Appendix A—Substance technical guideline for formalin. (1) The following substance technical guideline for formalin provides information on uninhibited formalin solution (thirty-seven percent formaldehyde, no methanol stabilizer). It is designed to inform employees at the production level of their rights and duties under the formaldehyde standard whether their job title defines them as workers or supervisors. Much of the information provided is general; however, some information is specific for formalin. When employee exposure to formaldehyde is from resins capable of releasing formaldehyde, the resin itself and other impurities or decomposition products may also be toxic, and employers should include this information as well when informing employees of the hazards associated with the materials they handle. The precise hazards associated with exposure to formaldehyde depend both on the form (solid, liquid, or gas) of the material and the concentration of formaldehyde present. For example, thirty-seven to fifty percent solutions of formaldehyde present a much greater hazard to the skin and eyes from spills or splashes than solutions containing less than one percent formaldehyde. Individual substance technical guidelines used by the employer for training employees should be modified to properly give information on the material actually being used.

(a) Substance identification.
   (i) Chemical name: Formaldehyde.
   (ii) Chemical family: Aldehyde.
   (iii) Chemical formula: HCHO.
   (iv) Molecular weight: 30.03.
   (v) Chemical abstracts service number (CAS number): 50-00-0.

Synonyms: Formalin; Formic Aldehyde; Paraform; Formol; Formalin (Methanol-free); Fyde; Formalith; Methanal; Methyl Aldehyde; Methylene Glycol; Methylene Oxide; Tetraoxymethalene; Oxomethane; Oxymethylene.

(b) Components and contaminants.
   (i) Percent: 37.0 Formaldehyde.
   (ii) Percent: 63.0 water.

Note: Inhibited solutions contain methanol.

(iii) Other contaminants: Formic acid (alcohol free).

Exposure limits:
(A) WISHA TWA-0.75 ppm.
(B) WISHA STEL-2 ppm.

(c) Physical data.
   (i) Description: Colorless liquid, pungent odor.
   (ii) Boiling point: 214°F (101°C).
   (iii) Specific gravity: 1.08 (H2O = 1 @ 20 C).
   (iv) pH: 2.8-4.0.
   (v) Solubility in water: Miscible.
   (vi) Solvent solubility: Soluble in alcohol and acetone.
   (vii) Vapor density: 1.04 (Air = 1 @ 20 C).
   (viii) Odor threshold: 0.8-1 ppm.

(d) Fire and explosion hazard.
   (i) Moderate fire and explosion hazard when exposed to heat or flame.
   (ii) The flash point of thirty-seven percent formaldehyde solutions is above normal room temperature, but the explosion range is very wide, from seven to seventy-three percent by volume in air.
   (iii) Reaction of formaldehyde with nitrogen dioxide, nitromethane, perchloric acid and aniline, or peroxyformic acid yields explosive compounds.
Flash point: 185°F (85°C) closed cup.

Lower explosion limit: Seven percent.

Upper explosion limit: Seventy-three percent.

Autoignition temperature: 806°F (430°C).

Flammable class (WISHA): III A.

Extinguishing media:

(I) Use dry chemical, "alcohol foam," carbon dioxide, or water in flooding amounts as fog. Solid streams may not be effective. Cool fire-exposed containers with water from side until well after fire is out.

(II) Use of water spray to flush spills can also dilute the spill to produce nonflammable mixtures. Water runoff, however, should be contained for treatment.

National Fire Protection Association Section 325M Designation:

(A) Health: 2-Materials hazardous to health, but areas may be entered with full-faced mask self-contained breathing apparatus which provides eye protection.

(B) Flammability: 2-Materials which must be moderately heated before ignition will occur. Water spray may be used to extinguish the fire because the material can be cooled below its flash point.

(C) Reactivity: D-Materials which (in themselves) are normally stable even under fire exposure conditions and which are not reactive with water. Normal firefighting procedures may be used.

Stability: Formaldehyde solutions may self-polymerize to form paraformaldehyde which precipitates.

Incompatibility (materials to avoid):

(A) Strong oxidizing agents, caustics, strong alkalies, isocyanates, anhydrides, oxides, and inorganic acids.

(B) Formaldehyde reacts with hydrochloric acid to form the potent carcinogen, bis-chloromethyl ether. Formaldehyde reacts with nitrogen dioxide, nitromethane, perchloric acid and aniline, or peroxyformic acid to yield explosive compounds. A violent reaction occurs when formaldehyde is mixed with strong oxidizers.

(C) Hazardous combustion or decomposition products: Oxygen from the air can oxidize formaldehyde to formic acid, especially when heated. Formic acid is corrosive.

Health hazard data.

