

IV. ENVIRONMENTAL DATA

Environmental Levels

The information available on atmospheric concentrations of benzoyl peroxide in industry is limited. One manufacturer of benzoyl peroxide reported the results of an analysis of breathing zone air samples containing benzoyl peroxide from two different operations within the plant [10 (p 16)]. At the dry packing station, the total dust concentration was 0.10 mg/cu m. Another sample taken during another packing operation indicated that the total dust concentration was 0.16 mg/cu m. Both of these dust concentrations were below the existing federal environmental limit for benzoyl peroxide of 5 mg/cu m.

Sampling and Analysis

During industrial operations, benzoyl peroxide may escape into the environment as airborne dust [10 (p 16)]; however, there currently are no validated sampling and analytical methods specific for airborne benzoyl peroxide.

Kaznina [54] used a method for sampling and analysis in which the air samples were drawn through a filter into an absorber containing 5 ml of ethyl alcohol. Analyses of the samples for benzoyl peroxide were performed by ultraviolet spectrophotometry. The method was sensitive for benzoyl peroxide to a concentration of 1.0 $\mu\text{g/ml}$. Benzoyl peroxide, styrene, and dimethylaniline are present simultaneously where styrene-containing plastics are prepared [54]. The method was reported to have limited use because of interference by dimethylaniline and styrene, which were also

present in the operation. Therefore, an analysis based on ultraviolet spectrophotometry would be of limited value because much of the benzoyl peroxide produced each year in the United States is used in the production of polystyrene [5].

Dugan [55] and Dugan and O'Neil [56] determined benzoyl peroxide by an analytical colorimetric method. A colored complex resulted when benzoyl peroxide was used to accelerate the reaction between methanol and N,N-dimethyl-p-phenylene diamine sulfate. The relationship of the color intensity and the amount of benzoyl peroxide present in solution followed Beer's Law at peroxide concentrations of 5-30 $\mu\text{g/ml}$ but deviated at 40 $\mu\text{g/ml}$. For this analytical method to be accurate, time and temperature must be held constant because the reaction proceeds slowly without the addition of peroxide [57]. The authors [56] stated that molecular oxygen might interfere with the reaction as it does with many colorimetric methods. The time and temperature requirements, as well as the possible interference of molecular oxygen, make this method undesirable for analysis.

Banerjee and Budke [58] also used a colorimetric method of analysis for benzoyl peroxide. Benzoyl peroxide was dissolved in a mixture of acetic acid and chloroform; potassium iodide was then added. The absorption of the liberated iodine was measured at 470 nm, and the amount of benzoyl peroxide in the sample was determined from a standard curve. This method may be hazardous because explosions have occurred when chloroform and benzoyl peroxide were mixed and then heated above room temperature [59-61]. Furthermore, NIOSH has concluded that chloroform is carcinogenic (letter from Director, NIOSH, to Assistant Secretary of Labor,

OSHA, June 1976). This analytical method is not specific for benzoyl peroxide but determines total peroxides.

Airborne methylethylketone peroxide (MEKO) was analyzed by a colorimetric method (T Anania, written communication, January 1977). A known volume of air containing MEKO was drawn through a U-tube filled with dimethyl phthalate in which the benzoyl peroxide dissolved. The solution was transferred to a test tube, and diphenylcarbohydrazide, a color reagent, was added. This solution was compared to a standard solution in a spectrophotometer. When benzoyl peroxide was analyzed by this method, at the lowest level, 50 $\mu\text{g}/\text{sample}$, the color intensity was equivalent to that produced by 1.5 μg of MEKO. After an initial relative linearity in the range of 0-100 $\mu\text{g}/\text{sample}$, benzoyl peroxide, in increasing quantities, developed a progressively lower color intensity/unit and gave a curvilinear standard curve. Although no recommendations were made by the author, this degree of curvature is undesirable for a quantitative analysis.

