NIOSH/OSHA STANDARDS COMPLETION PROGRAM

DRAFT TECHNICAL STANDARD AND

SUPPORTING DOCUMENTATION FOR

*** ETHYL SILICATE ***

NIOSH/OSHA Draft Technical Standard and Supporting Documentation for ETHYL SILICATE

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 ETHYL SILICATE.

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 ethyl silicate not in excess of 100 parts per million (ppm) (850 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 ethyl silicate averaged over an eight-hour work shift.

(b) Initial determination and exposure measurement. (1) Each employer who has a place of employment in which ethyl silicate is released into the workplace air shall determine if there is any possibility that any employee may be exposed to airborne concentrations of ethyl silicate above the permissible level. The initial determination shall be made each time there is a change in production, process, or control measures which may result in an increase in airborne concentrations of ethyl silicate.

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

(i) Any information, observations, or calculations which may indicate employee exposure to ethyl silicate;

(ii) Any measurements of ethyl silicate taken;

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

(iv) Date of initial determination, work being performed at the time, location within work site, and employees considered.

(3) If the employer determines that any employee may be exposed to ethyl silicate above the permissible exposure, 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 ethyl silicate above the action level, the employer shall:

(i) Identify all employees who may be exposed above the permissible level; and

(ii) Measure the exposure of the employees so identified.

(5) If an employee exposure measurement reveals that an employee is exposed to ethyl silicate above the action level, but not above the permissible exposure, the exposure of that employee shall be measured at least every three months.

(6) If an employee exposure measurement reveals that an employee is exposed to ethyl silicate 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 ethyl silicate above the permissible exposure. The employee shall also be notified of the results of the exposure measurements and of the corrective action being taken to reduce the exposure to below the permissible exposure.

(7) If two consecutive employee exposure measurements taken at least one week apart reveal that the employee is exposed to ethyl silicate 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 ethyl silicate above the permissible exposure as defined in paragraph (a)(1) of this section.

(2) Employee exposures to airborne concentrations of ethyl silicate 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 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. (i) When local exhaust is used to control exposure, measurements which demonstrate system effectiveness, for example, air velocity or static pressure, 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 ethyl silicate.

(ii) In the design of open surface tank ventilation for the purposes of § 1910.94(d), operations involving ethyl silicate shall be classified as B-3 at 21 degrees C (70 degrees F).

(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 not feasible; or

(iii) To supplement engineering and work practice controls when such controls fail to reduce airborne concentrations of ethyl silicate 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 ETHYL SILICATE

CONDITION	PERMISSIBLE RESPIRATORY PROTECTION
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and organic vapor cartridge(s).
	A gas mask with a chin-style or a front- or back-mounted organic vapor canister.
	Any supplied-air respirator with a full facepiece, helmet or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied - air respirator with a full facepiece operated in pressure - demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors.
	Any escape self-contained breathing apparatus.

(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 ethyl silicate.

(2) For the purpose of compliance with $ 1910.309, locations classified as hazardous locations due to the presence of ethyl silicate shall be Class I, Group D.

(3) For the purpose of compliance with $ 1910.157, ethyl silicate 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 ethyl silicate shall be Class I, Group D.

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

(6) Spray finishing operations shall be performed in accordance with $$ 1910.107 and 1910.94(c).

(7) Dip tank operations shall be performed in accordance with $$ 1910.108 and 1910.94(d).

(8) Where a fan is located in ductwork and where ethyl silicate is present in the ductwork in concentrations greater than 3500 ppm (approximately 25% 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.

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

(10) Ethyl silicate shall be stored so as not to come in contact with strong oxidizers or water.

(f) Personal protective equipment. (1) Employers shall provide and ensure that employees use appropriate protective clothing and equipment necessary to prevent repeated or prolonged skin contact with liquid ethyl silicate. Face shields shall comply with $ 1910.133(a)(2),(a)(4), (a)(5), and (a)(6).

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

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

(4) Employers shall provide and ensure that employees use splash-proof safety goggles which comply with $ 1910.133(a)(2)-(a)(6) where liquid ethyl silicate may contact the eyes.

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

(2) Liquid ethyl silicate shall not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of vapors are permitted.

(h) Sanitation. Employers shall ensure that employees whose skin becomes wet with liquid ethyl silicate promptly wash or shower with soap or mild detergent and water to remove any ethyl silicate from the skin.

