

NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND
SUPPORTING DOCUMENTATION FOR

*** KETENE ***

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for KETENE

The basic text of this document contains the draft technical standard approved by the Joint Review Committee of the NIOSH/OSHA Standards Completion Program and the supporting documentation for the substance KETENE.

The SCP draft technical standards are recommendations to the Department of Labor for its consideration in rulemaking and have no legal status until final rules have been promulgated by that agency. This draft standard is provided for your information only.

The References and Sources, Respirator Table Documentation and Use/Exposure and Control Documentation are the working documents used by the various SCP working groups during the development of the draft technical standard and serve as the technical foundation for the standard. The classification for each substance and the regulatory statements were derived following a decision logic established for the various sections of the standard.

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(a) DEFINITIONS

- (1) PERMISSIBLE EXPOSURE - "Permissible Exposure" means inhalation of ketene in concentrations not in excess of 0.5 parts per million (ppm) (0.9 milligrams per cubic meter, mg/cu.m.) averaged over an eight hour work shift, as stated in section 1910.93, Table G-1.
- (2) ACTION LEVEL - "Action Level" means one half (1/2) of the permissible exposure for ketene.

(b) EMPLOYEE INFORMATION - Each employer who has a workplace in which ketene is present shall:

- (1) STANDARD AVAILABILITY - Keep a copy of this section with its appendices A, B and C, at the workplace. This material shall be made readily available to affected employees; and
- (2) PRESENCE OF KETENE - Inform affected employees of the quantity, location, and manner of use or storage of ketene.

(c) EXPOSURE MEASUREMENT

- (1) INITIAL DETERMINATION - Each employer who has a place of employment in which ketene is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of ketene at or above the action level. The determination shall be made each time there is a change in production, process, or control measures which could result in an increase in airborne concentrations of ketene. A written determination shall be made and it shall contain at least the following information:

- (i) Any information, observations, or calculations which would indicate employee exposure to ketene;
- (ii) Any measurements of airborne concentrations of ketene taken;
- (iii) Any employee complaints of symptoms which may be attributable to exposure to ketene; and
- (iv) Date of determination, work being performed at the time, location within work site, name, and social security number of each employee considered.

- (2) INITIAL EXPOSURE MEASUREMENT - If the employer determines that any employee may be exposed to airborne concentrations of ketene at or above the action level, the exposure of the employee believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum exposure of the employee.

- (3) IDENTIFICATION OF EXPOSED EMPLOYEES - If the exposure measurement taken under paragraph (c)(2) of this section reveals employee exposure to airborne concentrations of ketene at or above the action level, the employer shall:

- (i) Identify all employees who may be exposed at or above the action level; and
- (ii) Measure the exposure of the employees so identified.

- (4) EXPOSURE ABOVE THE ACTION LEVEL - If an employee exposure measurement reveals that an employee is exposed to airborne concentrations of ketene at or above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every two months.

- (5) EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE - If an employee exposure measurement reveals that an employee is exposed to airborne

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concentrations of ketene above the permissible exposure, the employer shall:

- (i) Inform the employee of the exposure as required by paragraph (N)(1) of this section; and
- (ii) Measure the exposure of the employee at least monthly; and
- (iii) Institute control measures as required by paragraph (E) of this section.

(6) TERMINATION OF EXPOSURE MEASUREMENT - If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to airborne concentrations of ketene below the action level, the employer may terminate measurement for the employee. For purposes of this subparagraph, use of respirators shall not constitute reduction of employee exposure below the action level.

(d) METHODS OF MEASUREMENT - An employee's exposure shall be obtained by any combination of long term or short term samples which represents the employee's actual exposure averaged over an eight hour work shift (Appendix B (iv)). The method of measurement shall have an accuracy, to a confidence level of 95%, of not less than that given in Table 1 below.

Table 1

Concentration	Required Accuracy
Above permissible exposure	Plus or Minus 25%
At or below permissible exposure and above the action level	Plus or Minus 35%
At or below the action level	Plus or Minus 50%

(e) Methods of Compliance

(1) Engineering controls - No employee shall be exposed to ketene above the permissible limit as defined in paragraph (a)(1) of this section. Engineering and work practice controls shall be used to reduce exposure to ketene to at or below the permissible exposure.

