Occupational Health Guideline for Maleic Anhydride

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: (CHCO)₇O
- Synonyms: 2,5-Furanedione; cis-butenedioic anhydride: toxilic anhydride
- Appearance and odor: Colorless or white solid with a penetrating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for maleic anhydride is 0.25 part of maleic anhydride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1 milligram of maleic anhydride per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

Routes of exposure

Maleic anhydride 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: Maleic anhydride dust and vapor may cause irritation of the eyes, nose, throat, and skin. On contact with the skin, maleic anhydride may not cause an immediate burning sensation, especially if the skin is dry. If the solid form is allowed to remain in contact with moist tissues, burn may occur. Upon inhalation of dust or vapors, a person may experience coughing, sneezing, and burning of the throat. If the dust or vapors get into a person's eyes, irritation, sensitivity to light, and double vision may occur.

- 2. Long-term Exposure: Repeated or prolonged exposure to maleic anhydride may cause chronic skin or eye irritation. An allergic type of skin rash and asthma may also occur.
- 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 maleic anhydride.

· Recommended medical surveillance

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

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to maleic anhydride would be expected to be at increased risk from exposure. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual

Summary of toxicology

basis.

Maleic anhydride in the form of a vapor, fume, or dust is a severe irritant of the eyes; it is both an irritant and sensitizer of both the skin and respiratory tract, and may produce asthma on repeated exposures. In a carcinogenesis experiment with a few rats injected subcutaneously with 1 mg maleic anhydride in oil twice weekly for 61 weeks, 2 of 3 surviving animals developed fibrosarcomas which appeared 80 weeks after the start of the experiment. Workers exposed to vapors from heated maleic anhydride developed an intense burning sensation in the eyes and throat, with cough and vomiting; exposure to high fume concentrations caused photophobia, double vision, and a sensation of seeing rings around lights. Exposure of humans to a concentration of

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.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES

Public Health Service Centers for Disease Control National Institute for Occupational Safety and Health U.S. DEPARTMENT OF LABOR
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6 to 8 mg/m³ of air resulted in nasal irritation within 1 minute and eye irritation after 15 to 20 minutes. Among workers repeatedly exposed to 5 to 10 mg/m³ there was ulceration of nasal mucous membranes, chronic bronchitis, and some asthma. The dust on dry skin may result in a delayed burning sensation, but on moist skin the sensation is almost immediate, producing erythema which may progress to vesiculation. Prolonged or repeated exposure also may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data
 - 1. Molecular weight: 98.1
 - 2. Boiling point (760 mm Hg): 202 C (396 F)
- 3. Specific gravity (water = 1): 1.43 (solid); 1.3 (melt)
- 4. Vapor density (air = 1 at boiling point of maleic anhydride): 3.38
 - 5. Melting point: 53 C (127 F)
 - 6. Vapor pressure at 20 C (68 F): 0.16 mm Hg
- 7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble but reacts slowly and dissolves
- 8. Evaporation rate (butyl acetate = 1): Data not available
- Reactivity
- 1. Conditions contributing to instability: Maleic anhydride is decomposed by water at temperatures above 66 C (150 F).
- 2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with alkali metals, caustics, and amines may cause polymerization if temperature is greater than 66 C (150 F).
- 3. Hazardous decomposition products: Toxic gases and vapors (such as irritating fume of unburned material and carbon monoxide) may be released in a fire involving maleic anhydride.
 - 4. Special precautions: None
- Flammability
 - 1. Flash point: 102 C (215 F) (closed cup)
 - 2. Autoignition temperature: 477 C (890 F)
- 3. Flammable limits in air, % by volume: Lower: 3.4 (calculated); Upper: 7.1
- 4. Extinguishant: Alcohol foam, carbon dioxide. Dry chemical, multi-purpose dry chemical, or loaded stream fire extinguishing media should not be used because of the possibility of an explosion due to the probable reaction of basic compounds in these extinguishing media with maleic anhydride.
- Warning properties
- 1. Odor Threshold: According to the AIHA Hygienic Guide, "at a concentration of 2 mg/m³ a faint odor is noticed."
- 2. Eye Irritation Level: Exposure to a concentration of 6 to 8 mg/m³ maleic anhydride results in eye irritation within 15 to 20 minutes, according to the *Hygienic Guide*, which also states that "a tendency for eye irritation at levels of approximately 1 mg/m³ has been observed."

Grant reports that maleic anhydride is a "crystalline material which powders and sublimes readily, producing fumes which are powerfully irritating to the eyes and respiratory tract." Grant gives no quantitative information, however.