(i) Training and information. (1) Each employer who has a workplace in which ethyl silicate 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 ethyl silicate above the action level without regard to the use of respirators, or employees who may have repeated or prolonged skin contact or who may have eye contact with liquid ethyl silicate, or employees who work where ethyl silicate presents a fire or explosion hazard, shall annually:

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

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

(iii) Instruct affected employees to advise the employer of the development of signs and symptoms of overexposure to ethyl silicate 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 ethyl silicate.

(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) Each employer who has employees exposed to airborne concentrations of ethyl silicate above the action level, without regard to the use of respirators, or employees who may have repeated or prolonged skin contact or who may have eye contact with liquid ethyl silicate shall obtain information as to whether such employee has a history of any of the following medical conditions:

(i) Kidney disease
(ii) Liver disease
(iii) Chronic lung disease
(iv) Skin disease
(v) Blood 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 ethyl silicate which are listed in Appendix A which the employee suspects are caused by exposure to ethyl silicate.

(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 ethyl silicate;

(ii) A description of the affected employee's duties as they relate to his exposure to ethyl silicate;

(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 by the examining physician shall specifically state: (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 ethyl silicate;

(B) Any recommended limitations upon the employee's exposure to ethyl silicate 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 the employee's employment.

(iii) The employer shall provide the employee with a copy of the physician's written opinion.

(7) No employee shall be exposed to ethyl silicate in such a way as would put the employee at increased risk of material impairment of his health from such exposure. The employer shall base this decision on any information available including the physician's written opinion.

(8) The employer shall provide emergency medical treatment for any employee injured through exposure to ethyl silicate.

(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 ethyl silicate.

(ii) This record shall include:

(A) The date of measurement;
(B) Operations involving exposure to ethyl silicate which are being monitored;
(C) Sampling and analytical method used and evidence of their accuracy;
(D) Number, duration, and results of samples taken; and
(E) Name 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 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) The name of the employee;
(B) Information concerning medical conditions obtained from the employee pursuant to paragraph (j)(2) of this section;
(C) Any employee medical complaints relative to exposure to ethyl silicate;
(D) A copy of information provided to the physician pursuant to paragraph (j)(4)(ii), (iii), (iv), (v), and (vi) of this section.
(E) Physician's written opinion; and
(F) A signed statement of any refusal to be examined.
(iii) This record shall be maintained for the duration of and for one year after termination 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) Each employee or former employee shall have access to the exposure determination and exposure measurement records required to be maintained by this section which indicate his own exposure to ethyl silicate.
(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 each employee or his representative an opportunity to observe any measurement of his exposure to ethyl silicate which is conducted pursuant to this section.

(2) When observation of measurement of employee exposure to ethyl silicate 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 ethyl silicate that are being performed at the place of exposure; and

(iii) Record the results obtained.

NOTE: The information contained in the following appendix for ethyl silicate is neither intended, by itself, to create any additional obligations not otherwise imposed, nor detract from any existing obligation. To the extent the information supplements this regulation for ethyl silicate, it is advisory in nature.

APPENDIX A

SUBSTANCE SAFETY DATA SHEET FOR ETHYL SILICATE

I. SUBSTANCE IDENTIFICATION

A. Substance: Ethyl silicate

B. Permissible Exposure: 100 parts of ethyl silicate per million parts of air (ppm) (850 milligrams of ethyl silicate per cubic meter of air (mg/M3)) averaged over an eight-hour work shift.

C. Appearance and Odor: Colorless liquid with a mild, sweet alcohol-like odor

II. HEALTH HAZARD DATA

A. Ways in which the chemical affects your body: Ethyl silicate can affect your body if you inhale it or if it comes in contact with your eyes or skin. It may also affect your body if you swallow it.

B. Effects of Overexposure:

1. Exposure to ethyl silicate may irritate the eyes and nose. In animals, exposure to ethyl silicate has caused severe breathing difficulties, liver damage, kidney damage and anemia. Repeated application of ethyl

silicate to animal skin has caused the skin to become dry.

2. Reporting Symptoms: You should inform your employer if you develop any signs or symptoms and suspect that they are caused by exposure to ethyl silicate.

III. EMERGENCY FIRST AID PROCEDURES

A. Eye Exposure: If liquid ethyl silicate gets into your eyes, wash your 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 ethyl silicate gets on your skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid ethyl silicate soaks through your clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

C. Breathing: If you or any other person breathes in large amounts of ethyl silicate 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 liquid ethyl silicate has been swallowed and the person is conscious, 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 emergency rescue equipment before the need arises.