(i) When mechanical ventilation is used to control exposure, measurements which demonstrate system efficiency (for example: air velocity, static pressure, or air volume) shall be made at least every three months. Measurements of system efficiency shall also be made within five work days of any change in production, process or control which might result in a reduction in control.

(ii) Where a fan is located in duct work and where ketene is present in concentrations greater than 3500 ppm, the fan rotating element shall consist of, or be lined with, non-sparking material. There shall be sufficient clearance between the fan rotating element and the fan casing so as to prevent contact.

(2) Respirators

(i) Compliance with the permissible exposure may not be achieved by the use of respirators except:

- a. During the time period necessary to install engineering controls; or
- b. In work situations in which engineering controls are technically not feasible; or
- c. In work situations in which feasible engineering and work practice controls are insufficient to reduce

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employees exposure to at or below the permissible exposure. Where technically feasible engineering and work practice controls are not sufficient to reduce exposure to at or below permissible exposure, they shall be used to reduce exposure to the lowest level feasible; or

- d. For operations not exceeding 40 hours per year; or
- e. In emergencies.
- (ii) Respirators shall be jointly approved by the mining enforcement and safety administration (formerly Bureau of Mines) and by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.
- (iii) Employers shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.
- (iv) Employers shall institute a respiratory protection program in accordance with sections 1910.134(b), (d), (e), and (f).

TABLE 2 RESPIRATORY PROTECTION FOR KETENE

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Vapor Concentration	
Equal to or less than 25 ppm	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 escape and entry from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive-pressure mode A combination respirator which include 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.

(f) Fire and Safety

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Employers shall familiarize themselves with the information contained in the Substance Technical Guidelines for ketene which is contained in Appendix B in order to ensure the safe handling and use of ketene.

- (1) Electrical - For the purposes of compliance with section 1910.309, locations classified as hazardous locations due to the presence of ketene shall be Class I Group D.
 - (2) Portable fire extinguishers - For the purposes of compliance with section 1910.157, ketene is classified as a Class B fire hazard except that loaded stream or foam fire extinguishing media may not be used.
 - (3) Powered industrial trucks - For the purposes of compliance with section 1910.178, locations classified as hazardous locations due to the presence of ketene shall be Class I Group D.
 - (4) Sources of ignition - Sources of ignition such as smoking or open flames are prohibited where ketene is handled or used in a manner so as to create a potential fire or explosion hazard.
- (g) Reserved
- (h) Spills
- (1) Potential sources of ignition shall be eliminated and available ventilation utilized if ketene is accidentally released.
- (i) Reserved
- (j) Training and Information - Each employer who has employees exposed to ketene in excess of the action level, or employees who work where accidental release, fire, or explosion of ketene may occur, shall annually:
- (1) Substance Safety Data Sheet - Inform each employee of the information contained in the Substance Safety Data Sheet for ketene, which is contained in Appendix A; and
 - (2) Medical -
 - (I) Advise employees as to the signs and symptoms of exposure to ketene.
 - (II) Instruct the employees to advise the employer of the development of signs and symptoms of exposure to ketene which are listed in Appendix A.
 - (3) Procedures -
 - (I) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to ketene.
 - (II) The procedures required by (j)(1), (2), and (3)(I) shall be provided to employees at the expense of the employer during the employee's normal working hours.
- (k) Medical Surveillance
- (1) The employer shall provide medical procedures as required by paragraph (k). These procedures shall be provided at no cost to the employee.
 - (2) Preplacement Examination - The employer shall make available to each employee who is to be exposed to airborne concentrations of ketene at or above the action level, a medical examination which shall include as a minimum the following:
 - (i) A medical history and physical examination with emphasis on the lungs.

