NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND

SUPPORTING DOCUMENTATION FOR

*** MORPHOLINE ***

NIOSH/OSHA Draft Technical Standard and Supporting Documentation for MORPHOLINE

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 MORPHOLINE.

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.

(a) Definitions. (1) "Permissible exposure" means exposure of employees to airborne concentrations of morpholine not in excess of 20 parts per million (ppm) (70 milligrams per cubic meter, (mg/m3)) averaged over an eight-hour work shift (time weighted average), as stated in § 1910.1000, Table Z-1.

(2) "Action level" means one half of the permissible exposure for morpholine.

(b) Exposure determination and measurement. (1) Each employer who has a place of employment in which morpholine is released into the workplace air shall determine if any employee may be exposed to airborne concentrations of morpholine 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 morpholine.

(2) A written record of the determination shall be made and shall contain at least the following information:

(i) Any information, observations, or calculation which may indicate employee exposure to morpholine;

(ii) Any measurements of morpholine taken;

(iii) Any employee complaints of symptoms which may be attributable to exposure to morpholine; and

(iv) Date of determination, work being performed at the time, location within work site, name, and social security number of each employee considered.

(3) If the employer determines that any employee may be exposed to morpholine at or above the action level, the exposure of the employee in each work operation who is believed to have the greatest exposure shall be measured. The exposure measurement shall be representative of the maximum eight-hour time weighted average exposure of the employee.

(4) If the exposure measurement taken pursuant to paragraph (b) (3) of this section reveals employee exposure to morpholine 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.

(5) If an employee exposure measurement reveals that an employee is exposed to morpholine 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.

(6) If an employee exposure measurement reveals that an employee is exposed to morpholine above the permissible exposure, the employer shall:

(i) Measure the exposure monthly of the employee so exposed; and

(ii) Institute control measures as required by paragraph (d) of this section; and

(iii) Individually notify, in writing, within five days, every employee who is found to be exposed to morpholine above the permissible exposure. The employee shall also be notified of the corrective action being taken to reduce the exposure to at or below the permissible exposure.

(7) If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to morpholine below the action level, the employer may terminate measurement for the employee.

(8) For purposes of this paragraph, employee exposure is that which would occur if the employee were not using a respirator.

(c) Methods of measurement. (1) 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 (See Appendix B (iv) of this section).

(2) The method of measurement shall have an accuracy, to a confidence level of 95 percent, of not less than that given in Table 1.

Table 1

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

(d) Compliance. (1) No employee shall be exposed to morpholine above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of morpholine shall be controlled to at or below the permissible exposure by engineering and work practice controls:

(i) Engineering and work practice controls shall be instituted to reduce exposures to at or below the permissible exposure, except to the extent that such controls are not technically feasible.

(ii) Wherever engineering and work practice controls are not sufficient to reduce exposures to at or below the permissible exposure, they shall nonetheless be used to reduce exposure to the lowest level feasible and shall be supplemented by respirators in accordance with paragraph (d)(4) of this section.

(3) Engineering controls. When mechanical ventilation is used to control exposure, measurements which demonstrate system effectiveness, for example, air velocity, static pressure, or air volume, shall be made at least every three months. Measurements of system effectiveness shall also be made within five days of any change in production, process, or control which might result in an increase in airborne concentrations of morpholine.

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

(i) During the time period necessary to install or implement engineering or work practice controls; or

(ii) In work situations in which engineering and work practice controls are technically not feasible; or

(iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of morpholine to at or below the permissible exposure; or

(iv) For operations which require entry into tanks or closed vessels; or

(v) In emergencies.

(5) Where respirators are needed and permitted under this paragraph to reduce employee exposure, the employer shall select and provide the appropriate respirator from Table 2 and shall ensure that the employee uses the respirator provided.

TABLE 2 RESPIRATORY PROTECTION FOR MORPHOLINE

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Vapor Concentration	
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet or hood operated in continuous-flow mode.
Greater than 8000 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. (Supplied-air suits may be necessary.)
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.

(6) Respirators shall be approved by the Mining Enforcement and Safety Administration (formerly Bureau of Mines) or by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part 11.

(7) The employer shall institute a respiratory protection program in accordance with § 1910.134(b), (d), (e), and (f).

(e) Fire and safety. (1) The employer shall familiarize himself with the information contained in the Substance Technical Guidelines (Appendix B of this section) for morpholine.

(2) For the purpose of compliance with § 1910.309, locations classified as hazardous locations due to the presence of morpholine shall be Class I, Group C.

(3) For the purpose of compliance with § 1910.157, morpholine is classified as a Class B fire hazard.

(4) For the purpose of compliance with § 1910.178, locations classified as hazardous locations due to the presence of morpholine shall be Class I, Group C.

(5) For the purpose of compliance with § 1910.106, liquid morpholine is classified as a Class IC flammable liquid.

(6) Where a fan is located in ductwork and where morpholine is present in the ductwork in concentrations greater than 4500 ppm (approximately 25 percent of the lower flammable limit), the fan rotating element shall be of nonsparking material or the casing shall consist of, or be lined with, nonsparking material. There shall be sufficient clearance between the fan rotating element and the fan casing so as to prevent contact.