Dolin [62] used methods for sampling and analysis that were not specific for benzoyl peroxide. One cubic foot of air/minute was drawn through a Greenburg-Smith impinger containing 75 ml of doubly distilled water for times varying from 13 to 37 minutes. Aliquots of the sampling solution were added to flasks containing a mixture of 0.75% aqueous potassium iodide and a freshly prepared 0.50% starch solution, which were then allowed to stand from 1 hour to overnight. The color intensity was measured in a spectrophotometer or visually compared with a set of color standards prepared from known concentrations of benzoyl peroxide. The relationship of the developed color in the standards to the concentration of benzoyl peroxide followed Beer's Law, and a standard curve was

constructed. The concentrations of benzoyl peroxide in the samples were read from the standard curve. Dolin found that, unless the standards were prepared at the same time as the sample solutions, the measurement error was as high as 25%. With this method, a spectrophotometer can detect as little as 1 μg of benzoyl peroxide; as little as 3 μg can be detected visually. The method was not specific for benzoyl peroxide but indicated total peroxides. Dolin used a standard impinger in his sampling method but gave no data on the collection efficiency of the impinger with distilled water as an absorbent.

Sampling and analytical methods have been developed that allow specific analysis for benzoyl peroxide. A known volume of air is drawn through a membrane filter. The benzoyl peroxide is subsequently extracted from the filter and analyzed by high pressure liquid chromatography [63]. When an air sample size of 90 liters was collected, by drawing air at a rate of 1.5 liters/minute through a 37-mm diameter mixed cellulose ester membrane filter with a pore size of 0.8 μm , a collection efficiency of 1.00 was determined. Storage stability studies on samples collected from a test atmosphere at a concentration of 7.30 mg/cu m indicated that, after 1 week with the samples held in the filter cassettes at room temperature, there was a 9.3% decrease in the amount of benzoyl peroxide recovered from the filter.

Benzoyl peroxide was extracted from the filter with ethyl ether [63]. Tests showed that benzoyl peroxide is stable in ethyl ether at room temperature for at least 1 week. Thus, there may be up to a 9.3% loss of benzoyl peroxide if the samples are not extracted immediately or refrigerated.

Analysis of the samples by high pressure liquid chromatography is subject to interference from any compound that has the same retention time as benzoyl peroxide at the operating conditions used [63]. Although retention time data on a single column cannot be considered proof of chemical identity, an interfering compound can be eliminated as an interference by altering operating conditions, using a different column packing, or using a selective detector. The coefficient of variation for the total sampling and analytical method in the range of 3.12-19.10 mg/cu m was 0.060, which corresponds to a standard deviation of 0.30 mg/cu m at an air concentration of benzoyl peroxide of 5 mg/cu m. The sampling device is small and portable, and it involves no liquids. The samples collected on membrane filters are analyzed by means of a quick instrumental method. This method has been shown to provide sufficient accuracy, sensitivity, and precision within the range required to determine compliance with this standard for benzoyl peroxide.

Other methods have been reported for the determination of benzoyl peroxide in pharmaceuticals [64,65], flour [66], cheese [22], fats [67], and oils [67]. In 1967, Gruber and Klein [64] reported the comparison of spectrophotometric, titrimetric, and polarographic techniques in testing the stability of pharmaceuticals containing benzoyl peroxide. The results of the polarographic and spectrophotometric methods, when they were used to show the degradation of benzoyl peroxide at high temperatures, were in good agreement. The titrimetric method was far less sensitive than the other two and did not differentiate between benzoyl peroxide and some of its decomposition products. All three methods are colorimetric, and none is specific for benzoyl peroxide. In 1975, Daly et al [65] reported

difficulty in reproducing the results of Gruber and Klein [64] and suggested another titrimetric method as a more accurate means for determining the content of benzoyl peroxide in pharmaceuticals. The authors [65] noted that, although alkylhydroperoxides and dialkyl peroxides would interfere with this method, commercial pharmaceutical creams and lotions containing benzoyl peroxide would probably not contain these other classes of peroxides. The American Oil Chemists Society (AOCS) [67] published their official method for analyzing total peroxide in fats and oils in 1960; it was reapproved in 1973. The described method was a titrimetric procedure that was not specific for benzoyl peroxide.

