

Occupational Health Guideline for Formic Acid

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: HCOOH
- Synonyms: Formic acid 85%; formic acid 90%; formic acid 95%; hydrogen carboxylic acid; methanoic acid
- Appearance and odor: Colorless liquid that may fume with a pungent, penetrating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for formic acid is 5 parts of formic acid per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 9 milligrams of formic acid per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

• Routes of exposure

Formic acid 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

1. Short-term Exposure: Formic acid may cause irritation of the eyes, nose, throat, upper respiratory tract, and skin. These are often accompanied by watering of the eyes, nasal discharge, and coughing. Skin contact with concentrated solutions causes severe irritation and blistering. Swallowing formic acid has caused a number of cases of severe poisoning and death. The symptoms found in this type of poisoning include salivation, vomiting, burning sensation of the mouth, bloody vom-

iting, diarrhea, and pain. In severe poisoning, the person may go into shock. Later, the person may have trouble breathing and may die. The person may also have kidney damage. One death has been reported in a worker who had hot formic acid splashed in his face. This worker could not speak, had trouble breathing, and died six hours later.

2. Long-term Exposure: Prolonged or repeated exposure to formic acid may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to formic acid.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to formic acid 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 formic acid exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of formic acid might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Formic acid is a primary skin irritant and has caused skin sensitization. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although formic acid is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Liver disease: Although formic acid is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

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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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

—Eye disease: Formic acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.
2. **Periodic Medical Examination:** Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Formic acid vapor is a severe irritant of the eyes, mucous membranes, and skin. Exposure causes eye irritation with lacrimation, nasal discharge, throat irritation, and cough. A worker splashed in the face with hot formic acid developed marked dyspnea with dysphagia, and died within 6 hours. Workers exposed to a mixture of formic and acetic acids at an average concentration of 15 ppm of each complained of nausea. The liquid on the skin causes burns with vesiculation; keloid formation at the site of the burn often results. Skin sensitization may occur in persons previously exposed to formaldehyde. While ingestion of the liquid is unlikely in ordinary industrial use, the highly corrosive nature of the substance may be expected to produce serious burns of the mouth and esophagus.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 46.03
2. Boiling point (760 mm Hg): 85%: 107 C (224.6 F); 90%: 106.5 C (223.7 F); 95%: 102 C (215.6 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of formic acid): 1.6
5. Melting point: 85%: -15.3 C (4.5 F); 90%: -6.5 C (20.3 F); 95%: 1.4 C (34.5 F)
6. Vapor pressure at 20 C (68 F): 23–33 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 2.1

• Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers or strong caustics may cause fires and explosions. Contact with concentrated sulfuric acid causes formation of toxic and flammable carbon monoxide gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving formic acid.
4. Special precautions: Liquid formic acid will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point (90% solution): 50 C (122 F) (closed cup)
2. Autoignition temperature (90% solution): 435 C (813 F)
3. Flammable limits in air, % by volume: Lower: 18; Upper: 57
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• Warning properties

1. Odor Threshold: May reports an odor threshold of 21 ppm. Patty states that formic acid has a “pungent, penetrating” odor.
2. Eye Irritation Level: Grant notes, “It has been said that the vapors of formic acid are irritating to the eyes . . . , but there appears to be little in the literature on this subject.” According to Patty, “the principal hazard is that of severe primary damage to the skin, eye, or mucosal surfaces.” Deichmann and Gerarde also state that formic acid is irritating to the eyes.
3. Other Information: Grant, Patty, and Deichmann and Gerarde report that formic acid is a mucous membrane irritant, capable of irritating the upper respiratory tract and the eyes. The *Documentation of TLV's* states that “workers exposed to formic and acetic acids in a textile plant . . . at concentrations of each acid averaging 15 ppm” experienced irritation at these levels.
4. Evaluation of Warning Properties: Through its odor and irritant effects, formic acid is detectable at concentrations only several times the permissible exposure limit. For the purposes of this guideline, therefore, formic acid is judged to have adequate 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 formic acid on chromosorb 103, desorption with deionized water, and analysis by ion chromatography. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure formic acid may be used. An analytical method for formic acid is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

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 any possibility of skin contact with liquid formic acid.

- Clothing contaminated with formic acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of formic acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the formic acid, the person performing the operation should be informed of formic acid's hazardous properties.

- Where there is any possibility of exposure of an employee's body to liquid formic acid, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with formic acid should be removed immediately and not reworn until the formic acid 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 formic acid or solutions containing formic acid contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to liquid formic acid or solutions containing 1% or more of formic acid by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with formic acid should be immediately washed or showered to remove any formic acid.

COMMON OPERATIONS AND CONTROLS

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

Operation

Use in textile dyeing and finishing industry as a dye exhausting agent; chrome dyeing; to impart finishes to cotton; an acidifying agent; and shrink- and wrinkle-proofing compound

Use as a chemical intermediate as a strong reducing agent for acids, salts, dyes, fumigants, refrigerants, pharmaceuticals, and solvents

Use in leather processing industry as a deliming agent and neutralizer; as a preservative and levelling agent

Use in rubber industry as a coagulant for natural rubber latex and form making; as a preservative of latex

Use as a catalyst in hydrocarbon-formaldehyde resins and phenolic resins, and plasticizer for vinyl resins

Use in electroplating industry to control particle size and plating thickness

Use as an antiseptic in wine and beer brewing, preservative in animal feed additives and cleaning solution compounds

Use in miscellaneous operations as a wire stripping compound and preparing bare wires for soldering; laundry sour; and as an oil well acidifying agent

Controls

Local exhaust ventilation; general dilution ventilation; personal protective equipment

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 formic acid or solutions containing formic acid get 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 formic acid gets on the skin, immediately flush the contaminated skin with water. If formic acid soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of formic acid, 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

If formic acid has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the formic acid. Do not attempt to make the exposed 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 formic acid 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 collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Formic acid should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Formic acid may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR FORMIC ACID

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor of Particulate Concentration	
100 ppm or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 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 and particulates. Any escape self-contained breathing apparatus.

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