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- (ii) 14" x 17" chest roentgenogram.
 - (iii) Pulmonary function testing, FVC and FEV (1 sec).
- (3) The employer shall obtain from the physician, as a record of the examination, the following information:
- (i) The physician's written opinion stating whether or not the employee has any detected medical conditions which would place him at increased risk from exposure to ketene.
 - (ii) 14" x 17" chest roentgenogram or a medically acceptable copy.
 - (iii) Results of the pulmonary function testing.
- (4) Periodic Examinations - The employer shall make available to each employee, exposed to ketene in excess of the action level at 12 months from the date of the employee's first exposure, and at every 12 months of exposure in excess of the action level thereafter, a medical examination which must include the following:
- (i) A medical history and physical examination (see (k)(2)(1) of this section).
 - (ii) Pulmonary function testing, FVC and FEV (1 sec).
 - (iii) 14" x 17" chest roentgenogram (only when indicated by abnormalities in results of pulmonary function testing).
- (5) The employer shall obtain from the physician, as a record of the periodic examination, the following information:
- (i) The physician's written opinion stating whether or not the employee has any detected medical conditions which would place him at increased risk to further exposure to ketene.
 - (ii) 14" x 17" chest roentgenogram or a medically acceptable copy.
 - (iii) Results of the pulmonary function testing.
- (6) Exclusion or Removal from Exposure - No employee shall be exposed to ketene if such exposure could place the employee at increased risk of material impairment of his health.
- (7) Emergency Procedures - The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured through exposure to ketene.
- (8) Informing the Physician - The employer shall provide to the examining physician the following information:
- (i) A copy of this section with its Appendices A, B, and C;
 - (ii) A description of the employee's duties as they relate to his exposure to ketene;
 - (iii) A description of any personal protective equipment, including respirators, required to be used;
 - (iv) The results of any employee's exposure measurement, if available;
 - (v) The employee's anticipated exposure level; and
 - (vi) Upon request of the physician, information from previous medical examination of the employee.
- (9) Physician's Written Opinion
- (i) The physician's written opinion shall be a signed statement by the examining physician specifically stating:
 - (A) Whether the employee has any detected medical conditions which could be directly or indirectly aggravated by exposure to ketene or which could significantly interfere with the ability of the employee to follow

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- recommended or required procedures for protecting himself from unusual or emergency exposure.
- (B) Any recommended limitations on the employee's exposure to ketene.
 - (C) The employee has been informed by the physician of any detected medical conditions which require further medical examination or treatment.
- (ii) The written opinion shall not reveal medical information unrelated to exposure to ketene.
- (10) Alternative Medical Examinations - If the examining physician chooses to use alternative medical examinations to those specified in sections (2) and (4), the employer may accept such alternative medical surveillance examinations as meeting the requirements of this part provided that the employer:
- (i) Obtains a statement from the examining physician setting forth the alternative medical examinations and the rationale for substitution and evidence that they will be equally effective.
 - (ii) Informs each exposed employee of the fact that alternative medical examinations to those required in section (2) or (4) above are to be made available.
- (11) Refusal to be Medically Examined - If an employee refuses any required medical examination, the employer shall inform the employee of the possible health consequences of such refusal and obtain a signed statement from the employee indicating that the employee understands the risks involved by refusing to be examined.
- (1) Recordkeeping.
- (1) Initial determination.
 - (i) The employer shall keep an accurate record of all initial determinations required to be made pursuant to paragraph (c)(1) of this section.
 - (ii) The record shall include the written determination and any supporting documentation as required in paragraph (c)(1) of this section.
 - (iii) This record shall be maintained until replaced by a more recent record.
 - (2) Exposure measurements.
 - (i) The employer shall keep an accurate record of all measurements taken to determine employee exposure to ketene.
 - (ii) This record shall include:
 - (a) The date of measurement;
 - (b) A reference to the subparagraph of this regulation which required the measurement, if any;
 - (c) Operations involving exposure to ketene which is being monitored;
 - (d) Sampling and analytical methods used and evidence of their accuracy;
 - (e) Number, duration, and results of samples taken;
 - (f) Name, Social Security number, and exposure of the employee monitored.
 - (iii) This record shall be maintained until replaced by a more recent record but in no event for less than one year.