(7) Sources of ignition such as smoking or open flames are prohibited where morpholine presents a fire or explosion hazard.

(8) Morpholine shall be stored so as not to come in contact with strong oxidizers and strong acids.

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use impervious clothing, gloves, face shields (eight-inch minimum) and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid morpholine or solutions containing greater than 25% morpholine by weight and to prevent repeated or prolonged skin contact with solutions containing 25% or less of morpholine by weight. Face shields shall comply with § 1910.133(a)(2),(a)(4), (a)(5), and (a)(6).

(2) Employers shall ensure that clothing contaminated with morpholine is placed in closed containers for storage until it can be discarded or until the employer provides for the removal of morpholine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the morpholine, the employer shall inform the person performing the operation of the hazardous properties of morpholine.

(3) Where there is any possibility of exposure of an employee's body to liquid morpholine or solutions containing greater than 25% morpholine by weight, employers shall provide facilities for quick drenching of the body within the immediate work area for emergency use.

(4) Employers shall ensure that clothing which becomes wet with liquid morpholine be removed immediately and not reworn until the morpholine is removed from the clothing.

(5) Employers shall ensure that non-impervious clothing which becomes contaminated with morpholine be removed promptly and not reworn until the morpholine is removed from the clothing.

(6) Employers shall provide and ensure that employees use splash-proof safety goggles (cup-cover type dust and splash safety goggles) which comply with § 1910.133 (a)(2)-(a)(6) where there is any possibility of liquid morpholine or solutions containing morpholine contacting the eyes.

(7) Where there is any possibility that an employee's eyes may be exposed to liquid morpholine or solutions containing greater than 15% by weight of morpholine, employers shall provide an eye-wash fountain within the immediate work area for emergency use.

(g) Spills and disposal. (1) In the event that liquid morpholine is spilled the employer shall immediately eliminate potential sources of ignition, provide available ventilation and then clean up the spill.

(2) Liquid morpholine shall not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

(h) Sanitation. (1) Employers shall ensure that employees whose skin becomes contaminated with morpholine promptly wash or shower to remove

(2) Employers shall ensure that employees who handle liquid morpholine or solutions containing morpholine wash hands thoroughly before eating, smoking or using toilet facilities.

(i) Training and information. (1) Each employer who has a workplace in which morpholine is present shall keep a copy of this regulation with Appendixes A, B and C at the workplace. This material shall be made readily available to affected employees.

(2) Each employer who has employees exposed to morpholine above the action level or employees who may have skin or eye contact with liquid morpholine or solutions containing morpholine, or employees who work where morpholine presents a fire or explosion hazard, shall annually:

(i) Inform affected employees of the information contained in the Substance Safety Data Sheet for morpholine (Appendix A of this section);

(ii) Advise affected employees as to the signs and symptoms of exposure to morpholine.

(iii) Instruct affected employees to advise the employer of the development of signs and symptoms of exposure to morpholine which are listed in Appendix A of the section;

(iv) Instruct affected employees to inform the employer if they develop any of the medical conditions listed in paragraph (j)(2) of this section; and

(v) Provide training to ensure that employees understand the precautions of safe use, emergency procedures, and the correct use of protective equipment relative to morpholine.

(j) Medical surveillance. (1) The employer shall provide medical procedures as required by this paragraph. All medical procedures shall be performed by or under the supervision of a physician at no cost to the employee.

(2) The employer shall obtain from each employee who is exposed, or will be exposed, to liquid morpholine or airborne concentrations of morpholine at or above the action level, information as to whether such employee has a history of any of the following medical conditions:

(i) Eye disease

(ii) Liver disease

(iii) Chronic lung disease
(iv) Skin disease examining physician.
(v) Kidney disease
(3) The employer shall provide a medical examination for the employee if:
(i) The employee provides a history of any of the medical conditions listed in paragraph (j)(2) of this section; or
(ii) The employee informs the employer of the development of any of the medical conditions listed in paragraph (j)(2) of this section or any of the signs or symptoms of exposure to morpholine which are listed in Appendix A which the employee suspects are caused by exposure to morpholine.
(4) The employer shall provide to the examining physician the following information:
(i) A copy of this regulation with Appendixes A, B and C for morpholine;
(ii) A description of the affected employee's duties as they relate to his exposure to morpholine;
(iii) A description of any personal protective equipment and respirators required to be used;
(iv) The results of any measurements which may indicate the affected employee's exposure;
(v) The affected employee's anticipated exposure; and
(vi) Upon request of the physician, any available information from previous medical examinations of the affected employee.
(5) Where a medical examination is required by paragraph (j)(3) of this section, following such examination the employer shall obtain a written opinion from the examining physician which conforms with paragraph (j)(6) of this section.
(6)(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 condition which would place the employee at increased risk of material impairment of the employee's health from exposure to morpholine or would directly or indirectly aggravate any detected medical condition;
(B) Any recommended limitations upon the employee's exposure to morpholine including limitations upon the use of personal protective equipment and respirators;
(C) That the employee has been informed by the physician of any detected medical conditions which require further medical examination or treatment.
(ii) The physician's written opinion shall not reveal specific medical findings or diagnoses unrelated to exposure to morpholine.
(iii) The employer shall provide the employee with a copy of the physician's written opinion.
(7) No employee shall be exposed to liquid morpholine or airborne concentrations of morpholine in such a way as would put the employee at increased risk of material impairment of his health from such exposure. This determination may be based on the physician's written opinion.
(8) The employer shall provide emergency and follow-up medical examinations and treatment for any employee injured through exposure to morpholine.
(9) 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 risk involved by refusal to be examined.

