OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZOYL PEROXIDE

INTRODUCTION

This guideline summarizes pertinent information about benzoyl peroxide 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 Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

• Formula

 $C_{14}H_{10}O_4$

• Structure

 $(C_6H_5CO)_2O_2$

Synonyms

Benzoic acid, benzoperoxide; benzoyl superoxide; diphenylglyoxal peroxide; dibenzoyl peroxide; Acetoxyl; Acnegel; Benzac; Clearasil BP Acne Treatment; Cuticura Acne Cream; Debroxide; Dry and Clear Acne Cream; Epiclear; Fostex; Incidol; Lucidol; Luperco AA; Nayper B; Novadelox; Oxy-5; Oxy Wash; Panoxyl; Persadox; Quinolor Compound; Sulfoxyl; Topex; Vanoxide; Xerac

• Identifiers

1. CAS No.: 94-36-0

2. RTECS No.: DM8575000 (for the technical product)

3. DOT UN: 2085 49 (for the technical product)

4. DOT label: Organic Peroxide

Appearance and odor

Benzoyl peroxide is a white crystalline solid that has a faint benzaldehyde odor.

CHEMICAL AND PHYSICAL PROPERTIES

Physical data

1. Molecular weight: 242.2

2. Boiling point (at 760 mm Hg): Decomposes explosively at temperatures above 105°C (221°F)

3. Specific gravity (water = 1): 1.33 at 25°C (77°F)

4. Vapor density: Not applicable

5. Melting point: 103° to 105°C (217.4° to 221°F)

6. Vapor pressure at 20°C (68°F): Less than 0.1 mm Hg

7. Solubility: Sparingly soluble in water, alcohol, or vegetable oils; soluble in chloroform, ether, and benzene

8. Evaporation rate: Not applicable

Reactivity

- 1. Conditions contributing to instability: Heat, sparks, friction, or impact. Confined storage of dry benzoyl peroxide may lead to decomposition and explosion.
- 2. Incompatibilities: Benzoyl peroxide is extremely reactive, and fires and explosions may result from contact with strong acids, oxidizing and reducing agents, metals, metal oxides, amines, accelerators, methyl methacrylate, organic matter, carbon tetrachloride and ethylene, dimethylaniline, or lithium aluminum hydride.
- 3. Hazardous decomposition products: Toxic gases, vapors, and particulates (such as benzoic acid, phenyl benzoate, terphenyls, biphenyls, benzene, carbon monoxide, and carbon dioxide) may be released when benzoyl peroxide decomposes.
- 4. Special precautions: Benzoyl peroxide is highly reactive and may explode spontaneously; it must be kept wet in a mixture containing at least 1% water.

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Occupational Safety and Health Administration

• Flammability

The National Fire Protection Association has assigned a flammability rating of 4 (extreme fire hazard) to benzoyl peroxide.

1. Flash point: 80°C (176°F)

2. Autoignition temperature: 80°C (176°F)

3. Flammable limits in air: Data not available

4. Extinguishant: Use water only; do *not* use chemical or carbon dioxide extinguishants.

Fires involving benzoyl peroxide should be fought from an explosion proof location. In advanced or massive fires, the area should be evacuated. Isolate the hazard area and deny access to unnecessary personnel. If fire occurs in the vicinity of containers of benzoyl peroxide, water should be used to keep containers cool. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving benzoyl peroxide.

EXPOSURE LIMITS

OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzoyl peroxide is 5 mg/m³ of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• NIOSH REL

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

ACGIH TLV[®]

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned benzoyl peroxide a threshold limit value (TLV) of 5 mg/m³ as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of respiratory irritation associated with exposure to benzoyl peroxide.

HEALTH HAZARD INFORMATION

Routes of exposure

Exposure to benzoyl peroxide can occur through inhalation, ingestion, or contact with the skin or eyes.

Summary of toxicology

1. Effects on Animals: Benzoyl peroxide is an irritant of the eyes, mucous membranes, and skin in animals. When

instilled into the eyes of rabbits, benzoyl peroxide dust caused irritation [IARC 1985]. A 10% solution of benzoyl peroxide applied to the skin of guinea pigs caused a moderate degree of skin irritation [IARC 1985]. In rats, the 4-hr LC₅₀ is estimated to be 700 ppm, and the oral LD₅₀ is 7,710 mg/kg [ACGIH 1991a; NIOSH 1991]. During an acute 4-hr exposure to 2,458 ppm (24,300 mg/m³), rats showed eye tearing and squinting, difficult breathing, excessive salivation, erythema, and motor excitation followed by depression; all animals recovered within the 24- or 48-hr period following termination of exposure [NIOSH 1977]. In a chick embryo assay, embryo toxicity and malformations were induced by benzoyl peroxide [NLM 1991]. Chronic feeding studies in rats showed decreased weight gain in the medium- and high-dose groups and testicular atrophy among males in the high-dose group [IARC 1985].

2. Effects on Humans: Benzoyl peroxide is an irritant of the eyes, skin, and mucous membranes in humans. This substance is also a skin sensitizer. Workers exposed to 12.2 mg/m³ experienced strong irritation of the nose and upper respiratory tract [Proctor et al. 1988]. In prolonged and repeated contact with the skin, benzoyl peroxide has caused dermal irritation and sensitization [IARC 1985].

Signs and symptoms of exposure

- 1. Acute exposure: Acute exposure to benzoyl peroxide can cause moderate to severe irritation of the eyes, nose, and throat, with redness and tearing of the eyes, runny nose, cough, and difficult breathing. In contact with the skin, benzoyl peroxide causes redness and swelling.
- 2. Chronic exposure: Chronic exposure to benzoyl peroxide can cause dermatitis. Some sensitized individuals may also experience whorls, swelling, itching, and redness of the skin.