(A) Ingestion (swallowing): Liquids containing ten to forty percent formaldehyde cause severe irritation and inflammation of the mouth, throat, and stomach. Severe stomach pains will follow ingestion with possible loss of consciousness and death. Ingestion of dilute formaldehyde solutions (0.03-0.04%) may cause discomfort in the stomach and pharynx.

(B) Inhalation (breathing):

(I) Formaldehyde is highly irritating to the upper respiratory tract and eyes. Concentrations of 0.5 to 2.0 ppm may irritate the eyes, nose, and throat of some individuals.

(II) Concentrations of 3 to 5 ppm also cause tearing of the eyes and are intolerable to some persons.

(III) Concentrations of 10 to 20 ppm cause difficulty in breathing, burning of the nose and throat, coughing, and heavy tearing of the eyes, and 25 to 30 ppm causes severe respiratory tract injury leading to pulmonary edema and pneumonitis. A concentration of 100 ppm
is immediately dangerous to life and health. Deaths from accidental exposure to high concentrations of formaldehyde have been reported.

(C) Skin (dermal): Formalin is a severe skin irritant and a sensitizer. Contact with formalin causes white discoloration, smarting, drying, cracking, and scaling. Prolonged and repeated contact can cause numbness and a hardening or tanning of the skin. Previously exposed persons may react to future exposure with an allergic eczematous dermatitis or hives.

(D) Eye contact: Formaldehyde solutions splashed in the eye can cause injuries ranging from transient discomfort to severe, permanent corneal clouding and loss of vision. The severity of the effect depends on the concentration of formaldehyde in the solution and whether or not the eyes are flushed with water immediately after the accident.

Note: The perception of formaldehyde by odor and eye irritation becomes less sensitive with time as one adapts to formaldehyde. This can lead to overexposure if a worker is relying on formaldehyde's warning properties to alert him or her to the potential for exposure.

(E) Acute animal toxicity:
(I) Oral, rats: LD50=800 mg/kg.
(II) Oral, mouse: LD50=42 mg/kg.
(III) Inhalation, rats: LC50=250 mg/kg.
(IV) Inhalation, mouse: LC50=900 mg/kg.
(V) Inhalation, rats: LC50=590 mg/kg.

(g) Chronic effects of exposure.
(i) Carcinogenicity: Formaldehyde has the potential to cause cancer in humans. Repeated and prolonged exposure increases the risk. Various animal experiments have conclusively shown formaldehyde to be a carcinogen in rats. In humans, formaldehyde exposure has been associated with cancers of the lung, nasopharynx and oropharynx, and nasal passages.

(ii) Mutagenicity: Formaldehyde is genotoxic in several in vitro test systems showing properties of both an initiator and a promoter.

(iii) Toxicity: Prolonged or repeated exposure to formaldehyde may result in respiratory impairment. Rats exposed to formaldehyde at 2 ppm developed benign nasal tumors and changes of the cell structure in the nose as well as inflamed mucous membranes of the nose. Structural changes in the epithelial cells in the human nose have also been observed. Some persons have developed asthma or bronchitis following exposure to formaldehyde, most often as the result of an accidental spill involving a single exposure to a high concentration of formaldehyde.

(h) Emergency and first-aid procedures.
(i) Ingestion (swallowing): If the victim is conscious, dilute, inactivate, or absorb the ingested formaldehyde by giving milk, activated charcoal, or water. Any organic material will inactivate formaldehyde. Keep affected person warm and at rest. Get medical attention immediately. If vomiting occurs, keep head lower than hips.

(ii) Inhalation (breathing): Remove the victim from the exposure area to fresh air immediately. Where the formaldehyde concentration may be very high, each rescuer must put on a self-contained breathing apparatus before attempting to remove the victim, and medical personnel should be informed of the formaldehyde exposure immediately. If breathing has stopped, give artificial respiration. Keep the affected person warm and at rest. Qualified first-aid or medical personnel should administer oxygen, if available, and maintain the patient's airways and blood pressure until the victim can be transported to a medical facility. If exposure results in a highly irritated upper respiratory tract and coughing continues for more than ten minutes, the worker should be hospitalized for observation and treatment.
(iii) Skin contact: Remove contaminated clothing (including shoes) immediately. Wash the affected area of your body with soap or mild detergent and large amounts of water until no evidence of the chemical remains (at least fifteen to twenty minutes). If there are chemical burns, get first aid to cover the area with sterile, dry dressing, and bandages. Get medical attention if you experience appreciable eye or respiratory irritation.

(iv) Eye contact: Wash the eyes immediately with large amounts of water occasionally lifting lower and upper lids, until no evidence of chemical remains (at least fifteen to twenty minutes). In case of burns, apply sterile bandages loosely without medication. Get medical attention immediately. If you have experienced appreciable eye irritation from a splash or excessive exposure, you should be referred promptly to an ophthalmologist for evaluation.

(i) Emergency procedures.