It is recommended that total dust concentrations be monitored routinely by collecting breathing zone samples on a preweighed glass-fiber filter as detailed in Appendix I. Glass-fiber filters have been selected for sampling because they will efficiently collect airborne dust particles. In addition, being relatively free of organic matter, they are less likely to form explosive mixtures with benzoyl peroxide than filters like cellulose paper.

After the sample is collected, the weight of total dust is determined by gravimetric analysis. The filter is reweighed with the same balance that was used for the preweighing, and the difference between the tare and final weights is determined. Before each weighing, the filter should be equilibrated in a constant humidity chamber, and a static charge neutralizer should be used to improve the reproducibility of the weight determinations and thus enhance gravimetric accuracy. The recommended gravimetric method is described in detail in Appendix II.

In many applications, one should not have to do more than measure total dust. However, if the total airborne dust exceeds the recommended benzoyl peroxide environmental limit of 5 mg/cu m, the gravimetric analysis must be followed by a colorimetric analysis for total peroxide developed from a method by Dolin [62]. The filter is placed in a flask containing a mixture of potassium iodide and starch solution which is oxidized by benzoyl peroxide and other peroxides to form a blue iodide-starch complex. The filter should remain in the solution for 12 hours to permit the blue color to develop from the iodide-starch complex. The color intensity is measured in a spectrophotometer or visually compared with a set of color standards. The concentration of total peroxides should be calculated as benzoyl peroxide. Other oxidizing agents would also produce the iodide-starch complex and give erroneously high concentrations when they are present with benzoyl peroxide in the sample. This interference, however, would never produce a calculated benzoyl peroxide concentration lower than the actual concentration. The recommended analytical method is described in detail in Appendix II.

Engineering Controls

Benzoyl peroxide should be protected from contact with sparks, shocks, friction, and excessive heat. Electrical installations in all areas where pure benzoyl peroxide or formulations containing benzoyl peroxide are manufactured, used, or stored should conform to the National Electrical Code, NFPA No. 70-1975 [68]. Where benzoyl peroxide is used in spray applications, electrical installations and other engineering controls, including ventilation, should conform to the Standard for Spray

Application Using Flammable and Combustible Materials, NFPA No. 33-1973 [69]. Where it is used in the manufacture of organic coatings, electrical installations and other engineering controls, such as ventilation, should conform to the Standard for the Manufacture of Organic Coatings, NFPA No. 35-1971 [69].

Descriptions of two hazard classification systems, one under consideration by the NFPA (O Mageli, written communication, January 1977) and the other recommended by Factory Mutual Research Corporation [70], a loss prevention research and engineering organization, are found in Chapter XII, Appendix IV. The NFPA classification system provides a general description of the burning characteristics of organic peroxides. The Factory Mutual Research Corporation provides a more detailed description of the physical reactions to the tests used to generate the hazard classifications.

Nuclear static eliminators can be used to remove any static electric charge which might build up where benzoyl peroxide flows through an aperture [10 (p 7)]. All metal surfaces that benzoyl peroxide comes in contact with should be grounded and bonded [4]. Conductive flooring or mats will also aid in the control of static electricity [4].

Benzoyl peroxide and its formulations should be stored where there are no sources of excessive heat or ignition, [4] such as open flames, electrical devices [71], and exposed steam lines or wall radiators, in the storage area [4]. Furthermore, benzoyl peroxide should not be exposed to direct sunlight [4,71].

Buildings or facilities intended specifically for the storage of organic peroxides should be constructed in conformance with any applicable

local, state, or federal requirements [4] and any additional recommendations of manufacturers and insurance authorities [71]. Depending on the amount of organic peroxides stored at one time, manufacturers and users should provide detached storage buildings or storage rooms separated by fire-resistant walls [71]. Explosion venting should be provided where benzoyl peroxide is manufactured, used, or stored; the Factory Mutual Research Corporation [72] has recommended that there should never be less than 1 sq ft of venting area/30 cu ft of volume. However, supporting data were not included with this recommendation. In process areas where there are numerous operations, partitioning with fire- and explosion-resistant materials should be installed where needed.