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- (3) Mechanical ventilation.
 - (i) When mechanical ventilation is used as an engineering control, the employer shall maintain a record of measurements demonstrating the effectiveness of such ventilation as required by paragraph (e)(1)(i) of this section.
 - (ii) This record shall include:
 - (a) Date of measurement;
 - (b) Type of measurement taken;
 - (c) Result of measurement.
 - (iii) This record shall be maintained for at least one year.
- (4) Annual training.
 - (i) The employer shall keep an accurate record of all employee training and advice required by paragraph (j) of this section.
 - (ii) The record shall include:
 - (a) Date of training;
 - (b) Name and Social Security number of employee trained;
 - (c) Substance of training provided.
 - (iii) This record shall be maintained until replaced by a more recent record.
- (5) Medical records.
 - (i) The employer shall keep an accurate medical record for each employee.
 - (ii) The record shall include:
 - (a) Results of tests required in Section (k)(3) and (k)(5) of th
 - (b) Physician's written opinion;
 - (c) Any employee medical complaints relative to exposure to kete
 - (d) A signed statement of any refusal to be examined;
 - (e) A copy of information provided to the physician pursuant to paragraph (k)(8) (ii) through (vi) of this section
 - (iii) This record shall be maintained for the duration of the employment of the affected employee.
- (6) Access to records.
 - (i) All records required to be maintained by this section shall be made available upon request to authorized representatives of the Assistant Secretary and the Director.
 - (ii) Employee exposure measurement records required to be maintained by this section shall be made available to employee and former employees and their designated representatives.
 - (iii) Employee medical records required to be maintained by this section shall be made available upon written request to a physician designated by the employee or former employee.
- (m) Observation of monitoring.
 - (1) Duty.

The employer shall give affected employees or their representatives an opportunity to observe any monitoring of employee exposure to ketene which is conducted pursuant to this section.
 - (2) Exercise of opportunity to observe monitoring.
 - (i) When observation of the monitoring of employee exposure to ketene requires entry into an area where the use of personal protective devices is required, the observer shall use such

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equipment and comply with all other applicable safety procedures.

(ii) Without interfering with the measurement, observers shall be entitled to:

- (a) Receive an explanation of the measurement procedures;
- (b) Visually observe all steps related to the measurement of exposure to ketene that are being performed at the place of exposure.
- (c) Record the results obtained.

(n) Employee notification.

- (1) The employer shall notify in writing, within five work days, every employee who is found to be exposed to ketene above the permissible exposure. The employee shall also be notified of the level of his exposure and corrective action being taken to reduce the exposure to at or below the permissible exposure.
- (2) Pursuant to paragraph (k) of this Section, when an employee is medically examined the employer shall provide the employee with a copy of the physician's written opinion.

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APPENDIX A

SUBSTANCE SAFETY DATA SHEET

I. SUBSTANCE IDENTIFICATION

SUBSTANCE: Ketene

PERMISSIBLE EXPOSURE: 0.5 parts of ketene per million parts of air (ppm)
or 0.9 milligrams of ketene per cubic meter of air (mg/cu m)

APPEARANCE AND ODOR: Colorless gas with a sharp odor.

II. HEALTH HAZARD DATA

A. Ways in which the Chemical Affects Your Body: Ketene can affect your body if you inhale it or if it comes in contact with your eyes.

B. Effects of Overexposure:

1. Short-Term Overexposure: 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 Overexposure: Chronic overexposure to ketene may cause permanent lung damage.
3. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms associated with ketene exposure.

III. EMERGENCY FIRST AID PROCEDURES

A. Breathing: If you or any other person breathes in large amounts of ketene remove 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.

B. Rescue: Move 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 yourself. Understand your emergency rescue procedures and know the locations of the equipment before the need arises.

IV. RESPIRATORS AND PROTECTIVE CLOTHING

A. RESPIRATORS: Respirators are not the best way to control exposure to ketene. You can only be required to wear them for routine use if your employer is in the process of installing controls or if control measures prove inadequate. You may be required to wear respirators for non-routine activities or in emergencies. If respirators are worn, they must have a Mining Enforcement and Safety Administration

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(MESA)/National Institute for Occupational Safety and Health (NIOSH) approval label. (Older respirators may have a Bureau of Mines approval label.) For effective protection, respirators must fit your face and head snugly. Respirators should not be loosened or removed in work situations where their use is required. If you can smell ketene while wearing a respirator, the respirator is not working correctly; go immediately to fresh air. If you experience difficulty breathing while wearing a respirator, tell your employer.

