

IV. ENVIRONMENTAL DATA

Engineering Controls

Most glycidyl ethers are liquids with low vapor pressures, ranging from 0.01 mmHg at 25 C for PGE to 3.2 mmHg for BGE, 4.7 mmHg for AGE, and 9.4 mmHg for IGE at 25 C. The vapor pressures for BGE, AGE, and IGE are great enough to permit vapor concentrations of up to 4,000, 6,000, and 12,000 ppm, respectively. Glycidyl ether vapors are generated in certain processes, such as resin curing, and the inhalation of these vapors may be a health hazard. Engineering controls must therefore be installed wherever possible to maintain the concentration of glycidyl ethers at or below the recommended environmental limits. Closed-system operations should be used whenever feasible to control exposure to vapors produced during the manufacture or use of glycidyl ethers. Closed-system operations are effective only when the integrity of the system is maintained, so the equipment should be inspected frequently for leaks, and any that are found should be promptly repaired.

A sparkproof ventilation system may be required where a closed system proves to be impractical and is desirable as a standby if the closed system should fail. Industrial Ventilation--A Manual of Recommended Practice [69], published by the American Conference of Governmental Industrial Hygienists, and Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971 [70], published by the American National Standards Institute, provide useful guidelines for the design and installation of adequate ventilation systems. The air intake for ventilation systems should be sited so that exhaust air is not recirculated

in the work area. Ventilation systems will require regular inspection and maintenance to facilitate effective operation, and a regular schedule for inspections and repair should be established. These routine checks should include face velocity measurements of the collecting hood, inspection of the air mover, ducts, and collector, and measurements of airborne concentrations of glycidyl ethers in the workroom. Any process changes that may affect the ventilation system or the operations being ventilated must be assessed promptly to ensure that engineering controls will continue to provide adequate protection for employees.

If it is determined that glycidyl ether vapors are generated in a particular process in amounts sufficient to create a possible fire or explosion hazard, several precautions should be taken. If a fan is located in ductwork and the air concentration of glycidyl ether vapors may exceed 25% of the lower flammable limit, the rotating element should be constructed of nonsparking material and the casing should also be constructed of a nonsparking material. Devices to prevent flashback should be installed along the entire length of the ventilation system.

The addition of glycidyl ethers and other components to epoxy resin systems immediately before the resins are to be used should be done in a ventilated hood. Unnecessary worker exposure to and contamination of the physical plant by glycidyl ethers can be minimized by using separate areas of the plant for mixing, molding, and curing the resins [71,72].

Sampling and Analysis

Only a few reports describing procedures for the sampling and analysis of glycidyl ethers have been found. The sampling and analytical

methods recommended in Appendices I, II, and III have not been validated for detecting glycidyl ethers at concentrations as low as the recommended limits. Further testing of these methods is an important need.

The Intersociety Committee of the American Public Health Association, Inc., has reported an analytical method for organic solvent vapors in air [73]. The method was tested for AGE, BGE, and IGE; these compounds were reported to have greater than 80% desorption efficiency by this method. Air samples were collected with a charcoal tube and an air-sampling pump. The tube was glass, 7 cm long, with a 6-mm outer diameter and a 4-mm inner diameter, and contained two sections of 20/40-mesh activated charcoal separated by a 2-mm portion of urethane foam. After a known volume of air was drawn through the tubes at a specific flowrate (50-200 cc of air/minute), the collected organic vapors were desorbed separately from each section of charcoal in the tube with carbon disulfide and analyzed by gas chromatography with flame ionization detection. The area of the peaks was compared with a standard curve to determine the concentration of the samples.

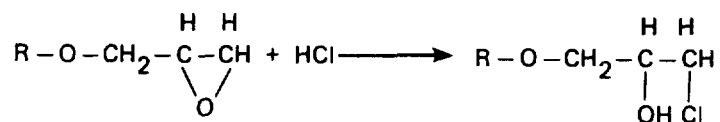
High humidity and high temperatures were reported to interfere with the adsorption capacity of the activated charcoal [73]. The precision of the method was limited by the reproducibility of the pressure drop across the tubes, and the amount of sample collected was limited by the adsorption efficiency of the charcoal. Advantages of the method are that the sampling device is small, portable, and requires no liquids, and there are few interferences; these can usually be eliminated by altering the gas chromatographic operating conditions.