(10) No medical procedure which would be performed pursuant to this section need be performed if records of a previous such procedure performed within the past six months are acceptable to the examining physician.

(k) Recordkeeping. (1) Exposure determination. (i) The employer shall keep an accurate record of all determinations required to be made pursuant to paragraph (b)(1) of this section.

(ii) This record shall include the written determination required in paragraph (b)(2) 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 morpholine.

(ii) This record shall include:

(A) The date of measurement;

(B) Operations involving exposure to morpholine which are being monitored;

(C) Sampling and analytical methods used and evidence of their accuracy, including the method, results and date of calibration of sampling equipment;

(D) Number, duration, and results of samples taken; and

(E) 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.

(3) Mechanical ventilation. (i) When mechanical ventilation is used as an engineering control, the employer shall maintain an accurate record of the measurements demonstrating the effectiveness of such ventilation required by paragraph (d)(3) of this section.

(ii) This record shall include:

(A) Date of measurement;

(B) Type of measurement taken;

(C) Result of measurement.

(iii) These records shall be maintained for at least one year.

(4) Employee training and information. (i) The employer shall keep an accurate record of all employee training and information required by paragraph (i) of this section.

(ii) This record shall include:

(A) Date of training;

(B) Name and social security number of employee trained;

(C) Content or scope of training provided.

(iii) This record shall be maintained until replaced by a more recent record.

(5) Medical surveillance. (i) The employer shall keep an accurate record of employee medical surveillance required by paragraph (j) of this section.

(ii) This record shall include:

(A) Information concerning medical conditions obtained from the employee pursuant to paragraph (j)(2) of this section;

(B) Any employee medical complaints relative to exposure to morpholine;

(C) A copy of information provided to the physician pursuant to paragraph (j)(4)(ii), (iii), (iv), (v), and (vi) of this section.

(D) Physician's written opinion; and

(E) A signed statement of any refusal to be examined.

(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 of Labor for Occupational Safety and Health and the Director of the National Institute for Occupational Safety and Health.

(ii) Employee exposure determination and exposure measurement records required to be maintained by this section shall be made available to employees 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.

(l) Employee observation of measurement. (1) The employer shall give affected employees or their representatives an opportunity to observe any measurement of employee exposure to morpholine which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to morpholine requires entry into an area where the use of personal protective devices, including respirators, is required, the observer shall be provided with and required to use such equipment and comply with all other applicable safety procedures.

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

(i) Receive an explanation of the measurement procedure.

(ii) Visually observe all steps related to the measurement of the airborne concentration of morpholine that are being performed at the place of exposure; and

(iii) Record the results obtained.

NOTE: The information contained in the following appendixes is advisory in nature and is not intended, by itself, to create any additional obligations not otherwise imposed or detract from any existing obligation.

APPENDIX A

SUBSTANCE SAFETY DATA SHEET FOR MORPHOLINE

I. SUBSTANCE IDENTIFICATION

A. Substance: Morpholine

B. Permissible Exposure: 20 parts of morpholine per million parts of air (ppm) (70 milligrams of morpholine per cubic

meter of air, (mg/m3)) averaged over an eight-hour work shift.

C. Appearance and Odor: Colorless liquid with a weak, ammonia-like odor.

II. HEALTH HAZARD DATA

A. Ways in Which the Chemical Affects Your Body: Morpholine can affect your body if you inhale it, if it comes in contact with your eyes or skin, or if you swallow it. It may enter your body through your skin.

B. Effects of Overexposure:

1. Short-Term Exposure: Morpholine may cause, irritation of the eyes, nose, throat, lungs, and skin.
2. Long-Term Exposure: Repeated or prolonged overexposure to morpholine may cause skin irritation.
3. Reporting Signs and Symptoms: You should inform your employer if you develop any signs or symptoms and suspect they are caused by exposure to morpholine.

III. EMERGENCY FIRST AID PROCEDURES

A. Eye Exposure: If liquid morpholine or solutions containing morpholine get into your eyes, wash the 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.

B. Skin Exposure: If liquid morpholine or solutions containing morpholine get on your skin, immediately flush skin with water. If liquid morpholine or solutions containing morpholine soak through your clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

C. Breathing: If you or any other person breathes in large amounts of morpholine 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.

D. Swallowing: When morpholine 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.

E. 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 morpholine. You can only be required to wear them for routine use if your employer is in the process of installing controls or 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 (MESA) or 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 there use is required. If you can smell morpholine 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. Supplied-air suits: in some work situations the wearing of supplied-air suits may be necessary. Your employer should instruct you in their proper use and operation.