IV. RESPIRATORS AND PROTECTIVE CLOTHING

A. Respirators: Respirators are not the best way to control exposure to ethyl silicate. 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 their use is required. If you can smell ethyl silicate 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: You must wear appropriate protective clothing and equipment to prevent repeated or prolonged skin contact with liquid ethyl silicate. Replace or repair impervious clothing that has developed leaks.

C. Eye Protection: You must wear splash-proof safety goggles where liquid ethyl silicate may contact your eyes.

V. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

A. Ethyl silicate is a flammable liquid and its vapors can easily form explosive mixtures with air.

B. Ethyl silicate must be stored in tightly closed containers in a cool, well ventilated area away from strong oxidizers and water.

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

D. Metal containers in operations involving the transfer of five gallons or more of ethyl silicate should be grounded and bonded.

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

F. If your skin becomes wet with liquid ethyl silicate, you must promptly wash or shower with soap or mild detergent and water to remove the ethyl silicate from your skin.

G. Fire extinguishers, where provided, must be readily available and you should know where they are and how to operate them.

H. Ask your supervisor where ethyl silicate is used in your work area and for any additional 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 ethyl silicate. In addition, your employer must instruct you in the safe use of ethyl silicate, emergency procedures, and the correct use of protective equipment.

B. Your employer is required to determine whether you are being exposed to ethyl silicate. 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 the actions which are being taken to reduce your exposure.

C. Your employer is required to keep records of your exposure and medical examinations. Your employer is required to keep exposure data for at least one year and to keep medical data during your employment, and for a period of one year following your termination of employment. Your employer is required to make the exposure data available to you upon your request. Your employer is also required to release your medical records to your physician upon your written request.

D. Your employer must give you a copy of the physicians written opinion for any physical examination required by this standard.

NOTE: The information contained in the following appendix for ethyl silicate is neither intended, by itself, to create any additional obligations not otherwise imposed, nor detract from any existing obligation. To the extent the information supplements this regulation for ethyl silicate, it is advisory in nature.

APPENDIX B

SUBSTANCE TECHNICAL GUIDELINES FOR ETHYL SILICATE

I. PHYSICAL AND CHEMICAL DATA

A. Substance Identification

1. Synonyms: Ethyl silicate, condensed; tetraethyl orthosilicate; tetraethyl silicate; ethyl orthosilicate tetraethoxysilane
2. Formula: $(C_2H_5O)_4Si$ or $(C_2H_5)_4SiO_4$
3. Molecular weight: 208.3

B. Physical Data

1. Boiling point (760 mm Hg): 169 C (336 F)
2. Specific gravity (water = 1): 0.94
3. Vapor density (air = 1 at boiling point of ethyl silicate): 7.2
4. Melting point: Less than -85 C (-121 F)
5. Vapor pressure at 20 C (68 F): 2 mm Hg
6. Solubility in water, % by weight at 20 C (68 F): Reacts slowly to form ethyl alcohol and silica gel
7. Evaporation rate (butyl acetate = 1): Data not available
8. Appearance and odor: Colorless liquid with a mild, sweet, alcohol-like odor

II. FIRE, EXPLOSION AND REACTIVITY HAZARD DATA

A. Fire

1. Flash point: 37.2 C (99 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 23
4. Extinguishing media: Carbon dioxide, dry chemical, and foam
5. Special fire-fighting procedures: Do not use a solid stream of water since a stream will scatter and spread the fire. Use water spray to cool containers exposed to a fire.

6. Unusual fire and explosion hazards: Ethyl silicate is a flammable liquid. Its vapors can easily form explosive mixtures with air. All ignition sources must be controlled where ethyl silicate is used, handled or stored in a manner that could create a potential fire or explosion hazard. Ethyl silicate 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 ethyl silicate is handled.
7. For purposes of conforming with the requirements of 29 CFR 1910.106, ethyl silicate is classified as a Class IC flammable liquid. For example, 3500 ppm, approximately one-fourth of the lower flammable limit, is one situation in which ethyl silicate 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 ethyl silicate shall be Class I, Group D.

B. Reactivity
1. Conditions contributing to instability: High temperatures may cause containers to explode.
2. Incompatibilites: Contact with strong oxidizers may cause fires and explosions. Contact with water causes formation of volatile and flammable ethyl alcohol.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl silicate.
4. Special precautions: Ethyl silicate will attack some forms of plastics, rubber and coatings.