All buildings where large quantities of pure benzoyl peroxide are stored should have automatic sprinkler systems [4]. Appropriate building codes should be consulted for specific requirements for installing these sprinkler systems.

Any area or room where pure benzoyl peroxide is manufactured and stored should have at least two exits; no part of the room should be more than 75 feet from an exit [4]. The doors should open outward, and they should be equipped with a "panic bar" if they are latched [4].

Respiratory protective equipment and protective clothing are not acceptable substitutes for proper engineering controls but should be available for emergency purposes and for nonroutine maintenance and repair situations.

If ventilation is necessary, it should conform to the National Electric Code, NFPA No. 70 [68]. The NIOSH Recommended Industrial Ventilation Guidelines [73] should also be consulted for guidance in

design. Recommendations in Industrial Ventilation--A Manual of Recommended Practice [74] and Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2 -1971 [75] should also be considered. Exhaust air should not be recirculated into workrooms. Ventilation ducts should be maintained so benzoyl peroxide does not accumulate.

The Factory Mutual Research Corporation [72] has recommended that stored flammable liquid peroxides and solid benzoyl peroxide formulations that are explosive or flammable should be provided with natural ventilation through permanent roof- and floor-level openings having at least 1 sq ft of free inlet and outlet opening/500 sq ft of floor area. Individual ventilators should be no more than 72 sq inches and covered with screen to prevent wastes, embers, or small animals from entering. Trapped drains leading to a safe, outdoor disposal point should be installed and, where waste water containing benzoyl peroxide could enter the drains, they should be flushed to prevent an accumulation of material in the trap.

V. WORK PRACTICES

The work practices and sanitation needs appropriate to the manufacture, handling, and storage of benzoyl peroxide differ for each benzoyl peroxide formulation. Improper use or negligent handling and storage of benzoyl peroxide formulations can lead to a separation or precipitation of benzoyl peroxide from the diluents [3,76]. If a formulation separates or dries out, the more stringent work practices appropriate for pure benzoyl peroxide should be observed.

Pure benzoyl peroxide is a very flammable solid which may decompose explosively if subjected to excessive heat, shock, sparks, or friction [4]. If benzoyl peroxide is exposed to temperatures of 75-80 C for prolonged periods of time, it becomes unstable and may spontaneously decompose; if heated to just above its melting point (104 C), it will instantaneously and violently decompose [4]. When benzoyl peroxide must be mixed with other materials, the temperature of these other materials should be below 50 C [4]. Benzoyl peroxide may react violently with various organic and inorganic acids, amines, alcohols, metallic naphthanates, polymerization accelerators, and other chemicals that are easily oxidized [4]. Benzoyl peroxide will decompose at room temperature in the presence of small amounts of tertiary arylalkylamines which are used in curing polyester resins. Many transition metal ions also catalyze the decomposition of benzoyl peroxide [77]. Direct or reflected sunlight may cause decomposition of benzoyl peroxide [71]. Decomposition of benzoyl peroxide is accompanied by a 200-fold increase in volume [5] and yields a dense white smoke consisting of benzoic acid, phenyl benzoate, terphenyls,

biphenyls, benzene, and carbon dioxide [7]. The decomposition of benzoyl peroxide may be preceded or followed by fire [5]. If benzoyl peroxide or its decomposition products catch fire, dense black smoke is produced [8]. The resulting biphenyls promote the further decomposition of benzoyl peroxide [5,7].