C. Protective Clothing: You must wear impervious clothing, gloves, face shield or other appropriate protective clothing to prevent any possibility of skin contact with liquid morpholine or solutions containing greater than 25% morpholine by weight or repeated or prolonged skin contact with solutions containing 25% or less of morpholine by weight. Replace or repair impervious clothing that has developed leaks.

D. Eye Protection: You must wear splash-proof safety goggles where there is any possibility of liquid morpholine or solutions containing morpholine contacting your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

A. Morpholine is a flammable liquid and its vapors can easily form explosive mixtures in air.

B. Morpholine must be stored in tightly closed containers in a cool, well ventilated area away from heat, sparks, flames, strong oxidizers, and strong acids.

C. Sources of ignition such as smoking and open flames are prohibited wherever morpholine is handled, used or stored in a manner that could create a potential fire or explosion hazard.

D. You must use non-sparking tools when opening or closing metal containers of morpholine, and containers must be bonded and grounded when pouring or transferring liquid morpholine.

E. You must promptly remove any non-impervious clothing that becomes contaminated with morpholine and this clothing must not be reworn until the morpholine is removed from the clothing.

F. Clothing wet with liquid morpholine can be easily ignited. You must immediately remove this clothing and it must not be reworn until the morpholine is removed from the clothing.

G. If your skin becomes contaminated with morpholine, you must promptly wash or shower to remove the morpholine from your skin.

H. If you handle liquid morpholine or solutions containing morpholine, you must wash your hands thoroughly with water before eating, smoking or using toilet facilities.

I. Fire extinguishers, eye flushing facilities and quick drenching facilities, where provided, must be readily available and you should know where they are and how to operate them.

J. Ask your supervisor where morpholine is used in your work area and for any additional plant safety and health rules.

VI. ACCESS TO INFORMATION

A. Each year your employer is required to inform you of the information contained in this Substance Safety Data Sheet for morpholine. In addition, your employer must instruct you in the safe use of morpholine, emergency procedures, and the correct use of protective equipment.

B. Your employer is required to determine whether you are being exposed to morpholine. You or your representative have the right to observe employee exposure measurements and to record the results obtained. If your employer determines that you are being overexposed, he is required to inform you of the exposure and of the actions which are being taken to reduce your exposure.

C. Your employer is required to keep records of exposure determinations, exposure measurements, and medical surveillance. Your employer is required to make records of exposure determinations and your exposure measurements available to you or your representative upon your request. Your employer is required to release your medical records to your physician upon your written request.

APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES FOR MORPHOLINE

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Tetrahydro-1,4-oxazine; diethyleneimide oxide
2. Formula: C_4H_9ON
3. Molecular weight: 87.1

B. Physical Data

1. Boiling point (760 mm Hg): 128 C (263 F)
2. Specific gravity (water = 1): 1.0
3. Vapor density (air = 1 at boiling point of morpholine): 3.0
4. Melting point: -4.8 C (23 F)
5. Vapor pressure at 20 C (68 F): 7 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): Miscible in all proportions
7. Evaporation rate (butyl acetate = 1): Less than 1
8. Appearance and odor: Colorless liquid with a weak

ammonia-like odor

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: 35 C (95 F) (closed cup)
2. Autoignition temperature: 310 C (590 F)
3. Flammable limits in air, % by volume: Lower: 1.8 (calcd.); Upper: 11 (est.)
4. Extinguishing media: Carbon dioxide, dry chemical, alcohol foam
5. Special fire-fighting procedures: Do not use a solid stream of water since the stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.
6. Unusual fire and explosion hazards: Morpholine is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where morpholine is handled, used or stored in a manner that could create a potential fire or explosion hazard. Morpholine vapors are heavier than air and may travel along the ground and be ignited by open flames or sparks at locations remote from the site at which morpholine is handled.
7. For purposes of conforming with the requirements of 29 CFR 1910.106, morpholine is classified as a Class IC flammable liquid. For example, 4500 ppm, approximately one-fourth of the lower flammable limit, is one situation in which morpholine is considered to be a potential fire and explosion hazard.
8. For purposes of complying with 29 CFR 1910.309, the classification of hazardous locations as described in Article 500 of the National Electrical Code for morpholine shall be Class I Group C.

B. Reactivity

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact of liquid with strong acids will cause violent spattering. Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving morpholine.
4. Special precautions: Liquid morpholine will attack some forms of plastics, rubber and coatings.

III. SPILL, LEAK, AND DISPOSAL PROCEDURES

A. If morpholine is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for vapors to completely clear hood ductwork, then burn the paper. Large quantities can be collected and atomized in a suitable combustion chamber equipped with

an appropriate effluent gas cleaning device. Morpholine may not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

B. Persons not wearing protective equipment should be restricted from areas of spills or leaks until cleanup has been completed.