Little information has been found on portable direct-reading instruments that can be used to perform immediate evaluations of concentrations of glycidyl ethers in the workplace. The Wilks Miran 1A is a portable instrument that uses infrared absorbance to detect many air contaminants. The reported minimum detectable concentrations for AGE and BGE were 0.07 ppm (0.33 mg/cu m) and 0.05 ppm (0.27 mg/cu m), respectively [74]. It is possible that this instrument might be useful for detecting other glycidyl ethers, but no data concerning the performance of the instrument with them are currently available.

In 1977, Terrill and Lee [39] described a paired sampling and analysis regimen for PGE and phenol. The sampling device was a midget impinger containing 15 ml of a 0.1 N sodium hydroxide solution in equal parts of ethyl alcohol and water. A 10-liter air sample was collected at a sampling rate of 1 liter/minute, and ultraviolet analysis was performed on it. A 5-ppm v/v solution of PGE had an absorbance of 0.4 (1-cm cell) at a maximum of 270 nm. Phenol had a lambda maximum at 288 nm and could be detected when the phenol concentration was 5% or more of the PGE concentration. The relative proximity of the two lambda maximums is a factor that limits the minimum detectability for the system. When phenol concentrations were greater than or equal to 0.05 ppm, 0.25 ppm, and 0.6 ppm, the minimum sensitivities for PGE were 1, 5, and 12 ppm (6, 30, and 74 mg/cu m), respectively. The phenol concentrations were monitored because trace amounts of phenol (found by gas chromatographic analysis) were present in the PGE that was sampled.

Jungnickel et al [7] have reviewed several methods for the analysis of materials containing alpha-epoxide rings, a group common to all glycidyl

ethers. The tendency of the epoxide group to react readily with nucleophilic reagents is the basis for all of the methods. Hydrogen chloride (HCl) is added to a flask containing the sample material and allowed to react. This reaction can be represented schematically as follows:



Since each dissociated molecule of HCl reacts with only one epoxide group, the calculated value for HCl is a measure of the number of epoxide groups present. When monoglycidyl ethers are analyzed, the number of moles HCl is equal to the amount of glycidyl ether in the sample. When diglycidyl ethers are sampled, the number of moles of HCl is equal to twice the number of moles of the diglycidyl ether in the sample.

The seven methods described by Jungnickel et al [7] differ principally in the solvent for HCl, the temperature at which the reaction is carried out, the specific indicator, and the solvent (water or methanol) in the solution of sodium hydroxide used as a titrant. The nature of the sample is one of the factors to be considered when selecting a particular hydrochlorination method. The reagents chosen should be good solvents for the sample, especially if it is in solid form. The conditions under which the reaction is carried out are also important. The method that allows the smallest number of side reactions (such as isomerization to the

corresponding carbonyl compound) should be selected. The authors [7] reported that glycidyl ethers of very high purity were sampled quite accurately unless alcoholic magnesium chloride hydrochlorinate was used as a reagent; then the results were 1-2% low. The authors did not report results of analysis of impure glycidyl ether samples, such as might be encountered in sampling workplace air. It can be seen, however, that any impurities that would react with the hydrochlorination agent or the glycidyl ether would affect the accuracy of the method. The possibility that other substances in the workplace environment will interfere with the determination of glycidyl ethers should be considered when the analyses are performed.

These hydrochlorination methods are not suitable for the sampling and analysis of glycidyl ethers in workplace air for a number of reasons. Solvent selection is extremely important and must be based on the knowledge of other substances that may be present as sample contaminants and the hydrochlorination reactions. Most of the solvents suggested (eg, dioxane, pyridine, diethyl ether) are toxic. Finally, because a dye is used as an indicator, these methods should be routinely performed by the same technician to provide reproducible results.