III. SPILL, LEAK, AND DISPOSAL PROCEDURES

A. If ethyl silicate 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. Remove to a safe place (such as a fume hood) and burn the paper. Large quantities can be collected and reclaimed or atomized in a suitable combustion chamber. Ethyl silicate must not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of ethyl silicate vapors are permitted.

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

C. Waste disposal methods: Ethyl silicate may be disposed of:
1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing 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 eight-hour exposure may be determined from a single eight-hour sample or two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). Sampling and analyses may be performed by collection of the particulates and vapors using a high efficiency membrane filter followed by an adsorption tube with subsequent chemical analysis of both the filter and adsorption tube. Detector tubes certified by NIOSH under 42 CFR part 84 or other direct-reading devices calibrated to measure ethyl silicate may be used. The method of measurement must determine the concentration of ethyl silicate 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 ethyl silicate 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 S" (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 ethyl silicate in tightly closed containers in a cool, well ventilated area.

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

C. Metal containers in operations involving the transfer of five gallons or more of ethyl silicate should be grounded and bonded.

D. Employers should advise employees of all areas and operations where their exposure to ethyl silicate could occur.

VI. COMMON OPERATIONS

Common operations in which exposure to ethyl silicate is likely to occur are: During its production and its use as a binder and gelling agent for metal-casting molds; as a vehicle for zinc-rich paints and coatings; as an impregnant for porous layers in oil

wells; as a delustrant in lacquers; as an intermediate in the manufacture of silicone resins; in the manufacture of refractories; and in the textile industry.

NOTE: The information contained in the following appendix for ethyl silicate is neither intended, by itself, to create any additional obligations not otherwise imposed, nor detract from any existing obligations. To the extent the information supplements this regulation for ethyl silicate, it is advisory in nature.

APPENDIX C - MEDICAL SURVEILLANCE GUIDELINES

I. ROUTE OF ENTRY

Inhalation.

II. TOXICOLOGY

Ethyl silicate vapor is an irritant of the eyes and nose and in animals causes lung, liver, and kidney damage. Exposure of guinea pigs to 2530 ppm for 4 hours was lethal to more than half of the animals; usually death was delayed and a result of pulmonary edema; effects were irritation of eyes and nose, lacrimation, tremor, dyspnea and narcosis; some surviving animals developed a delayed profound anemia. Exposure of rats to 1000 ppm for up to 3 seven-hour periods was fatal; autopsy findings were marked tubular degeneration and necrosis of the kidneys, mild liver damage, and slight pulmonary edema and hemorrhage. In rats exposed to 125 ppm for 15 to 20 seven-hour periods, slight to moderate kidney damage was observed but there were no pathologic changes detected in the liver or lungs. In humans, the eyes and nose are affected by brief exposures as follows: 3000 ppm, extremely irritating and intolerable; 1200 ppm, lacrimation and stinging; 700 ppm, mild stinging; 250 ppm, slight tingling. Instillation of the liquid into the rabbit eye caused immediate marked irritation which was reversible. Repeated or prolonged skin contact with the liquid may cause dermatitis due to its solvent effect.

III. SIGNS AND SYMPTOMS

Irritation of eyes and nose; by analogy to effects caused in animals, it may cause lacrimation, dyspnea, pulmonary edema; tremor, narcosis; damage to liver and kidneys; anemia.

IV. SPECIAL TESTS

None in common usage.

V. TREATMENT

Remove from exposure. Promptly flush eyes with water and wash skin with soap or mild detergent and water. If swallowed and the person is conscious, induce vomiting. Give artificial resuscitation and administer oxygen if indicated. Consideration should be given to hospitalization and observation for the possible delayed onset of pulmonary edema.

VI. SURVEILLANCE AND PREVENTIVE CONSIDERATIONS

A. GENERAL

Most reported effects of ethyl silicate are caused by its irritant properties. In animals it causes damage to the lungs, liver, and kidneys. It is important that the physician become familiar with plant operating conditions in which exposure to ethyl silicate 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 examinations 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 ethyl silicate exposure. Only those giving a positive history of these conditions must be referred for further medical examinations.

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

2. Liver disease -- Ethyl silicate 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 -- Ethyl silicate 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. Blood disease -- Ethyl silicate causes anemia in animals. Persons with preexisting blood disorders may be more susceptible to the effects of this agent.