C. Waste disposal methods: Morpholine may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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 8-hour exposure may be determined from a single eight-hour sample or two (2) 4-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). Sampling and analyses may be performed by instruments such as detector tubes certified by NIOSH under 42 CFR part 84, portable direct-reading instruments, dosimeters, or gas and vapor adsorption tubes with subsequent chemical analyses. The method of measurement must determine the concentration of morpholine to plus or minus 35%.

B. EXPOSURE ABOVE THE PERMISSIBLE EXPOSURE: The monitoring and measurements 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. The method of measurement must determine the concentration of morpholine to plus or minus 25%.

C. METHODS: Methods meeting these accuracy requirements are available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161 under the title "NIOSH Analytical Methods for Set K" (Order number XXXXXXXXXX).

D. QUALIFIED PERSONS: Since many of the duties relating to employee protection are dependent on the results of monitoring and measuring procedures, employers should assure that the evaluation of employee exposures is performed by a competent industrial hygienist or other technically qualified person.

V. MISCELLANEOUS PRECAUTIONS

A. Store morpholine in tightly closed containers in a cool, well ventilated area.

B. High exposures to morpholine can occur when transferring the liquid from one container to another.

C. Non-sparking tools must be used to open and close metal morpholine containers. These containers must be effectively grounded and bonded prior to pouring.

D. Use of supplied-air suits or other impervious coverings may be necessary to prevent skin contact with morpholine where the concentration of morpholine is unknown or is greater than 8000 ppm. Supplied-air suits should be selected, used, and maintained under the immediate supervision of persons knowledgeable in the limitations and potential life endangering characteristics of supplied-air suits.

E. Employers should advise employees of all areas and operations where exposure to morpholine could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to morpholine is likely to occur are: during its production and its use as a corrosion inhibitor in steam boilers; stabilizer for chlorinated solvents; in the manufacture of optical brighteners; as an intermediate in the manufacture of floor polishes, rubber chemicals, germicides, textile finishing agents, etc.

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation; skin absorption.

II. TOXICOLOGY

Morpholine vapor is an irritant to the skin, eyes, mucous membranes and the respiratory tract. Repeated daily exposure of rats to 18,000 ppm was lethal to some animals; those dying during the third to fifth days of exposure revealed damage to lungs, liver and kidneys. A human exposure to 12,000 ppm for 1 1/2 minutes in a laboratory produced nose irritation and cough; mouth pipetting of the liquid caused a severe sore throat and reddened mucous membranes. The liquid dropped in the eye of a rabbit caused moderate injury with ulceration of the conjunctiva and corneal clouding. Workers exposed for several hours to low vapor concentrations complained of foggy vision with rings around lights, the result of corneal edema which cleared within 3 to 4 hours after cessation of exposure. The liquid is a severe skin irritant. In industry, some instances of skin and respiratory tract irritation have been observed.

III. SIGNS AND SYMPTOMS

Visual aberrations; nose irritation; cough; respiratory irritation; may cause liver and kidney damage; severe eye and skin irritation from liquid splashes; skin irritation from repeated or prolonged overexposure.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Immediately flush eyes and skin with water. If swallowed and the person is conscious, immediately administer water by mouth and induce vomiting. Give artificial resuscitation if indicated. Recovery is usually rapid and complete.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of morpholine are caused by its irritant properties. Skin absorption is known to occur. It is important that the physician become familiar with plant operating conditions in which exposure to morpholine 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

Routine medical histories and physical examination are not required. However, the employer must screen employees for history of certain medical conditions (listed below) which might place the employee at increased risk from morpholine exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

1. Chronic respiratory disease -- Morpholine causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of morpholine might cause exacerbation of symptoms due to its irritant properties.

2. Liver disease -- Morpholine causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

3. Kidney disease -- Morpholine causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

4. Eye disease -- Morpholine is an eye irritant and has caused corneal edema in workers. Persons with preexisting eye disorders may be more susceptible to the effects of this agent.

5. Skin disease -- Morpholine is a primary skin irritant. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.

C. PERIODIC EXAMINATIONS

Routine periodic examinations are not required. However, if the employer becomes aware of an employee with the above listed conditions, he must refer such employee for further medical examination.

VII. REFERENCES

1. American Conference of Governmental Industrial Hygienists: "Morpholine," Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, pp. 175-176.

2. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 2202-2204.

3. Grant, W. Morton: Toxicology of the Eye (2d ed.), Charles C. Thomas, Illinois, 1974, pp. 722-723.

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REFERENCES AND SOURCES
MORPHOLINE
1910.93

(e) 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, p. 17.