- B. PROTECTIVE CLOTHING: None required
- C. EYE PROTECTION: Provided as part of respiratory protection.
- V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE
- A. Ketene is a combustible, highly reactive gas. It easily forms explosive mixtures with air.
- B. Sources of ignition such as smoking and open flames are prohibited wherever ketene is handled, used or stored in a manner that could create a potential fire or explosion hazard.
- C. Fire extinguishers, where provided, must be readily available and you should know where they are and how to operate them.
- D. Ask your supervisor where ketene is used in your work area and for any additional plant safety and health rules.

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APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES
KETENE

- I. PHYSICAL AND CHEMICAL DATA
- A. Substance Identification
1. Synonyms: none
 2. Formula: CH_2CO
 3. Molecular Weight: 42
- B. Physical Data
1. Boiling point (760 mm Hg): -56 C (-69 F)
 2. Specific gravity (water=1): not applicable
 3. Vapor density (air=1 at boiling point of ketene): 1.45
 4. Melting point: -151 C (-239 F)
 5. Vapor pressure at 20 C (68 F): not pertinent
 6. Solubility in water, % by weight at 20 C (68 F): Reacts with water to form acetic acid
 7. Evaporation rate (butyl acetate=1): not applicable
 8. Appearance and odor: Colorless gas with a sharp odor
- II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA
- A. Fire
1. Flash point: not applicable (gas)
 2. Autoignition temperature: data not available
 3. Flammable limits in air, % by volume: data not available
 4. Extinguishing media: stop flow of gas
 5. Special fire-fighting procedures: Use water spray to keep fire-exposed containers cool and to protect men fighting fire. Do not extinguish flame in an enclosed area since unburnt gas may form explosive mixtures with air.
 6. Unusual fire and explosion hazards: Ketene is a flammable, highly reactive gas. It can readily form explosive mixtures with air. It is heavier than air and can travel along the ground and be ignited at locations remote from the site where ketene is handled. All ignition sources must be controlled where ketene is used, or handled.
- B. 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.
- III. SPILL, LEAK AND DISPOSAL PROCEDURES
- A. If ketene is leaked, the following steps should be taken:
1. Remove all ignition sources
 2. Ventilate area of leak

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3. Stop flow of gas.

- B. Persons not wearing protective equipment should be restricted from areas of leaks until cleanup has been completed.
- C. Waste disposal methods: Ketene may be disposed of by burning at a safe location or in a suitable combustion chamber.

IV. MONITORING AND MEASUREMENT PROCEDURES

- a. EXPOSURE ABOVE THE ACTION LEVEL: Measurements taken for the purpose of determining employee exposure under this section are best taken such that the average eight-hour exposure may be determined from a single eight-hour sample or two (2) 4-hour samples. Short term interval samples (up to 30 minutes) may also be used to determine average exposure level if a minimum of five (5) measurements are taken in a random manner over the eight-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random equal duration samples taken on one (1) work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR Part 84, portable direct-reading instruments, gas and vapor adsorption tubes with subsequent chemical analyses or dosimeters. The method of measurement must determine the concentration of ketene to plus or minus 35%.
 - b. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring under this section should be essentially the same as described under paragraph IV. a. Laboratories performing chemical analyses should be accredited in Industrial Hygiene Chemistry by the American Industrial Hygiene Association (AIHA). The method of measurement must determine the concentration of ketene to plus or minus 25%. Methods meeting these accuracy requirements are available from NIOSH.
- V. MISCELLANEOUS PRECAUTIONS
- A. Do not use flame to detect leaks.
 - B. Employers must advise employees of all plant areas and operations where exposure to ketene could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to ketene is likely to occur are: during its preparation by the pyrolysis of acetic acid, acetic anhydride, acetone, and many other organic compounds; during its use to prepare acetic acid, acetic anhydride, diketene, and intermediates for acrylic ester monomers; and its use as an intermediate in the preparation of dyes, pigments, and pharmaceuticals.

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APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. 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 indicates that chronic pulmonary changes (emphysema and fibrosis) may result from repeated acute exposures.