5. Skin disease -- Ethyl silicate is a defatting agent and can cause dermatitis on prolonged exposure. 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: "Ethyl Silicate (Tetraethyl Orthosilicate)," Documentation of the Threshold Limit Values for Substances in Workroom Air (3d ed., 2d printing), Cincinnati, 1974, p. 108.

2. Hygienic Guide Series: "Ethyl Silicate," American Industrial Hygiene Association Journal, 29:624-626, 1968.

3. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II - Toxicology (2d ed. revised), Interscience Publishing Company, New York, 1963, pp. 1933-1934.

4. Browning, Ethel: Toxicity and Metabolism of Industrial Solvents, Elsevier Publishing Company, Amsterdam, 1965, pp. 693-695.

5. Pozzani, U.C. and C.P. Carpenter: "Response of Rodents to Repeated Inhalation of Vapors of Tetraethyl Orthosilicate," A.M.A. Archives of Industrial Hygiene and Occupational Medicine, 4:465-468, 1951.

6. Rowe, V.K., et al: "Toxicological Studies on Certain Commercial Silicones and Hydrolyzable Silane Intermediates," Journal of Industrial Hygiene and Toxicology, 30:332-352, 1948.

7. Smyth H.F., Jr. and J. Seaton: "Acute Response of Guinea Pigs and Rats to Inhalation of the Vapors of Tetraethyl Orthosilicate (Ethyl Silicate)," Journal of Industrial Hygiene and Toxicology, 23:288-296, 1940.

REFERENCES AND SOURCES
ETHYL SILICATE
1910.1000

(d) Compliance - Open surface tank classification based on relative evaporation rate of slow estimated from boiling point using guidelines from ANSI Z9.1.

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

Eye: Grant, "Toxicology of the Eye;" Patty, "Industrial Hygiene and Toxicology"

Skin: None

Ingestion: Sax, "Dangerous Properties of Industrial Materials;" Browning, "Toxicity and Metabolism of Industrial Solvents;" Spector, "Handbook of Toxicology"

COMMENTS

Eye - Classification: 2
Output statement number: 10
Exceptions: None

According to Grant, "a drop applied to rabbit eyes caused immediate signs of discomfort, but the eyes were found to be normal in twenty-four hours and the corneas took no fluorescein stain." He adds that ethyl silicate is insoluble in water, but slowly hydrolyzes to release ethyl alcohol and deposit silica.

Patty simply states that "precautions should be taken in industrial handling. . . to avoid contact of the vapor or liquid with the eyes."

A classification of 2 is concluded to be appropriate for this compound.

Skin - Classification: 2
Output statement numbers: 2, 7b, 17i, 21
Exceptions: None

No literature sources could be found which indicate that skin contact with ethyl silicate is hazardous. However, since it hydrolyzes in the presence of moisture to form ethyl alcohol and deposit silica, it can be inferred that prolonged or repeated contact may cause dermatitis due to the defatting action of the alcohol. Minimum requirements, based upon a classification of 2, are therefore specified.

Ethyl silicate has a vapor pressure of 2 mm Hg at 20 degrees, and a flash point of 99 degrees F.

Ingestion - Classification: 0
Output statement numbers: None
Exceptions: None

Sax considers the acute local effects of ingestion to be of severe toxic hazard and the acute systemic effects to be of moderate toxic hazard.

Browning reports that "the basic toxic response to ethyl silicate by any route of administration is rupture of the pulmonary capillaries."

Spector lists an oral LD100 for the rat of 3000 - 5000 mg/kg and an oral rat LD50 of 6270 mg/kg.

There is no clear indication in the literature that

ingestion of this compound, in the context of this standard, would be a hazard in the industrial environment. It is, therefore, assigned a classification of zero.