- 3. Other Information: The Hygienic Guide notes that at a concentration of 6 to 8 mg/m³ "persons not accustomed to handling maleic anhydride report definite nasal irritation within 1 minute."
- 4. Evaluation of Warning Properties: Through its odor maleic anhydride can be detected at a concentration of only twice the TLV. In addition, the *Hygienic Guide* states that eye irritation can occur at the TLV.

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

An analytical method for maleic anhydride 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

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minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid or liquid maleic anhydride or liquids containing maleic anhydride.

- Clothing contaminated with maleic anhydride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of maleic anhydride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the maleic anhydride, the person performing the operation should be informed of maleic anhydride's hazardous properties.
- Non-impervious clothing which becomes contaminated with maleic anhydride should be removed promptly and not reworn until the maleic anhydride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid maleic anhydride or liquids containing maleic anhydride contacting the eyes.
- Where there is any possibility of exposure of an employee's body to solid or liquid maleic anhydride or liquids containing maleic anhydride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid maleic anhydride or liquids containing maleic anhydride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with maleic anhydride should be promptly washed or showered with soap or mild detergent and water to remove any maleic anhydride.
- Employees who handle solid or liquid maleic anhydride or liquids containing maleic anhydride should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation

Use in manufacture of polyester resins for automobile bodies, structural building panels, molded boats, and chemical storage tanks

Use during manufacture of fumaric acid (as food acidulant) and polyester; use in manufacture of alkyld resins as enamels, interior flat finishes, automotive finishes, printing inks, reactive plasticizers, and marine paints and varnishes

Use in manufacture of detergents and lubricating additives as dispersant and wetting agent; use in manufacture of drying oils

Use in manufacture of tall oil resins as general coating and industrial dip cotaing; use in manufacture of terpene resins as shellac substitutes, in aniline inks, as protective coatings on paper, in metal foil, cellulose films, and natural and synthetic fiber

Use in manufacture of chlorendic anhydride for fire-retardant polyester resins, as expoxy hardener, component of military paints, manufacture of extreme pressure lubricants; and use in organic synthesis and in production of chemical intermediates

Controls

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.

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Eye Exposure

If maleic anhydride gets into the eyes, wash eyes immediately with copious amounts of water, lifting the lower and upper lids occasionally. If irritation or other eye problems are present after washing, get medical attention immediately. Contact lenses should not be worn when working with this chemical.

Skin Exposure

If maleic anhydride gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If maleic anhydride or liquids containing maleic anhydride penetrate through the clothing, remove the clothing immediately 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 maleic anhydride, 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 maleic anhydride 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 AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If maleic anhydride is spilled, the following steps should be taken:
- 1. Ventilate area of spill.
- 2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
- 3. Large quantities should be collected in the most convenient and safe manner for reclamation or disposal in a secured sanitary landfill.
- Waste disposal methods:

Maleic anhydride may be disposed of:

- 1. By making packages of maleic anhydride in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
- 2. By dissolving maleic anhydride in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
- 3. By placing maleic anhydride in closed containers and depositing in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Maleic Anhydride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Maleic Anhydride," *Hygienic Guide Series*, Detroit, Michigan, 1970.
- Dickens, F., and Jones, H. E. H.: "Further Studies on the Carcinogenic and Growth-Inhibitory Activity of Lactones and Related Substances," *British Journal of* Cancer, 17:100-108, 1963.
- Elkins, H. B.: Chemistry of Industrial Toxicology (2nd ed.), Wiley, New York, 1959.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: Clinical Toxicology of Commercial Products (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: Toxicology of the Eye (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Manufacturing Chemists Association, Inc.: Chemical Safety Data Sheet SD-88, Maleic Anhydride, Washington, D.C., 1962.
- Patty, F. A. (ed.): Toxicology, Vol. II of Industrial Hygiene and Toxicology (2nd ed. rev.), Interscience, New York, 1963.
- Smyth, H. F., and Carpenter, C. P.: "Chemical Burns of the Rabbit Cornea," *American Journal of Ophthalmology*, 29:1363-72, 1946.
- Survey of Compounds Which Have Been Tested for Carcinogenic Activity, U.S. Public Health Service Publication No. 149, Original, Supplements 1 and 2, 1961-1967, 1968-1969, and 1970-1971.

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RESPIRATORY PROTECTION FOR MALEIC ANHYDRIDE

Condition	Minimum Respiratory Protection* Required Above 0.25 ppm				
Particulate or Vapor Concentration					
12.5 ppm or 50 mg/m³ 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.				
250 ppm or 1000 mg/m² or less	A powered air-purifying respirator with an organic vapor cartridge and a high efficiency particulate filter and a full facepiece, helmet, or hood.				
500 ppm or 2000 mg/m³ 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 500 ppm or 2000 mg/m³ 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 with a full facepiece providing protection against organic vapor and particulates.				
	Any escape self-contained breathing apparatus.				

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

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