(f) Personal Protective Equipment, and, (h) Sanitation

Eyes: Smyth et al., "Range Finding Toxicity Data List V," Arch. Indu. Hyg. Occup. Med., 10:61, July 1954; ACGIH, "Documentation of the Threshold Limit Values;" Union Carbide Corporation, "Toxicology Studies - Morpholine;" Grant, "Toxicology of the Eye;" and "Encyclopedia of Occupational Safety and Health," International Labour Office

Skin: Smyth et al., "Range Finding Toxicity Data List V," Arch. Indus. Hyg. Occup. Med., 10:61, July 1954; ACGIH, "Documentation of Threshold Limit Values;" Union Carbide Corporation, "Toxicology Studies - Morpholine;" Sax, "Dangerous Properties of Industrial Materials;" Gleason, "Clinical Toxicology of Commercial Products;" Stecher, "The Merck Index;" Jefferson, "MSDS;" Shea, "The Acute and Sub-Acute Toxicity of Morpholine," Jour. Indus. Hyg. Tox., 21:7, Sept 1939; and "Encyclopedia of Occupational Safety and Health," International Labour Office

Ingestion: Smyth et al., "Range Finding Toxicity Data List V;" Arch. Indus. Hyg. Occup. Med., 10:61, July 1954; Union Carbide Corporation, "Toxicology Studies - Morpholine;" Sax, "Dangerous Properties of Industrial Materials;" ILO, "Encyclopedia of Occupational Health and Safety;" PHS-149, "Survey of Compounds Which Have Been Tested for Carcinogenic Activity;" Shea, "The Acute and Sub-Acute Toxicity of Morpholine," Jour. Indus. Hyg. Tox., 21:7, Sept. 1939

COMMENTS

Eyes - Classification: 1 and 2
Output statement numbers: 9, 13
Exceptions: Statement 10 is deleted and statement 9 is used to require eye protection for all situations involving potential eye exposure to morpholine.

Smyth et al. rated eye injury to rabbits at 7 on a scale of one to 10. This indicates that an excess of 15% solution causes less than severe injury while a 40% solution does produce severe injury. The Documentation of TLV's states "the undiluted compound is very irritating to the eyes." Union Carbide states that "one small drop of undiluted chemical p burns in rabbit eyes." Grant reports that morpholine causes ulceration of the conjunctiva and clouding of the cornea. Union Carbide and the ILO report that an excess of a 15% solution causes only minor effects. The ILO also notes that an excess of 40% aqueous solution and droplets of undiluted morpholine cause severe rabbit-eye injury. It is evident that many of these sources base their comments on the data of Smyth et al.

Since there are sufficient data on this substance to make a distinction, the pure substance and solutions greater than 15% in strength are given a classification of 1. More dilute solutions are assigned a classification of 2. It is to be noted that another concentration between 15 and 40% may be more technically correct for this differentiation but data do not presently exist to support a value higher than 15%.

Skin - Classification: 1 and 2
Output statement numbers: 1 and 2 combined, 7a, 8a, 17g, 17i, 20
Exceptions: See below

Smyth et al. found a rabbit 14 day LD50 due to skin penetration equal to .31 - .81 ml/kg. The primary skin irritancy was rated at 6 on a scale of one to 10. The Documentation of TLV's states "concentrated morpholine readily permeates the skin," and assesses the degree of hazards by skin contact as "moderately high." Union Carbide rates skin penetration as a "definite hazard, with a single skin penetration LD50 for rabbits of 0.5 ml/kg for the full strength chemical." When diluted with water to 25% strength, the LD50 drops to 5 ml/kg, representing only a slight hazard. Union Carbide tests produced "mild skin burns as shown by persistent redness and swelling" when morpholine was applied to the tender skin of the rabbit belly. Sax assesses the systemic hazards of an acute exposure through skin absorption as moderate. Gleason states that the liquid may cause necrosis of the skin. Merck states that morpholine is corrosive to the skin and is a strong base, pkb - 9.61. The Jefferson MSDS states "absorption through the skin may cause nausea and headache." For a discussion of chronic effects, see the work by Shea reported below; the same results were reported for skin absorption, at the same doses. The ILO notes "the warning properties of morpholine are sufficiently strong to obviate the likelihood of intoxication due to cutaneous absorption, but the contaminated skin should be irrigated with copious amounts of water before any skin burns are treated." Also noted is that "a 10% solution in acetone is not irritating." The vapor pressure of the substance is 7 mm Hg at 20 C. It is miscible in all proportions with water and has a flash point of 95 degrees F.

The data indicate that pure morpholine and concentrated solutions of it are not only corrosive but can be very readily absorbed through the skin. As would be expected, it is also noted that somewhat dilute solutions are non-irritating, and of note is that its skin penetration LD50 increases from 0.5 to 5.0 ml/kg as its concentration is diluted from 100% to 25% in water. Based on these data, solutions containing more than 25% of morpholine by weight are assigned a classification of 1 and more dilute solutions are given a classification of 2. It is again noted that some value greater than the chosen 25% may be more

technically correct for such differentiation but that data do not exist to support a higher value. Statement 6 is replaced by 7a because amounts of morpholine so small as to go undetected on clothing are not likely to cause significant injury and are most likely to evaporate before causing harm to someone cleaning or inadvertantly coming in contact with the clothing.