SUBSTANCE TECHNICAL GUIDELINES

The references cited for this document include:

National Fire Protection Association, "Fire Protection Guide on Hazardous Materials," 5th edition, 1975 (NFPA)

Union Carbide, Corp., Product Information Bulletin (UCC)

Stauffer Chemical Co., Product Data Sheet and Product Safety Information Bulletin (Stauff)

Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd edition, Vol. 18, p. 218, 253 (K-O)

"International Maritime Dangerous Goods Code," Inter-Governmental Maritime Consultative Organization, London, 1972 (IMCO)

Sources of data items used:

I. A. 1. Synonyms: UCC, Stauff, K-O
2. Formula: NFPA-325M
3. Molecular weight: UCC

B. 1. Boiling point: UCC, NFPA-325M
2. Specific gravity: UCC, NFPA-325M
3. Vapor density: NFPA-325M
4. Melting point: UCC
5. Vapor pressure: UCC, Stauff
6. Solubility in water: UCC, NFPA-325M
7. Evaporation rate: Data not available
8. Appearance and odor: UCC, Stauff

II. A. 1. Flash point: IMCO
2. Autoignition temperature: Data not available
3. Flammable limits: IMCO
4. Extinguishing media: Stauff
5. Special fire fighting procedures: Stauff, ADL
6. Unusual fire and explosion hazards: Stauff, ADL

B. 1. Conditions contributing to instability: Stauff
2. Incompatibilities: Stauff
3. Hazardous decomposition products: None
4. Special precautions: ADL

III. A. Steps if released or spilled: Stauff, ADL

C. Waste disposal method: Stauff

V. Miscellaneous precautions: UCC, Stauff

USE/EXPOSURE AND CONTROL DOCUMENT

References used in the preparation of this document include:

Browning, E., "Toxicity and Metabolism of Industrial Solvents," Elsevier Publishing Co., 1965 (Browning)

"Ethyl Silicate," Hygienic Guide Series, American Industrial Hygiene Association, Nov. - Dec. 1968 (Hygienic Guide)

"Ethyl Silicate," Product Information, Union Carbide Corp., Chemicals and Plastics (Carbide)

Kirk, R. and Othmer, D., "Encyclopedia of Chemical Technology," Interscience Publishers, 2nd edition, Vol. 18, 1969 (K-O)

Payne, H. F., "Organic Coating Technology," John Wiley and Sons, Vol. I, 1954 (Payne)

"Silbond - Ethyl Silicate," Product Data Sheet, Stauffer Chemical Co.,

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ETHYL SILICATE

March 31, 1972 (Stauffer - Data Sheet)
"Silbond Pure," Product Safety Information, Stauffer Chemical Co., March 1972 (Stauffer - Safety Infor.)

References for Specific Use/Exposure

1. K-O, Payne, Stauffer - Data Sheet
2. Carbide, K-O, Payne, Stauffer - Data Sheet
3. Carbide, K-O, Payne, Stauffer - Data Sheet
4. Carbide, K-O, Stauffer - Data Sheet
5. Browning, Carbide, Payne
6. Payne
7. K-O, Stauffer - Data Sheet
8. Carbide, Hygienic Guide
9. Hygienic Guide, K-O, Payne
10. Carbide, Stauffer - Data Sheet
11. Stauffer - Safety Infor.
12. Carbide, Stauffer - Data Sheet

References for Specific Control Methods

Hygienic Guide and Stauffer - Safety Infor. were the references used in all the Specific Control Methods.

RESPIRATOR TABLE DOCUMENTATION

SUBSTANCE: Ethyl silicate

D. O. L. STANDARD: 100 ppm

WARNING PROPERTIES:

Odor Threshold: According to Grant, ethyl silicate can be detected by odor at 85 ppm.

Irritation levels: Grant states that "observations were made of the effect of various concentrations on the human experimenters: 3,000 ppm was found to be extremely irritating to the eyes and nose; 1,200 ppm stings eyes and nose and produces tears; 700 ppm mildly stings eyes and nose; 250 ppm makes the eyes and nose tingle slightly . . ." For the purposes of this standard, only full facepiece respirators are permitted.

Evaluation of Warning Properties: Since the threshold of odor is below the permissible exposure limit, and since the thresholds of eye and nasal irritation are within three times of the permissible exposure limit, ethyl silicate is treated as a material with good warning properties. Gas sorbent respiratory equipment is permitted.

IDLH: 1000 ppm

Basis for IDLH Value: The chosen IDLH is based upon the report in the AIHA Hygienic Guides that "Smyth and Seaton reported that a concentration of 1740 ppm in dry air caused the first guinea pig death in 15 minutes while at 1170 ppm the first death was in two hours. In the presence of 70% humidity, effects were less pronounced, presumably because part of the ethyl silicate was hydrolyzed."