III. SIGNS AND SYMPTOMS

Severe irritation of eyes, nose, throat and lungs. Signs and symptoms of pulmonary edema may occur several hours after exposure.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Give artificial resuscitation if indicated. If overexposed, consideration should be given to hospitalization and observation for possible delayed onset of pulmonary edema.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of ketene are caused by its respiratory irritant properties. Those overexposed should be carefully observed for a delayed onset of pulmonary edema. It is important that the physician becomes familiar with plant operating conditions in which exposure to ketene occurs. Those with skin disease may not tolerate the wearing of protective clothing and those with chronic respiratory disease may not tolerate the wearing of negative pressure respirators.

B. PREPLACEMENT

The following medical procedures must be made available to each employee who is exposed to ketene:

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1. A complete history and physical examination -- The purpose is to detect preexisting 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.
2. 14" x 17" chest roentgenogram -- Ketene causes lung damage in animals.
3. FVC and FEV (1 sec) -- Ketene is a severe pulmonary irritant in animals.

C. PERIODIC EXAMINATIONS

The above medical examinations are to be repeated annually except that an x-ray is required only when indicated by pulmonary function testing.

References

1. American Conference of Governmental Industrial Hygienists: "Ketene," (3d ed., 2d printing), Documentation of the Threshold Limit Values for Substances in Workroom Air, Cincinnati, 1974, p. 143.
2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1976-1978.

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REFERENCES AND SOURCES

KETENE

1910.93

- (g) Methods of Compliance
 - (1) Engineering Controls - In the absence of definitive data on the lower flammable limit of ketene, 3500 ppm was estimated to be the level above which non-sparking materials are required to minimize fire or explosion hazards from fan construction.
- (f) Fire and Safety
 - (1) Electrical - Classification based on "Fire Hazard Classification of Chemical Vapors Relative to Explosion-Proof Electrical Equipment," H. Carhart et al, National Academy of Sciences, 1973, report to U. S. Coast Guard, report no. CG-D-92-74.
- (g) Personal Protective Equipment, and, (i) Sanitation

COMMENTS

Ketene has a boiling point of -56 deg. C. There is no indication in the literature that it is harmful by any route of exposure covered or considered by this section of the standard. It is highly unlikely that anyone would handle this material in liquid form.

References: none

Statements: reserved

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

"Beilstein's Handbuch der Organischen Chemie," I, 724 and supplements (Beil)

Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd edition, 12, 87 (K-0)

Sources of data items used:

- I. A. 1. Synonyms:
 - 2. Formula: Beil
 - 3. Molecular weight: calculated
- B. 1. Boiling point: Beil, K-0
 - 2. Specific gravity: not applicable
 - 3. Vapor density: calculated
 - 4. Melting point: Beil; K-0
 - 5. Vapor pressure: not applicable
 - 6. Solubility in water: Beil
 - 7. Evaporation rate: not applicable
 - 8. Appearance and odor: Beil; K-0
- II. A. 1. Flash point: not applicable
 - 2. Autoignition temperature: not available
 - 3. Flammable limits: not available
 - 4. Extinguishing media: analogy
 - 5. Special fire fighting procedures: analogy
 - 6. Unusual fire and explosion hazards: analogy
- B. 1. Conditions contributing to instability: ADL
 - 2. Incompatibilities: Beil
 - 3. Hazardous decomposition products: analogy
 - 4. Special precautions: none
- III. A. Steps if released or spilled: analogy
- C. Waste disposal method: NA
- V. Miscellaneous precautions: analogy

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VI. Common operations: K-0

USE/EXPOSURE AND CONTROL DOCUMENT

References used in the preparation of this document include:

- Considine, D. M., "Chemical and Process Technology Encyclopedia," McGraw Hill, 1974 (Considine)
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- Hamilton, A., and Hardy, H. L., "Industrial Toxicology," Publishing Sciences Group, Inc., 3rd edition, 1974 (Hamilton and Hardy)
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References for Specific Use/Exposure

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2. Considine, Faith, Stephenson
3. ILO, SRI
4. Celanese, HPI
5. Chem Tech, Celanese, Merck, SRI
6. HPI, SRI
7. Chem Tech, ILO, Merck, Plunkett

References for Specific Control Methods

Hamilton and Hardy, ILO, Plunkett and Sax were the references used in the Specific Control Methods for numbers 1 - 7.