Ingestion - Classification: 2
Output statement numbers: 20a
Exceptions: None

Smyth et al. found a single-dose oral LD50 for rats of 0.95 - 1.16 g/kg, 14 days following the exposure. Union Carbide sets a single-dose oral rat LD50 at 1.05 gm/kg and rates it as a "moderate hazard." Sax lists the local and systemic effects of acute ingestion exposures as moderate. ILO reports that "daily intubation of 0.16 g/kg body weight of 1 - 2% aqueous solution of morpholine for 30 days caused stomach irritation due to the alkalinity of the substance and produced certain pathological effects in liver and kidney." It is also noted that "guinea pigs that received 0.09 g/kg body weight per day gained weight and had normal stomachs and only reversible, light cloudy swelling of livers and kidneys." Malignant lymph tumors and lung adenomas have been produced in laboratory mice following ingestion of doses of 6.33 g/kg food for 28 weeks, according to PHS-149. Shea found that neither rats nor guinea pigs survived oral dosing of 0.1 gm/kg body weight undiluted morpholine. When diluted to 25%, the LD50 for rats was found to be 1.6 gm/kg at the end of one week. In chronic studies, daily dosing by mouth of 0.08 gm of undiluted free base per kg and upwards produces death or presumably permanent pathological change in animal organs, increasing directly with dose," according to Shea. It was determined that "the principal damage when fed (was) to the secreting tubulis of the kidney (where) changes progress to necrosis as the dose increases and the concentration is greater." Other morphological changes observed were necrotic stomach glands and fatty changes in the liver. A classification of 2 is concluded adequate for prevention of chronic ingestion of small amounts of this substance.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

National Fire Protection Association, "Fire Protection Guide on Hazardous Materials," 5th edition, 1973 (NFPA)
Dow Chemical U.S.A., Material Safety Data Sheet (Dow)
Jefferson Chemical Co., Inc., Material Safety Data Sheet (Jeff)
Union Carbide Corp., Material Safety Data Sheet and "Chemicals and Plastics - Physical Properties," 1974 (UCC)
Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd edition, Vol. 13, p. 659 (K-O)

Sources of data items used:

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I. A. 1. Synonyms: UCC; K-O
2. Formula: NFPA-49
3. Molecular weight: ADL
B. 1. Boiling point: NFPA-325M; UCC
2. Specific gravity: Dow; UCC
3. Vapor density: NFPA-325M; Dow; UCC
4. Melting point: UCC
5. Vapor pressure: UCC; Jeff
6. Solubility in water: Dow
7. Evaporation rate: Jeff; UCC
8. Appearance and odor: NFPA-49; Dow

II. A. 1. Flash point: Measured by ADL
2. Autoignition temperature: NFPA-49; Dow; UCC
3. Flammable limits: Jeff; UCC
4. Extinguishing media: NFPA-49; Dow
5. Special fire fighting procedures: NFPA-49; Dow; Jeff
6. Unusual fire and explosion hazards: NFPA-49; ADL
B. 1. Conditions contributing to instability: ADL
2. Incompatibilities: NFPA-49
3. Hazardous decomposition products: UCC
4. Special precautions: ADL

III. A. Steps if released or spilled: NFPA-49; UCC; Dow
C. Waste disposal method: Dow; Jeff; UCC

V. Miscellaneous precautions: ADL

USE/EXPOSURE AND CONTROL DOCUMENT

References used in the preparation of this document include:

"Chemical Abstracts," American Chemical Society, Vol. 66-79, 1967-1973 (CA)
"Chemical Marketing Reporter," June 3, 1974 (Chem Mkt R)
Considine, D. M., "Chemical and Process Technology Encyclopedia," McGraw Hill, 1974 (Considine)
Gleason, M. N., et al., "Chemical Toxicology of Commercial Products," Williams and Wilkins Co., 1969 (Gleason)
International Labour Office, "Encyclopedia of Occupational Health and Safety," 1972 (ILO)
"Jefferson Chemicals," Manufacturers Bulletin, Jefferson Chemical Company, Inc. 1972 (Jefferson)
Kirk, R. and Othmer, D., "Encyclopedia of Chemical Technology," Interscience Publishers, 2nd edition, 1972 (K-O)
"Merck Index of Chemicals and Drugs," Merck and Co., Inc., 8th edition, 1968 (Merck)
"Morpholine," Material Safety Data Sheet, Union Carbide (MSDS)
Noble, R. J., "Latex in Industry," Rubber Age, 2nd edition, 1953 (Noble)

References for Specific Use/Exposure

1. CA, ILO, K-O, Noble
2. CA, K-O
3. Chem Mkt R, K-O
4. Gleason, Jefferson, K-O
5. Chem Mkt R, ILO, Jefferson, K-O
6. ILO
7. ADL estimate
8. Merck
9. Considine, K-O

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References for Specific Control Methods

1. K-0, MSDS
2. K-0, MSDS
3. K-0, MSDS
4. K-0, MSDS
5. K-0, MSDS
6. K-0, MSDS
7. K-0, MSDS
8. K-0, MSDS
9. K-0, MSDS

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Morpholine

D. O. L. STANDARD: 20 ppm

WARNING PROPERTIES:

Odor Threshold: Grant states that morpholine has a characteristic amine odor. No quantitative information is available concerning the odor threshold, however.