NIOSH has validated methods for the sampling and analysis of BGE [75], IGE [76], and PGE [77]. A draft report on validated sampling and analytical methods for AGE [78] indicates that the methods for these four glycidyl ethers are similar. The attempts to determine methods of sampling and analysis for DGE failed because desorption efficiency was not adequate to permit acceptable recovery [79].

The method tested for DGE under the NIOSH Standards Completion Program involved the use of a charcoal tube to collect the vapors; methylene chloride was used to desorb the DGE from the charcoal [79]. The samples were then analyzed by gas chromatography. When the method was tested, 15-minute samples were collected from chambers containing concentrations of airborne DGE at 0.5, 1, and 2 times the current Federal standard (2.8 mg/cu m). The amounts recovered were 71.6, 75.6, and 68.8%, respectively, which were considered too low to be acceptable. For this reason, and because the experimental work exceeded the time allotted to the project, the method received a "failure report." A review of the data indicates that the desorption efficiency ranged from 0.783 to 0.976 when 0.02 to 0.85 mg of DGE was placed on, and desorbed from, charcoal. The experimenters inferred from preliminary data that desorption efficiency may be, to some extent, a function of storage temperature and time; the time allotted for the investigation did not allow the experimenters to ascertain and clarify the role of storage times and temperature. It is reasonable to conclude that if these variables are determined, as they have to be with any method relying on sorption on, and desorption from, charcoal, the method will be useful for sampling airborne DGE.

Because of the similarities in the chemical structures of all glycidyl ethers, the methods presented in Appendices I, II, and III may be adequate for sampling and analysis of any glycidyl ether if certain parameters, such as the desorption solvents and operating conditions for the gas chromatograph, are appropriately modified. These modifications have not yet been tested by NIOSH.

To sample for concentrations of airborne BGE, IGE, and PGE, a known volume of air is drawn through a charcoal tube that traps the organic vapors. The analytes are desorbed with carbon disulfide and analyzed by gas chromatography. Further details of this procedure are presented in Appendix I.

To sample for concentrations of airborne AGE, a known volume of air is drawn through a Tenax-GC resin tube and the organic vapors are adsorbed on the resin. The sample is then desorbed with ether, and an aliquot is analyzed in a gas chromatograph. Further details of this procedure are presented in Appendix II.

To sample for concentrations of airborne DGE, a known volume of air is drawn through a charcoal tube that traps the organic vapors. The analyte is then immediately desorbed with methylene chloride and analyzed with a gas chromatograph. Further details of this procedure are presented in Appendix III.

Certain conditions may interfere with the analysis of these five glycidyl ethers. High humidity in the sampling environment may decrease the collection efficiency of the collecting tube, and the presence in the sample of compounds that have similar retention times at the prescribed operating conditions of the gas chromatograph will interfere with the detection of the ether being analyzed. If the possibility of interference exists, separation conditions (column packing, temperature, etc) must be changed to alter the retention times of the ether and the interfering compounds in order to circumvent the problem.

The upper limits of the ranges of the methods are dependent on the adsorptive capacity of the charcoal or Tenax-GC resin tubes. The

efficiency of the collecting tubes will change drastically as the tube becomes heavily loaded with organic vapors. In practice, lower limits are often dependent on the desorption efficiency, ie, the percentage of the glycidyl ether that is desorbed and dissolved in the solvent. Desorption efficiency must be determined over the range used for each ether being analyzed.

The NIOSH recommended methods for the sampling and analysis of AGE, BGE, IGE, PGE, and DGE have several advantages over the other methods discussed in this section. The recommended sample tubes contain either activated charcoal or, for AGE, Tenax-GC, and both of these are solid sorbents. A method that requires no liquids during sampling eliminates the possibility of spills and evaporation. The chosen sorbents involve no exposure to a toxic chemical used as a sampling medium, such as the solvents required for the hydrochlorination methods [7]. The sampling device is small and portable. Furthermore, interferences are few, and those that occur can be eliminated by altering chromatographic conditions. In the hydrochlorination method [7], interferences during sampling may alter the reaction that is the basis of the analysis and invalidate the results of the titration. In ultraviolet analysis of a liquid sample [39], the limit of detectability for PGE was seriously affected by the presence of phenol.

