

Occupational Health Guideline for Ethyl Silicate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_2H_5O)_4Si$ or $(C_2H_5)_4SiO_4$
- Synonyms: Ethyl silicate, condensed; tetraethyl orthosilicate; tetraethyl silicate; ethyl orthosilicate tetraethoxysilane
- Appearance and odor: Colorless liquid with a mild, sweet, alcohol-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl silicate is 100 parts of ethyl silicate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 850 milligrams of ethyl silicate per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for ethyl silicate a Threshold Limit Value of 10 ppm.

HEALTH HAZARD INFORMATION

• Routes of exposure

Ethyl silicate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

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 applications of ethyl silicate to animal skin has caused the skin to become dry.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any

signs or symptoms and suspects that they are caused by exposure to ethyl silicate.

• Recommended medical surveillance

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

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl silicate exposure.

—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.

—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.

—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.

—Blood disease: Ethyl silicate causes anemia in animals. Persons with pre-existing blood disorders may be more susceptible to the effects of this agent.

—Skin disease: Ethyl silicate is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Ethyl silicate vapor irritates 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

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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irritation of eyes and nose, lacrimation, tremor, dyspnea, and narcosis; some surviving animals later developed a delayed profound anemia. Exposure of rats to 1000 ppm for up to three 7-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 7-hour periods, slight to moderate kidney damage was observed, but no pathologic changes were 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.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 169 C (336 F)
3. Specific gravity (water = 1): 0.94
4. Vapor density (air = 1 at boiling point of ethyl silicate): 7.2
5. Melting point: Less than -85 C (-121 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts slowly to form ethyl alcohol and silica gel
8. Evaporation rate (butyl acetate = 1): Data not available

• Reactivity

1. Conditions contributing to instability: High temperatures may cause containers to explode.
2. Incompatibilities: 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.

• Flammability

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. Extinguishant: Carbon dioxide, dry chemical, foam

• Warning properties

1. Odor Threshold: According to Grant, ethyl silicate can be detected by odor at 85 ppm.
2. Irritation levels: Grant states that "observations were made of the effect of various concentrations on the human experimenters: 3000 ppm was found to be extremely irritating to the eyes and nose; 1200 ppm stings eyes and nose and produces tears; 700 ppm mildly

stings eyes and nose; 250 ppm makes the eyes and nose tingle slightly"

3. 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 the permissible exposure limit, ethyl silicate is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube packed with XAD-2 resin, followed by desorption with carbon disulfide and gas chromatographic analysis. Detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ethyl silicate may be used. An analytical method for ethyl silicate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid ethyl silicate.

- Clothing wet with liquid ethyl silicate should be placed in closed containers for storage until it can be discarded or until provision is made 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 person performing the operation should be informed of ethyl silicate's hazardous properties.
- Any clothing which becomes wet with liquid ethyl silicate should be removed immediately and not reworn until the ethyl silicate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid ethyl silicate contacting the eyes.

SANITATION

- Skin that becomes wet with liquid ethyl silicate should be promptly washed or showered with soap or mild detergent and water to remove any ethyl silicate.

COMMON OPERATIONS AND CONTROLS

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

| Operation | Controls |
|--------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|
| Use as a bonding agent for investment castings, ceramic shells, crucibles, and types of refractory shapes | Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment |
| Use as a protective coating for paints, lacquers, and films | General dilution ventilation; personal protective equipment |
| Use in manufacture of protective and preservative coatings for protection from corrosion, chemicals, heat, scratches, and fire | Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment |
| Use in impregnation of porous materials to increase strength, hardness, stiffness, and abrasion | Local exhaust ventilation; general dilution ventilation; personal protective equipment |
| Use as a waterproofing and weatherproofing agent in porous rock | General dilution ventilation; personal protective equipment |

Operation

Use as a chemical intermediate; use as a gelling agent in organic liquids; use as a coating agent inside electric lamp bulbs, and in the synthesis of fused quartz

Use in textile industry in aqueous emulsions, deluster and fireproofing, and to increase strength; use as a component of lubricants as mold release agent

Controls

Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If liquid ethyl silicate gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If liquid ethyl silicate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid ethyl silicate soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a 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.

• 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.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

- 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. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Ethyl silicate should 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.

- 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.

REFERENCES

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RESPIRATORY PROTECTION FOR ETHYL SILICATE

| Condition | Minimum Respiratory Protection* Required Above 100 ppm |
|-----------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Vapor Concentration | |
| 1000 ppm or less | Any chemical cartridge respirator with a full facepiece and an 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. |

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