Occupational Health Guideline for Methylamine

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: CH₄NH₄
- Synonyms: Monomethylamine; anhydrous methylamine
- Appearance and odor: Colorless gas with an odor like ammonia, but more fishy, particularly at lower concentrations. It can be stored under pressure as a liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylamine is 10 parts of methylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 12 milligrams of methylamine per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

Routes of exposure

Methylamine can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

Effects of overexposure

- 1. Short-term Exposure: Methylamine may cause irritation of the eyes, nose, throat, and lungs. It may also cause coughing and sneezing. Both the liquid and vapor of methylamine are highly irritating to the eyes. Eye injury may occur if proper care is not given immediately. Methylamine solutions may burn the skin.
- 2. Long-term Exposure: Repeated or prolonged exposure to methylamine may cause irritation of the skin or eyes.

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 methylamine.

· Recommended medical surveillance

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

- 1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylamine exposure.
- —Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylamine might cause exacerbation of symptoms due to its irritant properties.
- -Eye disease: Methylamine causes eye damage in animals and eye irritation in humans. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.
- —Skin disease: Methylamine in solution is a primary skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent. 2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

Summary of toxicology

Methylamine gas is a severe eye and respiratory irritant. The LD50 was 0.1 to 0.2 g/kg in rats exposed orally to a 40% aqueous solution of methylamine. One case of bronchitis in a chemical worker has been reported; concentrations measured in the workroom ranged from 2 to 60 ppm; the duration of the exposure was not given. Brief exposures to 20 to 100 ppm are said to produce transient irritation of the eyes, nose, and throat. No symptoms of irritation are produced from longer exposures at less than 10 ppm. One drop of 5% aqueous solution caused conjunctival hemorrhage, superficial corneal opacities, and edema in experimental animals; a

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.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

40% solution caused corneal damage in rabbits. A 40% solution caused necrosis when applied to the skin of a rabbit. Dermatitis and conjunctivitis are occasionally observed in workers after prolonged exposure to the vapor.

CHEMICAL AND PHYSICAL PROPERTIES

Physical data

- 1. Molecular weight: 31.1
- 2. Boiling point (760 mm Hg): -6.32 C (20.6 F)
- 3. Specific gravity (water = 1): 0.656
- 4. Vapor density (air = 1 at boiling point of methylamine): 1.1
 - 5. Melting point: -93.5 C (-136.3 F)
 - 6. Vapor pressure at 20 C (68 F): Not pertinent
- 7. Solubility in water, g/100 g water at 25 C (77 F): 959 cc/100 ml
 - 8. Evaporation rate (butyl acetate = 1): Greater than

• Reactivity

- 1. Conditions contributing to instability: Heat
- 2. Incompatibilities: Contact of gas or liquid methylamine with mercury or with strong oxidizers will cause fires and explosions.
- Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving methylamine.
- 4. Special precautions: Liquid methylamine will attack some forms of plastics, rubber, and coatings.
 Flammability
 - 1. Flash point: Not applicable (gas)
 - 2. Autoignition temperature: 430 C (806 F)
- 3. Flammable limits in air, % by volume: Lower: 5; Upper: 21
- 4. Extinguishant: Stop flow of gas; use carbon dioxide, alcohol foam, or dry chemical for water solutions
 Warning properties
- 1. Odor Threshold: May reports an odor threshold of 3.3 ppm. Patty reports that "olfactory fatigue occurs readily" upon exposure to methylamine.
- 2. Eye Irritation Level: Grant reports that methylamine is an eye irritant, but the concentrations producing irritation are not given. Patty, however, reports that "brief exposures to 20 to 100 ppm produce transient eye ... irritation."
- 3. Other Information: Patty reports that transitory nose and throat irritation is caused by short exposures to 20 to 100 ppm.
- 4. Evaluation of Warning Properties: Although the odor threshold of methylamine (3.3 ppm) is well below the permissible exposure limit, methylamine is treated as a material with poor warning properties, since "olfactory fatigue occurs readily." In addition, the irritant effects produced by brief exposures to methylamine are not considered to give adequate warning, since these effects are only transient.

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

An analytical method for methylamine is in the NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

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 methylamine or solutions containing methylamine or from becoming frozen from contact with vessels containing methylamine.
- Clothing wet with liquid methylamine or solutions containing methylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylamine, the person performing the operation should be informed of methylamine's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid methylamine or solutions

2 Methylamine September 1978

containing methylamine, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Any clothing which becomes wet with methylamine or non-impervious clothing which becomes contaminated with methylamine should be removed immediately and not reworn until the methylamine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid methylamine or solutions containing methylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid methylamine or solutions containing methylamine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

 Skin that becomes contaminated with methylamine should be immediately washed or showered to remove any methylamine.

COMMON OPERATIONS AND CONTROLS

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

Operation

Use as a chemical intermediate in production of insecticides, herbicides, and fungicides; use as a chemical intermediate in production of surfactants

Use in production of rocket fuels and explosives

Use in production of pharmaceuticals and photographic chemicals; intermediate for dyes, textiles, dye assists, rubber, and anti-corrosive chemicals

Controls

Local exhaust ventilation; general dilution ventilation

Local exhaust ventilation; general dilution ventilation

Local exhaust ventilation; general dilution ventilation

Operation

Use as a polymerization inhibitor of hydrocarbons during distillization; use to prevent coagulation and webbing in natural and synthetic latex; use to prevent polymerization in paint removers

Controls

General dilution 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 methylamine or solutions containing methylamine 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 methylamine or solutions containing methylamine get on the skin, immediately flush the contaminated skin with water. If liquid methylamine or solutions containing methylamine 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 methylamine, 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

When a solution of methylamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. 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.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

September 1978 Methylamine 3

- If methylamine is spilled or leaked, the following steps should be taken:
- 1. Remove all ignition sources.
- 2. Ventilate area of leak to disperse gas.
- 3. If in the gaseous form, 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:

Methylamine may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methylamine," Documentation of the Threshold Limit Values for Substances in Workroom Air (3rd ed., 2nd printing), Cincinnati, 1974.
- Commercial Solvents Corporation: "Methylamine," Manufacturers Bulletin, 1965.
- Deichmann, W. B., and Gerarde, H. W.: Toxicology of Drugs and Chemicals, Academic Press, New York, 1969.
- Grant, W. M.: Toxicology of the Eye (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Kirk, R., and Othmer, D.: Encyclopedia of Chemical Technology (2nd ed.), Interscience, New York, 1968.
- Manufacturing Chemists Association, Inc.: Chemical Safety Data Sheet SD-57, Methylamine, Washington, D.C., 1955.
- May, J.: "Solvent Odor Thresholds for the Evaluation of Solvent Odors in the Atmosphere," Staub-Reinhalt, 26:9, 385-389, 1966.
- Patty, F. A. (ed.): Toxicology, Vol. II of Industrial Hygiene and Toxicology (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: Dangerous Properties of Industrial Materials (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR METHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
100 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 100 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 with a full facepiece providing protection against methylamine.
	Any escape self-contained breathing apparatus with a full facepiece.

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