Formulations of benzoyl peroxide are generally less hazardous than the pure compound [9,77]. In safety tests, the burning rate of a benzoyl peroxide formulation containing 25% water was not as intensive as that of pure benzoyl peroxide [7]. Formulations containing plasticizers also generally burn slower than does pure benzoyl peroxide; however, a 50% benzoyl peroxide paste with tricresyl phosphate decomposed at a lower temperature than that required to explode pure benzoyl peroxide [78]. Appendix IV explains two hazard classification systems that relate to the physical properties of all organic peroxides and indicate the precautions that should be observed for their safe handling, use, and transportation; they give no indication of toxicity. Tests that evaluate the total energy release of a compound, the rate at which the energy is released, and the ease of ignition and decomposition are the basis for such hazard classifications. Employers should be aware of the appropriate hazard classification of the benzoyl peroxide formulations used in the workplace and should institute pertinent work practices.

Accidents

The flammability and explosiveness of benzoyl peroxide have caused accidents; those which resulted in injuries or fatalities are discussed in Chapter III. Other accidents, involving damage, have been described.

Knowledge of the physical properties of benzoyl peroxide and correct work practices might have prevented some of the accidents or at least lessened their severity. Malkemus [5] reported that 1 pound of benzoyl peroxide exploded after it had been removed from its original shipping container, placed in an open 1-quart can, and set under a window exposed to the sun. He [5] stated that the heat from the sunlight contributed to the explosion and that the can may have been contaminated with a reactive chemical.

A report from the American Insurance Association [3] included accounts of several accidents. A tractor-trailer carrying 300 pounds of benzoyl peroxide in 1-pound containers sideswiped another trailer, and the benzoyl peroxide exploded. All of the benzoyl peroxide was consumed in the explosion, and no fire resulted.

In another accident, an unspecified quantity of benzoyl peroxide caught fire because friction was generated by a broom used to sweep it off the floor. The fire spread to benzoyl peroxide stored on the second floor of the building.

A third accident reported by the American Insurance Association [3] occurred at a reinforced-plastics manufacturing plant. There was an explosion in a warehouse where 1,000 pounds of organic peroxides were stored. The report implied that benzoyl peroxide was present. The resulting fire spread to several adjoining buildings. Spilled peroxide and careless smoking were given in the report as possible causes of the accident.

A blended mixture of 30% benzoyl peroxide and unknown quantities of magnesium carbonate, hydrogen peroxide, sodium hydroxide, and oleic acid exploded while being dried in a steam-heated continuous drying oven [3].

There was a secondary explosion and flash fire in the building. The benzoyl peroxide apparently decomposed inside the oven, releasing what was described as a white, copious, flammable gas. Three sides and the top of the oven were blown out as much as 2 feet.

In 1974, Bolt and Joyce [79] described explosions which occurred during the alkylation of polyhalomethanes by alkanes and alkadienes in the presence of catalytic amounts of benzoyl peroxide. A reactor was charged with 100 g of carbon tetrachloride and 0.40 g of benzoyl peroxide. The reactor was then pressurized with ethylene and heated with agitation. Twenty minutes after the reaction had started, when the temperature was 94 C and the pressure was about 14,230 pounds per square inch (psi), an explosion occurred which blew out the gas inlet line near the reactor. An increased ratio of water to carbon tetrachloride resulted in no further explosions when the reactor was operated at 9,600 psi and 110 C; 100 g of carbon tetrachloride, 100 g of water, and 0.23 g of benzoyl peroxide were used.

The investigators [79] stated that the reaction can occur without incident at a lower pressure, such as 1,400 psi with a temperature as high as 120 C when 0.45 g of benzoyl peroxide and 200 g of carbon tetrachloride are used. However, a violent reaction occurred when equal weights of water and carbon tetrachloride were used at 1,400 psi and 165 C, although there was no explosion.

Storage, Handling, and Transportation

All areas, rooms, and buildings where benzoyl peroxide and its formulations are stored should be inspected frequently. Any area where

benzoyl peroxide is manufactured or stored should have smoke and heat detectors. Any conditions that may cause benzoyl peroxide to burn or explode should be eliminated. Unopened containers should be returned to a central storage area; opened containers may be kept in a special dispensing or premixing area, although they are safer in an isolated building. Benzoyl peroxide formulations containing more than 75% benzoyl peroxide should be stored alone. Other benzoyl peroxide formulations should not be stored with chemicals, such as explosives, reactive metals, and accelerators, that will readily react with benzoyl peroxide [3].

