Occupational Health Guideline for Ketene

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_2CO
- Synonyms: None
- Appearance and odor: Colorless gas with a sharp odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ketene is 0.5 parts of ketene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.9 milligrams of ketene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ketene can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to ketene may cause irritation of the eyes, nose, throat, and lungs. It may also cause cough, chest pain, and severe breathing difficulty. This may occur several hours after exposure and may be severe enough to cause death.

2. Long-term Exposure: Chronic overexposure to ketene may cause permanent lung damage.

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 ketene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to ketene 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 the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ketene causes lung damage in animals.

—FVC and FEV (1 sec): Ketene is a severe pulmonary irritant in animals.

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

- **Summary of toxicology**

Ketene is a severe respiratory irritant. Concentrations over 100 ppm were invariably fatal to mice, rats, and guinea pigs; death occurred rapidly with symptoms of marked eye, nose, throat, and pulmonary irritation; autopsies showed major damage to alveolar walls with pulmonary edema. The LC50 for mice was established at 17 ppm for 10 minutes, but 1 ppm was tolerated without apparent chronic injury by several animal species exposed for 6 hours daily for 6 months. Although it has not been reported in humans, animal data indicate that chronic pulmonary changes (emphysema and fibrosis) may result from repeated acute exposures.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 42
  2. Boiling point (760 mm Hg): −56 C (−69 F)
  3. Specific gravity (water = 1): Not applicable

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4. Vapor density (air = 1 at boiling point of ketene): 1.45

5. Melting point: −151 C (−239 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 with water to form acetic acid

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

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Ketene reacts vigorously with water and with a wide variety of organic compounds.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ketene.

4. Special precautions: Dimerization of ketene to diketene occurs even at low temperatures.

• **Flammability**

1. Flash point: Not applicable (gas)

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Stop flow of gas

• **Warning properties**

1. Odor Threshold: No quantitative information is available.

2. Eye Irritation Level: Grant states that "exposure of monkeys to 23 ppm in air for 4 hours caused the animals to rub their eyes, cough, and become lethargic. . . . The dimer, diketene, is said to be lacrimatory and to cause marked irritation of the conjunctiva."

3. Evaluation of Warning Properties: Since there is no quantitative information relating its warning properties to air concentrations, ketene 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 ketene in a bubbler containing alkaline hydroxlammonium chloride, followed by treatment with ferric chloride, and colorimetric analysis. An analytical method for ketene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

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.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as an intermediate in production of acetic anhydride, cellulose and vinyl acetate resins and plastics, acrylic resins, dyes, pigments, and pharmaceuticals	Process enclosure; local exhaust ventilation; personal protective equipment
Use in industrial organic synthesis in manufacture of acetyl chloride, acid anhydrides, esters, nitriles, and diketene	Process enclosure; local exhaust ventilation; personal protective equipment
Use during laboratory operations as an acetylating agent	Process enclosure; 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.

• **Breathing**

If a person breathes in large amounts of ketene, move the exposed person to fresh air at once. If breathing is difficult, properly trained personnel may assist the affected person by administering oxygen. If breathing has stopped, perform artificial respiration. Keep the

affected person warm and at rest. Get medical attention as soon as possible.

• 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 ketene is leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of leak.
3. Stop flow of gas.

• Waste disposal method:

Ketene may be disposed of by burning at a safe location or in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Ketene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• American Industrial Hygiene Association: "Phosgene," *Hygienic Guide Series*, Detroit, Michigan, 1968.

• 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.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadelphia, 1956-1959.

RESPIRATORY PROTECTION FOR KETENE

Condition	Minimum Respiratory Protection* Required Above 0.5 ppm
Vapor Concentration	
25 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 25 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.