Other Toxicological Information: The AIHA Hygienic Guides state that the studies by Smyth and Seaton indicated that the responses of animals during exposure were, in order of appearance, irritation of eyes and nose, lachrymation, tremors, respiratory difficulty and narcosis. When animals were fatally injured, death frequently was due to pulmonary edema with secondary pneumonia sometimes developing several days after the exposure. In a few cases there was evidence that death was due to acute nephritis.

According to the Documentation of TLV's, "Smyth and Seaton found that approximately 2000 ppm was the maximal concentration that did not produce serious disturbances in guinea pigs and rats after an exposure period of 60 minutes. Five hundred ppm was the maximal exposure for several hours without causing serious disturbances . . .

"The 100 ppm threshold limit is believed to be sufficiently low to prevent irritation to the eyes and nose. Patty noted that this value apparently has not been confirmed by human experience. Workers exposed for prolonged periods at concentrations approaching this level should be watched for signs and symptoms of lung, kidney or other injury."

LFL: 13,000 ppm
VAPOR PRESSURE AT 20 C: 2 mm Hg
SATURATED CONCENTRATION AT 20 C: Approximately 2630 ppm

NIOSH/OSHA Draft Technical Standard
and Supporting Documentation for ETHYL SILICATE

USE/EXPOSURE AND CONTROL DOCUMENT
ETHYL SILICATE

	Use/Exposure	Principal Route of Entry	Currently Used Control Methods
1.	Inhalation of vapor and skin contact with liquid during use in the manufacture of refractories (bonding agent for investment castings, ceramic shells, crucibles, all types of refractory shapes and coatings)	A,B	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
2.	Inhalation of vapor and skin contact with liquid during the application (brushing, spraying, dipping) of protective coatings (paints, lacquers, films)	A,B	General dilution ventilation; personal protective equipment (goggles, gloves, protective clothing)
3.	Inhalation of vapor and skin contact with liquid during use in the manufacture of protective and preservative coatings (vehicle and binder). Ethyl silicate is used in zinc dust paints, in polymer system coatings (amine, silicone, vinyl, nitrocellulose and urea-formaldehyde resins) and lacquers for the purpose of creating hard, corrosion-, chemical-, heat-, scratch- and fire-resistant coatings. These coatings are used for maintenance paint, primer coatings, mural paints, lacquers which adhere to glass, metal protective coatings and glass marking inks.	A,B	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
4.	Inhalation of vapor and skin contact with liquid during use as an agent for impregnation of porous materials to increase strength, hardness,	A,B	Local exhaust ventilation; general dilution ventilation; personal protective equipment (goggles, gloves, protective clothing)

	stiffness and abrasion resistance (clay pellets, silica bricks, graphite molds, catalysts, asbestos materials, paper, leather, textile products)		
5.	Inhalation of vapor and skin contact with liquid during use as a water-proofing and weather-proofing agent (sealing porous rock formations in oil wells; brick; artistic and architectural stonework; concrete)	A,B	General dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
6.	Inhalation of vapor and skin contact with liquid during the synthesis and processing of ethyl silicate (reaction of silicone tetrachloride with ethyl alcohol)	A,B	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
7.	Inhalation of vapor and skin contact with liquid during use as a chemical intermediate (phosphorous and higher orthosilicate acid esters, siloxane elastomers, soluble silicas, silicones)	A,B	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
8.	Inhalation of vapor and skin contact with liquid during use as a gelling agent for organic liquids (stable gels, solid fuels)	A,B	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
9.	Inhalation of vapor and skin contact with liquid during use as a source of finely divided amorphous silica (to coat inside of electric lamp bulbs, preparation of synthetic fused quartz)	A,B	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
10.	Inhalation of vapor and skin contact with liquid	A,B	Process enclosure; local exhaust ventilation; general

	during use in the textile industry (aqueous emulsions prevent slippage of textile fibers on each other; deluster and fireproof textiles and increase strength of textile products - wool, cotton, synthetic fibers and fabrics)		dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)
11.	Inhalation of vapor and skin contact with liquid during cleaning and maintenance of storage vessels and equipment and during clean up of accidental spills	A,B	Local exhaust ventilation; personal protective equipment (gloves, goggles, protective clothing, respiratory protective devices)
12.	Inhalation of vapor and skin contact with liquid during use as a component of lubricants used as mold release agents (prevents clay from sticking to dye in the extrusion of clay shapes)	A,B	Local exhaust ventilation; general dilution ventilation; personal protective equipment (gloves, goggles, protective clothing)

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