

Occupational Health Guideline for Diazomethane *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2N_2
- Synonyms: Azimethylene; diazirine
- Appearance: Yellow gas. When stored under pressure, diazomethane can be in the liquid form.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for diazomethane is 0.2 part of diazomethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of diazomethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- Routes of exposure
Diazomethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.
- Effects of overexposure
1. Short-term Exposure: Exposure to diazomethane vapor may cause severe irritation of the eyes, nose, throat, skin, and lungs. Symptoms include headache, weakness, cough, fever, chest pains, shortness of breath, and wheezing. The onset of symptoms after exposure may be delayed. Skin and mucous membrane exposure to liquids containing diazomethane may cause burns with the loss of the skin or mucous membrane. If any of these symptoms appear, get medical attention immediately.

2. Long-term Exposure: Prolonged or repeated exposure to diazomethane may lead to sensitization. Should sensitization occur, a person may experience asthma-like symptoms or fever from exposure to concentrations of diazomethane which had previously caused no symptoms. Diazomethane has been reported to cause cancer of the lungs in animals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to diazomethane.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to diazomethane at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of respiratory system should be stressed.

—14" x 17" chest roentgenogram: Diazomethane may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Diazomethane is reported to cause temporary pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

• Summary of toxicology

Diazomethane gas is a severe respiratory irritant and sensitizer. It is one of the most dangerous products of the chemical laboratory, causing irritation of the eyes, chest pain, cough, fever, and severe asthmatic attacks. Exposure of cats to 175 ppm for 10 minutes resulted in pulmonary edema and hemorrhage, with death occurring in 3 days. A chemist briefly exposed to an unknown concentration in a laboratory developed a violent cough and shortness of breath leading to severe pul-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

monary edema; symptoms completely subsided within 2 weeks. In a fatal incident, another chemist exposed to an unknown concentration of diazomethane, as well as other irritant gases, experienced immediate respiratory distress leading to pneumonitis and death on the fourth day after exposure. A physician exposed to diazomethane from a laboratory spill noted only a faint odor, but immediately experienced severe headache, cough, mild anterior chest pain, generalized aching of muscles, and a sensation of overwhelming tiredness. Within 5 minutes he was stuporous, and on early admission to hospital was markedly flushed and feverish; he recovered in approximately 48 hours. Subsequent exposure to trace amounts of the gas produced wheezing, cough, and malaise, leading to the suspicion that this substance may have a sensitizing, as well as an irritating, effect upon the respiratory system. Skin irritation and sensitization occurs. Also mutagenic and carcinogenic effects have been reported in animals.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 42
2. Boiling point (760 mm Hg): $-23\text{ C } (-9\text{ F})$
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of diazomethane): 1.4
5. Melting point: $-145\text{ C } (-229\text{ F})$
6. Vapor pressure at 20 C (68 F): Not pertinent
7. Solubility in water, g/100 g water at 20 C (68 F):

Reacts

8. Evaporation rate (butyl acetate = 1): Not pertinent

• Reactivity

1. Conditions contributing to instability: Diazomethane may explode when not diluted with other inert gases such as nitrogen. Exposure of diazomethane gas or solutions in solvents to sunlight or other bright illumination may cause explosions. Contact with rough edges such as ground glass may cause explosions.

2. Incompatibilities: Contact of diazomethane gas with alkali metals or drying agents such as calcium sulfate will cause explosions.

3. Hazardous decomposition products: Data not available

4. Special precautions: Barriers or shields should be utilized to protect employees from accidental explosions.

• Flammability

1. Flash point: Not pertinent
2. Autoignition temperature: Pure material explodes above 150 C (302 F). Impure material explodes at lower temperature.
3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Stop flow of gas.

• Warning properties

1. Odor Threshold: Patty reports that diazomethane

has a musty odor. No quantitative data are available, however, relating the odor to air concentrations.

2. Eye Irritation Level: Grant reports that "irritation of the eye from exposure to the gas has developed occasionally among those working with this substance." The concentrations causing eye irritation are not given.

3. Other Information: Patty reports that diazomethane is a severe respiratory tract irritant, but the concentrations producing this irritation are not given.

4. Evaluation of Warning Properties: Patty reports that "the warning properties of diazomethane are not adequate to prevent serious intoxication or fatalities." Based upon this report and upon the lack of quantitative data relating warning properties to air concentrations of diazomethane, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube containing XAD-2 resin coated with octanoic acid, followed by desorption with carbon disulfide and gas chromatographic analysis. An analytical method for diazomethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

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 technically feasible, when such controls are in the process of being installed, or when they 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 Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent the skin from becoming contaminated with liquid diazomethane or solutions containing diazomethane or from becoming frozen from contact with vessels containing liquid diazomethane.
- Clothing wet with flammable solutions containing diazomethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of diazomethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the diazomethane, the person performing the operation should be informed of diazomethane's hazardous properties.
- Any clothing which becomes wet with liquid diazomethane or flammable solutions containing diazomethane should be removed immediately and not reworn until the flammable liquids are removed from the clothing.
- Non-impervious clothing which becomes contaminated with solutions containing diazomethane should be removed promptly and not reworn until the diazomethane is removed from the clothing.
- Employees should be provided with and required to use safety goggles where there is any possibility of liquid diazomethane or solutions containing diazomethane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid diazomethane or solutions containing diazomethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with solutions containing diazomethane should be promptly washed or showered with soap or mild detergent and water to remove any solutions.

COMMON OPERATIONS AND CONTROLS

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

Operation

Use as methylating agent in chemical analysis and laboratory organic synthesis

Controls

Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If liquid diazomethane or solutions containing diazomethane get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If liquid diazomethane or solutions containing diazomethane get on the skin, immediately flush the contaminated skin with water. If liquid diazomethane or solutions containing diazomethane soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of diazomethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

If diazomethane has been swallowed, do not induce vomiting. Get medical attention immediately.

• Rescue

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

LEAK AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

- If diazomethane is leaked, the following steps should be taken:

1. Remove all ignition sources.
 2. Ventilate area of leak.
 3. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
 4. If in the liquid form, allow to vaporize.
- Waste disposal method:

Diazomethane may be disposed of by burning at a safe location or in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 7, 1974.

RESPIRATORY PROTECTION FOR DIAZOMETHANE

Condition	Minimum Respiratory Protection* Required Above 0.2 ppm
Gas Concentration	
2 ppm or less**	Any supplied-air respirator. Any self-contained breathing apparatus.
10 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. 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.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