The primary disadvantage of the recommended sampling and analytical methods is that they have not been tested at the recommended sampling rate and size. However, the methods are capable of determining concentrations of airborne glycidyl ethers at the recommended limits. The method for DGE has the distinct disadvantage of requiring desorption immediately after

sampling because desorption efficiency decreases with time. Immediate desorption creates a need for the proper packaging of the methylene chloride-desorbed analyte for shipment. The substitution of Tenax-GC for charcoal may eliminate the need for these procedures, but the recommended method has not been tested by NIOSH with Tenax-GC in the tube.

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A manufacturer of BGE and PGE used the NIOSH-validated sampling and analytical methods [75,77] to monitor these compounds during two production runs [17(p 155)]. Airborne concentrations below 1 ppm were recorded for both ethers. During drumming operations at the same facility, airborne concentrations of BGE were determined to be 2-4 ppm. No other data on concentrations of airborne glycidyl ethers have been found.

V. WORK PRACTICES

Human skin contact with glycidyl ethers has resulted in rashes, burns, and sensitization [23,25,80], and studies in animals indicate that skin irritation, sensitization, and systemic effects can result from dermal exposure to these compounds [23,31,32,34]. Glycidyl ethers have also caused hemopoietic and other systemic effects in animals exposed by inhalation [23,33,41], but, for glycidyl ethers other than DGE, these effects have occurred only at high concentrations. Eye irritation has resulted from both direct contact with liquid glycidyl ethers and exposure to airborne vapors [23,41,47]. Glycidyl ethers have proven to be cytotoxic or mutagenic or have caused radiomimetic effects in tests using several different routes of exposure, including dermal contact [56,58]. DGE and resorcinol diglycidyl ether have caused nonmalignant skin tumors in mice [51], and triethylene glycol diglycidyl ether was carcinogenic to mice at very high doses [52].

Work practices and sanitation measures applied in the manufacture, handling, and storage of glycidyl ethers must therefore be designed to minimize or prevent inhalation of glycidyl ether vapors or mists and to protect workers' skin and eyes from contact with liquid glycidyl ethers. Most glycidyl ethers are liquids. All of them have relatively low vapor pressures (Table XIV-2), but because of their toxicity, precautions to prevent inhalation of vapors or mists should nevertheless be taken. Throughout the process of manufacturing epoxy resin systems, glycidyl ethers can be present along with other components of the system, such as

amine hardeners. Good work practices designed to protect the worker from contact with glycidyl ethers should therefore be observed until the resin is fully polymerized. A fully polymerized resin has been considered to be inert [71,81,82], but wet or uncured resins, and the chemicals used to thin, strengthen, or harden them, should be considered hazardous substances [71]. Work practices appropriate for handling the other components of the epoxy resin system, such as the amine hardeners, should also be followed.

Workers should be provided with protective clothing that is impervious to glycidyl ethers and, if possible, fire-resistant. They should be protected against contact with liquids by the use of gloves, aprons, boots, faceshields (8-inch minimum), and other protective equipment or clothing. For processes in which manual dexterity requirements limit the types of gloves that can be worn, protective hand creams have been suggested as supplements to gloves that will permit the required dexterity [17(pp 5,141),83]. Extreme care should be taken to avoid contamination inside gloves. Tests done at Argonne National Laboratory in 1964 indicated that only 2 of 10 glove materials tested provide acceptable protection for work with AGE and PGE [84]. Milled butyl rubber and polyvinyl alcohol were found to be acceptable materials. Unacceptable glove materials were natural rubber (latex), neoprene-natural rubber (latex), milled neoprene, neoprene with nylon, milled Buna-N, vinyl and polyethylene (disposable), and polyvinyl chloride [84]. Gloves made of polyvinyl chloride or polyethylene-coated fabric may be used for a single workshift exposure (BW Karrh, M.D., written communication, January 1978). Only adequate test data should be used as a basis for deciding which glove materials provide proper protection against specific glycidyl ethers. At the end of the workshift,

workers should use conditioners to keep the skin on their hands and arms supple because absorption of, and sensitization to, glycidyl ethers occurs more readily through irritated or cracked skin [44,72]. Neutral or acid soaps that protect the skin from drying and cracking should be used instead of alkaline, powdered, and abrasive cleaning agents or lipid solvents [71,72].