Eye Irritation Level: Grant reports that lacrimation has been observed among experimental animals and among industrial workers who have been exposed to high vapor concentrations. "At low concentrations in air, morpholine has been listed with its N-ethyl and N-methyl derivatives among the amines which have been observed to cause transient edema of the cornea and temporary foggy vision with haloes around lights in workers exposed to the vapors for many hours, the symptoms usually coming on after work and clearing spontaneously by the next day."

Patty also reports that morpholine irritates the mucous membranes.

No quantitative information is available, however, concerning the threshold of eye irritation.

Other Information: Both Patty and Grant note that morpholine is a respiratory tract irritant, but no quantiative information is available concerning the threshold of this irritation.

Evaluation of Warning Properties: Since no quantitative information relating warning properties to air concentrations is available, morpholine is treated as a substance with poor warning properties. Gas sorbent respiratory equipment is not permitted.

IDLH: 8000 ppm

Basis for IDLH: This IDLH is based upon the ILO's report that 1 out of 6 rats died following an 8-hour exposure to 8497 ppm morpholine. This IDLH concentration is also supported by Patty's report that one hour was the maximum survival time for rats exposed to the saturated vapor (9200 ppm).

Other Toxicological Information: Patty reports that "morpholine acts like a secondary amine and resembles this group of compounds in its chemical and toxicological properties." Morpholine is a potent irritant of both the skin and the mucous membranes.

Patty reports that 1 hour was the maximum survival time for rats exposed to the saturated vapor, and that a 4-hour exposure to the saturated vapor killed all rats. "Exposure to 8000 ppm (calculated) for 8 hours resulted in no deaths in 6 rats."

Patty reports that Shea observed "fractional mortality, (and)

respiratory tract injury" among rats and guinea pigs which had been exposed to 18,000 ppm morpholine for 6 8-hour exposure periods. Shea also observed "no deaths (and) reversible respiratory tract and systemic injury" among rats and guinea pigs exposed to 12,000 ppm morpholine for 1 8-hour exposure. According to the Documentation of TLV's, among the animals which had died, Shea observed liver, kidney, and lung damage.

Union Carbide Corporation's Chemical Company Guides also note that "breathing the vapors of a known concentration of 8000 parts per million killed no animals (rats) in eight hours of exposure."

The ILO reports that no rats out of 12 succumbed to a concentration of 6734 ppm morpholine in a 4-hour exposure, but that 1 out of 6 rats died following an 8-hour exposure to 8497 ppm morpholine. Among the surviving animals, "no visible lesions" were apparent when the animals were autopsied. Union Carbide Corporation's Chemical Company Guides and Patty report a skin absorption LD50 of 0.5 ml/kg in rabbits.

LFL: 18,000 ppm
VAPOR PRESSURE AT 20 DEG. C.: 7 mm Hg
SATURATED CONCENTRATION AT 20 DEG. C.: 9200 ppm

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USE/EXPOSURE AND CONTROL DOCUMENT
MORPHOLINE

	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of vapor and skin contact with liquid during the manufacture of rubber chemicals (derivatives of morpholine are used as rubber accelerators, catalysts, plasticizers, curing agents, stabilizers of halogenated butyl rubber, emulsifying agents)	A,B,D	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles)
2.	Inhalation of vapor and skin contact with liquid during use as a corrosion inhibitor (especially useful in steam boiler systems, petroleum refining, sterilization autoclaves, natural gas processing). Morpholine derivatives are used as corrosion inhibitors (antioxidants for lubricating and fuel oils).	A,B,D	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles)
3.	Inhalation of vapor and skin contact with liquid during the manufacture of optical brighteners (whitening agents for bleaches and detergents for commercial and household use)	A,B,D	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles)
4.	Inhalation of vapor and skin contact with liquid during use in the compounding of waxes and polishes (compounded in situ with a fatty acid to form emulsifying agents for household and automotive waxes and polishes, rubless waxes and polishes, water-resistant polishes)	A,B,D	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, aprons)
5.	Inhalation of vapor and	A,B,D	Process enclosure; local

	skin contact with liquid during use as a chemical intermediate for: Textile industry - textile lubricants, sizing emulsifiers, softening agents, antifouling agents; Pharmaceutical industry - bactericides, analgesics, local anesthetics, antispasmotics, antimalarials; Chemical industry - alkyl morpholines, emulsifying agents, defoaming agents, surface active agents; Cosmetics - emulsifiers for soaps, shampoos, deodorants, creams; Agriculture - protective coatings for fresh fruits and vegetables, pesticide emulsifiers, insecticides, fumigants, herbicides.		exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, aprons)
6.	Inhalation of vapor and skin contact with liquid during the manufacture and processing of morpholine (dehydration of diethanolamine)	A,B,D	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, aprons)
7.	Inhalation of vapor and skin contact with liquid during cleaning and maintenance of storage vessels and during clean up of accidental spills	A,B,D	Local exhaust ventilation; General dilution ventilation; personal protective equipment (goggles, gloves, respiratory protective devices, aprons)
8.	Inhalation of vapor and skin contact with liquid during use as a solvent. (Morpholine is an economical solvent for dyes, waxes, resins, and casein).	A,B,D	Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, aprons)

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