Benzoyl peroxide and its formulations should always be stored in their original containers. In addition, because of possible contamination, no benzoyl peroxide which has been removed should be returned to its original container. Benzoyl peroxide containers should be kept closed when not in use to prevent contamination [71]. Contamination of benzoyl peroxide may result in decomposition or fire [3]. No screw tops should be permitted on containers used for formulations of benzoyl peroxide if pure benzoyl peroxide could accumulate in the screw threads [78]; an accident occurred when a screwcap bottle of benzoyl peroxide was being opened [40]. Precautions should be taken so that wet benzoyl peroxide formulations do not dry out.

Ultraviolet radiation will, like heat, increase the rate of decomposition of benzoyl peroxide [80]. Sufficient open space should be left between stacks of peroxide containers in storage areas. When hazardous benzoyl peroxide formulations must be refrigerated, explosion-proof refrigerators should be used for this purpose [72].

Only clean, properly designed equipment should be used for benzoyl peroxide and its formulations; containers should be made of polyethylene or stainless steel. The use of copper, brass, lead, zinc, and galvanized equipment should be avoided because reactions in such equipment may accelerate decomposition of organic peroxides [71]. Benzoyl peroxide should be brought into the process area in the original shipping container and in quantities limited to the amounts required for daily use. Only small quantities of pure benzoyl peroxide, definitely not more than 1 pound, should be handled at a time [5]. If large quantities of the peroxide start to decompose, the decomposition of the outside layer confines the inner mass and increases the rate of decomposition, causing an explosion [5].

A separate area should be provided for premixing benzoyl peroxide with resins [72]. The accelerator should be mixed with the resin before benzoyl peroxide is added to prevent violent decomposition [71]. Work practices for fibrous glass and plastic fabricators have been recommended to minimize the hazardous properties of benzoyl peroxide [81,82].

No pure benzoyl peroxide, without diluents, should be allowed in any grinding operation because explosive decomposition may occur [71]. Benzoyl peroxide may explode if it is recrystallized from hot chloroform [59-61]. The peroxide can be safely recrystallized from chloroform at room temperature if methanol is added to the solution [59]. However, as was mentioned in Chapter IV, Sampling and Analysis, chloroform has been implicated as a carcinogen, so an alternative solvent should be considered.

All containers of benzoyl peroxide and its formulations should be properly labeled. Labels for benzoyl peroxide formulations should follow

the regulations in Hazardous Industrial Chemicals, ANSI, Z129.1. Shipping labels should comply with the US Department of Transportation regulations and other applicable statutes, regulations, and ordinances [4].

Warnings should be posted in places where benzoyl peroxide is used and stored. The warnings should briefly and concisely state the important safety precautions to be adhered to within the area [4]. These warning placards should also indicate that these areas are accessible only to authorized personnel. Exits should be easily accessible and clearly marked. The location of emergency and first-aid equipment should also be easily accessible and clearly marked.

The Department of Transportation regulations, 49 CFR 173.157 and 178.58, specify that benzoyl peroxide wet with at least 30% water by weight should be packaged in quantities not to exceed 1 pound. It is important that fire-resistant material separates the individual bags so that the decomposition of benzoyl peroxide in one bag is less apt to affect the other bags in the box [5].