Safety showers and eyewash fountains should be readily accessible to employees working in or near areas where splashes of glycidyl ethers are possible, and this equipment should be properly maintained. Handwashing facilities, with neutral or acid soap or an alternative cleanser, must be available to the employees, who shall be instructed to wash their hands before eating or using toilet facilities. The preparation, dispensing, consumption, or storage of food or beverages in exposure areas should be prohibited.

The effects of glycidyl ethers on workers are intensified by the penetration of the ethers into clothing and shoes, which act as reservoirs and prolong the contact [23]. For this reason, clothing contaminated with any of the ethers must be removed as soon as possible and stored in a closed container until it is either laundered or discarded. The employer should inform the persons laundering or otherwise handling the contaminated clothing of the hazardous properties of glycidyl ethers. Shoes or other leather apparel on which glycidyl ethers have been spilled should be made unfit for use and discarded [17(p 5)].

To protect workers' eyes, the employer should provide chemical safety goggles (splashproof) meeting the requirements of 29 CFR 1910.133 and ANSI Z87.1-1968 and should ensure that they are worn whenever there is a

reasonable probability that glycidyl ethers could be splashed into the eyes. Workers should be cautioned to avoid rubbing their eyes with hands that may be contaminated with glycidyl ethers. If eye contact occurs, the eyelid should be lifted, the eye should be flushed with copious amounts of water, and the worker should be referred to a physician.

When concentrations of airborne glycidyl ethers cannot be kept at or below prescribed limits by engineering controls, eg, because of spills or equipment failure or during maintenance or entry into confined spaces, special respiratory protection is required. Employers should establish and enforce a respiratory protective program meeting the requirements of 29 CFR 1910.134 and should provide proper respiratory devices as outlined in Tables I-1, I-2, I-3, and I-4.

Because the glycidyl ethers vary in their physical properties and toxic effects, no single respirator selection guide can be devised that would be applicable to all compounds. Instead, the selection of a respirator that will provide adequate protection at a given concentration of airborne glycidyl ethers must be performed on a compound-by-compound basis for each glycidyl ether. Respirator guidelines have been developed for five of the glycidyl ethers, and these are presented in Tables I-1, I-2, I-3, and I-4. These guidelines should not be followed in choosing respirators for use with other glycidyl ethers unless additional information indicates that there are very close similarities in their physical properties and toxic effects.

However, available information on the glycidyl ethers as a class permits certain general recommendations. Quarter-mask and half-mask respirators should not be used with any glycidyl ether because all of the

compounds are potentially irritating to the eyes. Full-body protective clothing should also be provided in any situation that requires the use of a respirator because of the hazard of skin absorption and skin irritation and sensitization.

Protective clothing and equipment, including respirators, should be kept clean and maintained in good condition. This equipment should be cleaned and inspected by trained personnel after each use and should be replaced when necessary. The employer must ensure that all equipment is in working order and that it is stored properly when not in use.

If evacuation of the process or work area might be required in an emergency, a program permitting rapid egress from the area should be designed, and the employer should ensure that it is implemented. All potentially exposed employees must be aware of escape procedures, of the location of and proper use of respirators designated for emergency situations, and of firefighting methods. Instructions should be given for transporting injured employees to areas where emergency medical care can be given.

