service life of 12 minutes before a breakthrough of 5 ppm. Since it has been shown that charcoal can absorb 6 times as much carbon tetrachloride as methylene chloride, it can be estimated that the service life for an industrial size canister is estimated at 40 minutes in an atmosphere of 1,000 ppm, methylene chloride. The chin-type canister and the chemical cartridge respirator with much smaller volumes of sorbent are not recommended for use in methylene chloride contaminated atmospheres because of the very short breakthrough time of methylene chloride.

NIOSH periodically issues a list of approved or certified respiratory protective devices. All devices approved by the Bureau of Mines are listed in Information Circular 8559 and supplements. All types of devices certified by the Testing and Certification Laboratory of NIOSH are listed in a separate publication. These are available from the Testing and Certification Laboratory, NIOSH, Morgantown, West Virginia 26505.

VII. Research Needs

The finding that carbon monoxide is a major metabolite of methylene chloride opened up an entirely new field in methylene chloride toxicity. That this metabolic conversion occurs is well established. However, the biochemical mechanism by which it is accomplished is only speculation. There is evidence that other methylene chloride metabolites include formaldehyde and formic acid. It is important to study the metabolism of methylene chloride to determine the enzyme systems involved in these transformations in order to establish the significance of the intake, both in and out of the work environment, of other substances. For example, the effects on methylene chloride toxicity of alcohols, barbiturates and other enzyme-inducing substances has received little attention.

Whether similar COHb values obtained from inhaling CO and from metabolizing methylene chloride have the same significance has not been the subject of a specific study. It could be assumed that a level of COHb obtained from metabolism of methylene chloride would be more significant than the same level acquired from inhaling CO. The reasoning for such an assumption would be the premise that the ratio of tissue concentrations of CO to blood concentration should be greater when the CO is moving from the tissues to the blood. Information relative to this point is needed in order to adequately evaluate methylene chloride exposures. The affinity of hemoglobin for CO may be alerted when methylene chloride is present. This is of concern because there is some evidence that methylene chloride combines in some way with hemoglobin, and similar substances, to alter the CO, and oxygen, dissociation curves. There was some indication in the data reviewed that the ratio of % COHb to alveolar CO concentration was different following methylene chloride exposure than had been determined following CO exposure. Information is needed on these relationships in order to use alveolar breath samples to monitor COHb values of workers.

In the realm of cellular oxidation, there are potential problems that need investigation. Among these are indications that methylene chloride could interfere by direct combination with heme pigments, making them unavailable for transport purposes, and that oxygen dissociation curves may be altered. An important need for evaluating methylene chloride toxicity is knowledge of the shape of these curves at low tension.

Additional information is also needed on the chronic effects of methylene chloride, both animal experimentation, studies of exposed workers, and experimental human exposures at 25-75 ppm.

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