

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICYCLOPENTADIENE

INTRODUCTION

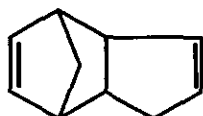
This guideline summarizes pertinent information about dicyclopentadiene for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

• Formula



• Structure



• Synonyms

1,3-Cyclopentadiene, dimer; alpha-dicyclopentadiene (endo form); bicyclopentadiene; biscyclopentadiene; cyclopentadiene dimer; 3a,4,7,7a-tetrahydro-4,7-methanoindene

• Identifiers

1. CAS No.: 77-73-6
2. RTECS No.: PC1050000
3. DOT UN: 2048 26
4. DOT label: Flammable liquid (or solid)

• Appearance and odor

Dicyclopentadiene is a flammable tricyclic compound that exists either as a solid or a clear liquid, depending on temperature. In the solid state, dicyclopentadiene is a colorless, combustible crystalline substance that has a disagreeable camphor-like odor. Dicyclopentadiene exists in two stereoisomeric forms, the endo and exo isomers; the commercial product consists predominantly of the endo isomer. The odor is detectable below 0.2 ppm, but does not become noticeably irritating below 10 ppm.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 132.21
2. Boiling point (760 mm Hg): 172°C (342°F); depolymerizes at boiling point to form two molecules of cyclopentadiene.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

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

3. Specific gravity (water = 1): 0.98 at 35°C (95°F)
4. Vapor density (air = 1 at boiling point of dicyclopentadiene): 4.6
5. Melting point: 32°C (89.6°F)
6. Vapor pressure at 20°C (68°F): 1.4 mm Hg
7. Solubility: Insoluble in water; soluble in acetic acid and alcohol; very soluble in ether and carbon tetrachloride.
8. Evaporation rate: Data not available

Reactivity

1. Conditions contributing to instability: Heat, sparks, and open flame
2. Incompatibilities: Contact of dicyclopentadiene with oxidizing agents can cause fires and explosions.
3. Hazardous decomposition products: Thermal-oxidative degradation products can include cyclopentadiene and partial oxidation products of carbon monoxide and carbon dioxide. When heated to decomposition, dicyclopentadiene emits acrid smoke and fumes.
4. Special precautions: Dicyclopentadiene must be inhibited and maintained under an inert atmosphere to prevent hazardous polymerization. In contact with air, especially when heated, dicyclopentadiene forms peroxides; the level of these can be controlled by the addition of an inhibitor.

Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to dicyclopentadiene.

1. Flash point: 32°C (90°F) (open cup)
2. Autoignition temperature: 503°C (937°F)
3. Flammable limits in air: Lower, 0.8; upper, 6.3
4. Extinguishant: Use dry chemical, carbon dioxide, alcohol-resistant foam, or water fog to fight fires involving dicyclopentadiene.

Fires involving dicyclopentadiene should be fought upwind from the maximum distance possible. Isolate the

hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of dicyclopentadiene may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half a mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving dicyclopentadiene. Structural firefighters' protective clothing may provide limited protection against fires involving dicyclopentadiene.

EXPOSURE LIMITS

• OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicyclopentadiene [29 CFR 1910.1000, Table Z-1].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 ppm (30 mg/m³) as a TWA for up to a 10-hr workday and a 40-hr workweek for dicyclopentadiene [NIOSH 1992].

• ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicyclopentadiene a threshold limit value (TLV) of 5 ppm (27 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

• Rationale for limits

The NIOSH limit is based on the risk of eye and skin irritation associated with dicyclopentadiene exposure. The ACGIH limit is based on the risk of irritation, kidney damage, and pulmonary effects associated with exposure to dicyclopentadiene.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to dicyclopentadiene can occur through inhalation, ingestion, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals:* Dicyclopentadiene is an irritant of the eyes and skin and a narcotic on acute exposure; chronic exposure causes kidney and lung damage. Applied to the skin of rabbits, dicyclopentadiene causes moderate to severe irritation; instilled into the rabbit eye, this substance causes mild and reversible irritation [NIOSH 1993; Clayton and Clayton 1981]. The dermal LD₅₀ in rabbits is 5,080 mg/kg [NIOSH 1993]. The 4-hr LC₅₀ is 145 ppm in mice and 372 ppm in rats [NIOSH 1993; Sax and Lewis 1989]. The oral LD₅₀ is 353 mg/kg in rats and 190 mg/kg in mice [NIOSH 1993]. Acutely poisoned animals showed signs of eye irritation, lost coordination, and convulsed before death [ACGIH 1991]. Rats exposed daily for 10 days to dicyclopentadiene concentrations of 72 or 146 ppm survived, but rats exposed on the same regimen to a concentration of 332 ppm died [ACGIH 1991]. Rats exposed to a 35- or 74-ppm concentration of dicyclopentadiene for 7 hours/day for 89 days showed, at autopsy, kidney damage and some lung involvement [ACGIH 1991]. Leukocytosis was found in rats 96-hr post-subcutaneous administration of dicyclopentadiene [Clayton and Clayton 1981; NLM 1992].