There is considerable variation in the fire and explosion hazards associated with the use, handling, and storage of various glycidyl ethers. IGE is classified, under the provisions of 29 CFR 1910.106, as a Class IC flammable liquid, which is a liquid with a flashpoint at or above 73 F (22.8 C) and below 100 F (37.8 C). AGE and BGE are Class II combustible liquids, and PGE is a Class III A combustible liquid. A Class II combustible liquid has a flashpoint at or above 100 F (37.8 C) and below 140 F (60 C), and a Class III A liquid has a flashpoint at or above 140 F (60 C) and below 200 F (93.3 C) (29 CFR 1910.106). Whenever a combustible

liquid is heated to within 30 F (16.7 C) of its flashpoint, the compound should be handled as if it belonged to the next lower class (29 CFR 1910.106). No data were found on the other glycidyl ethers covered in this document that would permit their classification as either flammable or combustible.

The vapor of IGE can easily form explosive mixtures in air; consequently, all sources of ignition must be controlled where IGE is used, handled, or stored. Furthermore, because this glycidyl ether is heavier than air, distant ignition sources can present problems [85]. Although the fire and explosion hazards associated with the use of AGE, BGE, and PGE are not as severe, it is necessary to ensure that flames or other sources of ignition, such as smoking, are not permitted in areas where these glycidyl ethers are used, stored, or handled. Should a fire involving glycidyl ethers occur, a medium such as water, carbon dioxide, or dry chemicals should be used to extinguish it [3]. Fire extinguishers should be readily accessible to all employees exposed to glycidyl ethers and should be maintained in good condition.

The storage of bulk amounts of glycidyl ethers must meet the requirements for their classification (flammable or combustible as specified in 29 CFR 1910.106(f)). There is evidence that PGE and BGE will undergo violent polymerization when subjected to high temperatures, whether alone or in the presence of catalysts or strong oxidizing agents such as acids, bases, and salts [17(pp 62,69)]. IGE will react in a similar fashion [85]. No data concerning violent polymerization by other glycidyl ethers have been found; nonetheless, since all glycidyl ethers have structural similarities, it seems reasonable to assume that at least some

of the rest of the glycidyl ethers might also polymerize violently under similar circumstances. Consequently, glycidyl ethers should be stored in a cool place where they will not be subjected to extreme temperatures, and they should not be stored near acids, bases, and salts.

Special precautions are necessary for entering confined spaces, such as tanks or reaction vessels and enclosed application sites, that may contain glycidyl ethers, for performing flame- or spark-generating operations such as welding and cutting, and for transferring glycidyl ethers. Before any employee enters a vessel, all pipelines leading into or out of the vessel must be blanked to prevent the entry of liquid or vapors. The vessel interior should be rinsed with water and then purged with air or with nitrogen followed by air. After the purging, and during all operations in the vessel, its atmosphere should be tested with an oxygen meter, a combustible gas meter, and other approved instruments. No employee should enter any tank or vessel that does not have an entrance large enough to admit the employee equipped with safety harness, lifeline, and appropriate respiratory equipment. The employee must be able to leave the tank or vessel by the same opening. Employees entering contaminated tanks or vessels should wear full-body protective clothing until inspection and testing assure safety for personnel in the tank. When employees are working in confined spaces, another employee should be stationed at the entrance to keep them under constant observation, and one or more additional employees shall be readily available in case of an emergency. A positive pressure respiratory protective device with safety harness and lifeline should be located outside the tank or vessel for emergency use. The use of portable lights to illuminate the interior of tanks, vessels, or

reactors when they are undergoing cleaning or repairs should be prohibited. Such interiors should be illuminated by reflected light or explosion-proof light sources. Only nonferrous (sparkproof) tools should be used for scraping away clinging residues or accumulated deposits, and rags and other materials used to wipe and absorb ethers should be placed in standard safety containers for subsequent disposal. Cutting or welding must be performed only after an authorized representative of the employer has signed a permit indicating that all actions prescribed in pertinent sections of 29 CFR 1910.252 have been taken.

Whenever flammable or combustible liquids are transferred from one container to another, both containers must be effectively bonded and grounded to prevent the buildup and discharge of static electricity.

The employer should assume responsibility for providing proper initial training and periodic retraining of employees on correct operating procedures and use of protective equipment. If all recommended work practices are observed, good engineering controls as discussed in Chapter IV are installed, and adequate educational programs are conducted, employees working with glycidyl ethers can be adequately protected from the hazards associated with them.