Housekeeping and Maintenance

The hazardous nature of benzoyl peroxide makes it imperative that housekeeping duties be performed continually under adequate supervision. Failure to follow these procedures has caused fires and accidents [71]. Even small amounts of benzoyl peroxide are potentially dangerous, and they may unpredictably decompose if subjected to any friction, heat, or shock [4]. Benzoyl peroxide formulations, such as pastes or the wet peroxide, may separate into their respective components through evaporation or freezing [6,76,83]. Thus, these small amounts of benzoyl peroxide

formulations may be dangerous if not cleaned up from the floor and from the equipment in the process areas. The accidental decomposition of these traces of benzoyl peroxide could initiate the decomposition of all the benzoyl peroxide in the surrounding area [61]. Wet mops or other implements that will minimize sparks and friction should be used to clean up spills; a fire has resulted when the friction between a broom and benzoyl peroxide on the floor ignited the peroxide [3].

All equipment should be cleaned meticulously to avoid possible violent reactions between benzoyl peroxide and reactive chemicals. Ducts should be cleaned and inspected regularly to prevent the accumulation of benzoyl peroxide. Benzoyl peroxide should either be removed or covered during maintenance and repair work [71]. Where benzoyl peroxide formulations are used to bleach flour or catalyze certain organic reactions, the proportion of benzoyl peroxide is generally so small in relation to other chemicals present that the nature of these chemicals, rather than that of benzoyl peroxide, may dictate the housekeeping and maintenance procedures [4].

The grounds surrounding process and storage buildings must be kept cleared of vegetation and all other combustible materials, such as trash, to prevent the spread of fire if one should occur [71,72]. Maintenance and repair work in areas where benzoyl peroxide is used, stored, or manufactured should be authorized by the appropriate supervisor [3,71].

Spills and Waste Disposal

Spills should be wetted with water and cleaned up immediately with a wet mop or other nonsparking implements [10 (p 9)]. Vacuum units should be

operated from a remote location away from electrical contacts; filter bags, as well as the vacuum lines, should be grounded to prevent static charge buildup. Care should be taken that benzoyl peroxide wastes are not mixed with other materials or chemicals, such as oxidizing or reducing agents, that might create hazardous conditions. A nonreactive container, such as one made of polyethylene, reserved only for benzoyl peroxide wastes, should be used to store the wastes until their disposal.

Benzoyl peroxide should not be disposed of by burning unless it has been thoroughly wetted down or mixed with water-wetted vermiculite, perlite, or another inert substance [84]. Water slurries of benzoyl peroxide wastes may be destroyed by gradually adding small amounts of the slurry to 10 times its weight of 10% sodium hydroxide solutions [4,84]. There should be sufficient agitation or stirring of the mixture so that there is no lump formation or settling. Water may be added to prevent thickening of the mixture that would make stirring difficult. The resulting slurry of sodium benzoate should be checked for neutrality and may be flushed into the sewage system if local regulations permit. Pure benzoyl peroxide itself should never be flushed into the sewage system [78]. Additional details of inactivating and disposing of benzoyl peroxide are described in Appendix V.

If wetted vermiculite or perlite has been added to a benzoyl peroxide spill, the water should be drained off and the waste water added to the waste slurry. The remaining material may be burned in an open incinerator or otherwise disposed of in accordance with local, state, and federal laws. If the material is burned, it should be placed in a shallow trench and ignited from a distance of at least 6 feet. When benzoyl peroxide becomes

mixed with an unknown material, it should be considered contaminated and disposed of properly [72].

If bags and cartons that formerly contained benzoyl peroxide are to be destroyed, they should be placed in a special waste collection drum provided for that purpose. The contents of the drum should be kept wet until they can be carefully burned in an area reserved for that purpose [4]. When the bags and cartons are ready for disposal, they should be burned in open piles or disposed of in accordance with local, state, and federal regulations. Empty 1-pound bags and cartons should not be recycled unless properly cleaned of all traces of benzoyl peroxide.

Disposal containers made of plastic or other flexible material should be used because, while they may rupture thereby releasing the contents, they are unlikely to explode [85]. Extreme caution should be taken to ensure that wet benzoyl peroxide wastes and other wastes containing pastes and liquid solutions of benzoyl peroxide are not allowed to dry out and thus increase the hazards of fire and explosion. The waste containers should be placed in a cool, well-ventilated place and disposed of frequently.