Emergency procedures



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! Immediately and thoroughly flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.
- 2. Skin exposure: Irritation may result. Immediately and thoroughly wash contaminated skin with soap and water.

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Inhalation exposure: Move the victim to fresh air immediately.

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 benzoyl peroxide 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 giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.
- —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 uses of benzoyl peroxide may result in worker exposures to this substance:

- -Use as an initiator in free radical polymerization
- -Use in production of polystyrene and related resins
- —Use in auto-repair kits, optical and dental castings, and other molding applications
- -Use in vulcanization of natural and synthetic rubbers
- —Use in textile manufacture as a burn-out agent for cellulose acetate to produce lace-like appearance in mixed fabrics
- -Use in printing pastes
- —Use in topical non-prescription medications as a treatment of acne, burns, dermatitis, poisoning, and external wounds, and as an antiseptic and local anesthetic
- --- Use as a bleaching agent for flour, cheese, fats, oils, and waxes
- —Use in the manufacture of special fast-drying inks for printing on plastic surfaces and in the embossing of vinyl flooring
- —Use as a fixing agent in light microscopy

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

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

Good sources of information about 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.
- 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, placement of workers in jobs that do not jeopardize their safety or health, 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 workrelated 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 benzoyl peroxide, a licensed health care professional 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 respiratory tract and skin and on a history of skin allergies. 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 assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to benzoyl peroxide at or below the prescribed exposure limit. The examining licensed health care professional 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 skin or respiratory system diseases.

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 licensed medical practitioner. Additional examinations may be necessary if a worker develops symptoms attributable to benzoyl peroxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of benzoyl peroxide on the skin and 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 benzoyl peroxide.

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 job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne benzoyl peroxide is determined by using a cellulose ester membrane filter (0.8 micron). Samples are collected at a maximum flow rate of 3 liters/min until a maximum air volume of 400 liters is collected. Immediately after sampling, the sample filters are transferred into a 20-ml scintillation vial and are then sealed and shipped under refrigeration. Upon receipt by the laboratory, the samples are frozen until they are to be analyzed. The sample is then treated with ethyl ether to extract the benzoyl peroxide. Analysis is conducted by high-performance liquid chromatography using ultraviolet light detection. The limit of detection for this procedure is 0.01 mg per sample. This method is described in Method 5009 of the NIOSH Manual of Analytical Methods [NIOSH 1984].

PERSONAL HYGIENE

If benzoyl peroxide contacts the skin, workers should remove any contaminated clothing immediately while drenching the affected area with water and then wash with soap and water.

Clothing and shoes contaminated with benzoyl peroxide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of benzoyl peroxide.

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

Workers should not eat, drink, or use tobacco products in areas where benzoyl peroxide is handled, processed, or stored.

STORAGE

Benzoyl peroxide should be stored in a cool, dry, wellventilated, fireproof area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Isolated, remote, or detached storage is preferred. The storage area should be equipped with an automatic fire suppression system. To prevent static sparks, all containers and equipment used in shipping, receiving, or transferring operations should be bonded and grounded. Only nonsparking tools may be used with benzoyl peroxide. Any storage system should have an explosion-relief design, and electrical installations and heating facilities should be prohibited in these storage areas. Only the small amount of benzoyl peroxide that is needed for a single work shift should be removed from storage at one time. Containers of benzoyl peroxide should be protected from incompatible chemicals, physical damage, shock, rough handling, friction,

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sunlight, heat, sparks, and open flame. Because containers that formerly contained benzoyl peroxide may still hold product residues, they should be handled appropriately.

SPILLS

Before benzoyl peroxide is used in the workplace, an emergency plan to handle any contingencies, including spills, should be developed and practiced. In the event of a spill involving benzoyl peroxide, the plan should be implemented. The following steps should be undertaken following a spill:

- 1. Do not touch the spilled material.
- 2. Notify safety personnel.
- 3. Remove all sources of heat and ignition.
- 4. Ventilate potentially explosive atmospheres using maximum explosion proof ventilation.
- 5. Cleanup personnel must wear fire-resistant and antistatic protective clothing.
- 6. Use nonsparking tools for cleanup. Do *not* use cellulosic materials (rags, paper, straw, etc.) to clean up spilled benzoyl peroxide.
- 7. All benzoyl peroxide spills should be inactivated by adding cold, 10% sodium hydroxide solution to the spilled material in an amount equal to 10 times the weight of the spill. This process takes up to 3 hr to complete.

SPECIAL REQUIREMENTS

The U.S. Environmental Protection Agency (EPA) 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

Benzoyl peroxide 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 benzoyl peroxide; there is no reportable quantity for this substance.

• Community right-to-know requirements

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture

25,000 lb or more or otherwise use 10,000 lb or more of benzoyl peroxide per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of benzoyl peroxide 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 benzoyl peroxide 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 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 benzoyl peroxide 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, 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 on the selection and use of respirators and on the medical screening of respirator users, consult the NIOSH Respirator Decision Logic [NIOSH 1987b] and the NIOSH Guide to Industrial Respiratory Protection [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Fire- and static-resistant protective clothing should be worn to prevent skin contact with benzoyl peroxide. Gloves, boots, aprons, and gauntlets are recommended to prevent prolonged or repeated skin contact. 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 benzoyl peroxide 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 benzoyl peroxide.

If benzoyl peroxide is dissolved in water or 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 benzoyl peroxide might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with benzoyl peroxide. Contact lenses should not be worn if the potential exists for benzoyl peroxide exposure.

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