2. *Effects on Humans:* Dicyclopentadiene is an irritant of the eyes, nose, throat, and skin in humans [NJDH 1989]. Exposed workers also experience headaches and other central nervous system effects [NLM 1992]. Workers exposed accidentally to a high but unspecified concentration of dicyclopentadiene experienced headaches for the first two months after exposure but did not continue to experience this symptom indicating a certain degree of inurement [ACGIH 1991].

• Signs and symptoms of exposure

1. *Acute exposure:* The signs and symptoms of acute exposure to dicyclopentadiene include redness, tearing, and inflammation of the eyes, sneezing, and coughing. Contact of the skin with this substance causes redness and may cause blistering. Headaches and loss of coordination also may occur after an acute overexposure.

2. *Chronic exposure:* Based on effects seen in animals, the signs and symptoms of chronic exposure to dicyclopentadiene may include those associated with kidney damage, such as blood, pus, or protein in the urine, or with lung damage, such as difficult breathing, rales, and fluid in the lungs.

• Emergency procedures

<p style="text-align: center;">WARNING!</p> <p style="text-align: center;">Exposed victims may die!</p> <p style="text-align: center;">Transport immediately to emergency medical facility!</p>
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Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure:* Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dicyclopentadiene. **Immediately and thoroughly** flush eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Irritation may result. **Immediately** remove contaminated clothing and **thoroughly** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air **immediately**. Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure:* Take the following steps if dicyclopentadiene or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by having the victim touch the back of the throat with a finger until productive vomiting ceases. Do **not** give syrup of ipecac

because of possible onset of respiratory depression and seizures.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve dicyclopentadiene and lead to worker exposures to this substance:

- Use as a chemical intermediate during chlorinated hydrocarbon pesticide synthesis and to stabilize organophosphorus insecticides
- Use in the production of ferrocene and other metallocene compounds
- Use as an intermediate in the production of plasticizers, elastomers, pharmaceuticals, resins, paints, varnishes, paint driers, and perfumes
- Use as a polyhalogenated flame retardant for plastics

The following methods are effective in controlling worker exposures to dicyclopentadiene, depending on the feasibility of implementation:

- Process enclosure
- Local exhaust ventilation
- General dilution ventilation
- Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. *Industrial ventilation—a manual of recommended practice*. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. *Industrial ventilation—a self study companion*. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. *Design of industrial ventilation systems*. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. *Engineering design for control of workplace hazards*. New York, NY: McGraw-Hill.

5. Plog BA [1988]. *Fundamentals of industrial hygiene*. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to dicyclopentadiene, the examining physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, kidneys, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is

exposed to dicyclopentadiene at or below the prescribed exposure limit. The examining physician should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes, skin, kidneys, or respiratory system.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to dicyclopentadiene exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicyclopentadiene on the eyes, skin, kidneys, or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for dicyclopentadiene.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicyclopentadiene is made using a charcoal tube (100/50 mg sections, 20/40 mesh). Samples are collected at a maxi-

mum flow rate of 0.1 liter/min until a maximum air volume of 10 liters is collected. The sample is then treated with carbon disulfide to extract the dicyclopentadiene. Analysis is conducted by gas chromatography using a flame ionization detector. This method is abstracted in the *OSHA Chemical Information Manual* [OSHA 1987] and can be found in the OSHA Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If dicyclopentadiene contacts the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with dicyclopentadiene should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of dicyclopentadiene, particularly its potential to cause skin irritation.

A worker who handles dicyclopentadiene should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where dicyclopentadiene or a solution containing dicyclopentadiene is handled, processed, or stored.

STORAGE

Dicyclopentadiene should be stored in a cool, dry, well-ventilated area in tightly sealed, stainless steel containers that are maintained under an inert blanket and are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. The storage area must meet requirements for an OSHA Class IB flammable liquid. Only explosion-proof ventilation may be used. Containers of dicyclopentadiene should be protected from physical damage and should be stored separately from oxidizing materials, heat, sparks, and open flame. To prevent static sparks, containers should be grounded and bonded for transfers. Because containers that formerly contained dicyclopentadiene may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving dicyclopentadiene, persons not wearing protective equipment and clothing

should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.
6. Use non-sparking tools for cleanup.
7. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
8. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
9. For large liquid spills, build dikes far ahead of the spill to contain the dicyclopentadiene for later reclamation or disposal.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) regulatory requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

• Emergency planning requirements

Dicyclopentadiene is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

• Reportable quantity requirements for hazardous releases

Employers are not required by the emergency release notification provisions of the Comprehensive

Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of dicyclopentadiene; there is no reportable quantity for this substance.

• Community right-to-know requirements

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicyclopentadiene emitted or released from their facility annually.

• Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity, as defined in 40 CFR 261.21-261.24. Although dicyclopentadiene is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat any waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

• Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicyclopentadiene exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as

maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent any skin contact with dicyclopentadiene. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to dicyclopentadiene permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to dicyclopentadiene.

If dicyclopentadiene is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which dicyclopentadiene might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available

within the immediate work area whenever the potential exists for eye or skin contact with dicyclopentadiene. Contact lenses should not be worn if the potential exists for dicyclopentadiene exposure.

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