Protective Clothing and Equipment

Protective clothing and safety glasses with side shields or safety goggles should be worn by employees to reduce the possibility of skin contact and eye irritation. Such protection is especially important where benzoyl peroxide and other powder or granular benzoyl peroxide formulations

may become airborne or where liquid or paste formulations of benzoyl peroxide might be spattered or spilled.

Protective clothing should be fire resistant. Any fabric that generates static electricity is not recommended. To prevent the buildup of static electricity, appropriate conductive footwear should be worn [4,10 (p 6)]. Gloves made of rubber, leather, or other appropriate material should be worn by employees for protection when they are opening shipping boxes of pure benzoyl peroxide [4] or otherwise handling pure benzoyl peroxide. Aprons made of rubber or another appropriate material are recommended for added protection when handling benzoyl peroxide and its formulations. Plastic aprons that generate static electricity should not be used [4].

All personal protective clothing and equipment should be cleaned, inspected on a regular schedule, and replaced when worn out or broken. The employer is responsible for ensuring that such clothing and equipment are stored in suitable designated containers or locations when not in use.

When the protective clothing is laundered, an antistatic rinse should be used to reduce static electricity [10 (p 6)]. Employers should inform launderers of the hazards of benzoyl peroxide, including the danger of smoking in the vicinity of the soiled clothing.

Workers must not carry sources of ignition, such as lighters and matches, into areas where benzoyl peroxide is being used or stored [10 (p 86)]. Workers whose uniforms become grossly contaminated with benzoyl peroxide should remove them before going to areas where smoking is permitted, where chemicals that may react explosively with benzoyl peroxide are present, or where there are any sources of ignition, such as soldering irons or welding equipment. In addition, employees should work behind a

safety shield made of a transparent shatterproof material when they are performing particularly hazardous tasks, such as packaging benzoyl peroxide [10 (p 6)].

Respiratory protection as specified in Chapter I must be used whenever airborne concentrations of benzoyl peroxide cannot be controlled to the recommended workplace environmental limit by either engineering or administrative controls.

Sanitation

Protective clothing should be kept apart from the workers' street clothing in lockers with two compartments provided for that purpose.

To minimize the potential for explosion or fire, workers must not eat or smoke where benzoyl peroxide is manufactured, used, or stored. Workers should also wash their hands before eating, smoking, or using the lavatory. A supply of potable water must be available near all places where there is potential contact with benzoyl peroxide and its formulations. A water supply may be provided by a free-running hose at low pressure or by emergency showers. Soap should be available at emergency showers. Where contact with the eyes is likely, eyewash fountains or bottles should be provided [10 (p 6)].

Emergency Procedures

Drills and training for all personnel should be an integral part of on-the-job training [10 (p 8)], and the employer should continually update emergency procedures. The employer should provide all emergency equipment

and ensure that it is clearly marked, located in an easily accessible place, and maintained in working order.

Firefighters should be informed that the dense smoke produced by benzoyl peroxide necessitates the use of a lifeline and a self-contained breathing apparatus [4,10 (p 86)] in addition to their standard firefighting clothing [4].

Local fire units and rescue squads should be apprised of the types of emergencies that may arise before any emergencies occur. The necessary phone numbers for such emergency assistance must be prominently posted in areas where emergencies are likely to occur.

Areas where pure benzoyl peroxide is manufactured, packaged, and stored should not contain firefighting equipment; if a fire occurs, these areas should be evacuated immediately; employees should not attempt to control this type of fire. However, firefighting equipment should be well marked and located in every room and area where formulations of benzoyl peroxide are stored. If a fire occurs near an organic peroxide storage area, the containers within the storage area should be kept continually wetted to prevent overheating.

Appropriate warning alarms that are automatically activated by heat or smoke should be installed in all benzoyl peroxide storage and work areas. In addition, an independent alarm system that can be controlled manually and whose controls are readily accessible to employees is advisable if smoke or heat is considered insufficient to trigger the automatic alarms.