RESPIRATOR TABLE JUSTIFICATION

Patty reports that ketene concentrations of over 100 ppm invariably proved fatal in tests with mice, rats and guinea pigs. Investigators concluded that ketene resembled phosgene closely in its ability to cause delayed pulmonary edema. Repeated inhalations of 1 ppm by cats, rats and monkeys resulted in lung damage detected on autopsy.

Documentation of TLV's reports an LC50 for mice of 17 ppm ketene for 10 minutes. Patty reports a rat LC50 of 130 ppm for 30 minutes and further states that four two-hour exposures of a cat to 23 ppm did not cause death. Spector lists MLC's for mice, rats, guinea pigs, cats and monkeys, the lowest value reported being the mouse MLC of 52 ppm. Deichman and Gerarde refer the reader to their phosgene entry which states that a brief exposure to 50 ppm "may be fatal."

AIHA Hygienic Guide Series considers 50 ppm the IDLH concentration for phosgene, with exposure to concentrations above 50 ppm likely to be fatal.

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Plunkett states that ketene causes conjunctivitis, anosmia (loss of the sense of smell), and irritation of the throat.

WARNING PROPERTIES: There is no quantitative data available to relate the warning properties of ketene to its toxicological effects. Because of the severity of the potential health hazard, ketene is treated as a material not having adequate warning properties.

EYE IRRITATION: Conjunctivitis is reported as an effect of ketene exposure. **GRANT:** Exposure of monkeys to 23 ppm in air for 4 hours caused the animals to rub their eyes, cough, and become lethargic. Only full facepiece respirators are permissible.

IDLH: Based upon the AIHA's IDLH recommendation for the more hazardous phosgene (50 ppm) and the animal studies cited by Spector and Deichman and Gerarde, an IDLH concentration of 50 ppm is assumed.

LFL: The lower flammable limit of ketene is higher than its IDLH concentration.

PERMISSIBLE EXPOSURE: 0.5 ppm

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USE/EXPOSURE AND CONTROL DOCUMENT
KETENE

Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1. Inhalation of gas and irritation of eyes and mucous membranes during use as an intermediate in the production of acetic anhydride	A,B	Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective device, goggles)
2. Inhalation of gas and irritation of eyes and mucous membranes during use as an intermediate in the production of cellulose acetate and vinyl acetate resins and plastics	A,B	Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective devices, goggles)
3. Inhalation of gas and irritation of eyes and mucous membranes during use as an intermediate in the production of acrylic resins (used in surface coatings, textiles, paper, polishes, leather)	A,B	Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective devices, goggles)
4. Inhalation of gas and irritation of eyes and mucous membranes during use as an intermediate in the preparation of dyes, pigments, and pharmaceuticals (aspirin, vitamin A)	A,B	Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective devices, goggles)
5. Inhalation of gas and irritation of eyes and mucous membranes during the preparation of ketene in laboratory and commercial amounts. (Ketene is prepared and used directly for further synthesis by most users because of its instability. It tends to dimerize unless stored below -60 C)	A,B	Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective devices, goggles)

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| 6. | Inhalation of gas and irritation of eyes and mucous membranes during use in the preparation of diketene (an intermediate in the manufacture of dyestuffs, pigments, and pharmaceuticals) | A,B | Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective devices, goggles) |
| 7. | Inhalation of gas and irritation of eyes and mucous membranes during use in industrial organic synthesis (manufacture of acetyl chloride, acid anhydrides, esters, nitriles) | A,B | Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective devices, goggles) |
| 8. | Inhalation of gas and irritation of eyes and mucous membranes during laboratory use for many organic synthetic processes (ketene is an acetylating agent) | A,B | Process enclosure; local exhaust ventilation; personal protective equipment in case of leakage or accident (respiratory protective devices, gloves goggles) |

- A -- Inhalation
- B -- Skin contact resulting in localized irritation
- C -- Ingestion
- D -- Skin contact resulting in absorption and subsequent systemic poisoning