(ii) Emergencies:

(A) If you work in an area where a large amount of formaldehyde could be released in an accident or from equipment failure, your employer must develop procedures to be followed in event of an emergency. You should be trained in your specific duties in the event of an emergency, and it is important that you clearly understand these duties. Emergency equipment must be accessible and you should be trained to use any equipment that you might need. Formaldehyde contaminated equipment must be cleaned before reuse.

(B) If a spill of appreciable quantity occurs, leave the area quickly unless you have specific emergency duties. Do not touch spilled material. Designated persons may stop the leak and shut off ignition sources if these procedures can be done without risk. Designated persons should isolate the hazard area and deny entry except for necessary people protected by suitable protective clothing and respirators adequate for the exposure. Use water spray to reduce vapors. Do not smoke, and prohibit all flames or flares in the hazard area.

(ii) Special firefighting procedures:

(A) Learn procedures and responsibilities in the event of a fire in your workplace.

(B) Become familiar with the appropriate equipment and supplies and their location.

(C) In firefighting, withdraw immediately in case of rising sound from venting safety device or any discoloration of storage tank due to fire.

(j) Spill, leak, and disposal procedures.

(i) Occupational spill: For small containers, place the leaking container in a well ventilated area. Take up small spills with absorbent material and place the waste into properly labeled containers for later disposal. For larger spills, dike the spill to minimize contamination and facilitate salvage or disposal. You may be able to neutralize the spill with sodium hydroxide or sodium sulfite. Your employer must comply with EPA rules regarding the clean-up of toxic waste and notify state and local authorities, if required. If the spill is greater than 1,000 lb/day, it is reportable under EPA's superfund legislation.

(ii) Waste disposal: Your employer must dispose of waste containing formaldehyde in accordance with applicable local, state, and federal law and in a manner that minimizes exposure of employees at the site and of the clean-up crew.

(k) Monitoring and measurement procedures.
(i) Monitoring requirements: If your exposure to formaldehyde exceeds the 0.5 ppm action level or the 2 ppm STEL, your employer must monitor your exposure. Your employer need not measure every exposure if a "high exposure" employee can be identified. This person usually spends the greatest amount of time nearest the process equipment. If you are a "representative employee," you will be asked to wear a sampling device to collect formaldehyde. This device may be a passive badge, a sorbent tube attached to a pump, or an impinger containing liquid. You should perform your work as usual, but inform the person who is conducting the monitoring of any difficulties you are having wearing the device.

(ii) Evaluation of 8-hour exposure: Measurements taken for the purpose of determining time-weighted average (TWA) exposures are best taken with samples covering the full shift. Samples collected must be taken from the employee's breathing zone air.

(iii) Short-term exposure evaluation: If there are tasks that involve brief but intense exposure to formaldehyde, employee exposure must be measured to assure compliance with the STEL. Sample collections are for brief periods, only fifteen minutes, but several samples may be needed to identify the peak exposure.

(iv) Monitoring techniques: WISHA's only requirement for selecting a method for sampling and analysis is that the methods used accurately evaluate the concentration of formaldehyde in employees' breathing zones. Sampling and analysis may be performed by collection of formaldehyde on liquid or solid sorbents with subsequent chemical analysis. Sampling and analysis may also be performed by passive diffusion monitors and short-term exposure may be measured by instruments such as real-time continuous monitoring systems and portable direct reading instruments.

(v) Notification of results: Your employer must inform you of the results of exposure monitoring representative of your job. You may be informed in writing, but posting the results where you have ready access to them constitutes compliance with the standard.

(l) Protective equipment and clothing.

(Material impervious to formaldehyde is needed if the employee handles formaldehyde solutions of one percent or more. Other employees may also require protective clothing or equipment to prevent dermatitis.)

(i) Respiratory protection. Use NIOSH-approved full facepiece negative pressure respirators equipped with approved cartridges or canisters within the use limitations of these devices. (Present restrictions on cartridges and canisters do not permit them to be used for a full workshift.) In all other situations, use positive pressure respirators such as the positive-pressure air purifying respirator or the self-contained breathing apparatus (SCBA).

(ii) Protective gloves:

(A) Wear protective (impervious) gloves provided by your employer, at no cost, to prevent contact with formalin.

(B) Your employer should select these gloves based on the results of permeation testing and in accordance with the ACGIH guidelines for selection of chemical protective clothing.

(iii) Eye protection:

(A) If you might be splashed in the eyes with formalin, it is essential that you wear goggles or some other type of complete protection for the eye.

(B) You may also need a face shield if your face is likely to be splashed with formalin, but you must not substitute face shields for
eye protection. (This section pertains to formaldehyde solutions of one percent or more.)

(iv) Other protective equipment:
(A) You must wear protective (impervious) clothing and equipment provided by your employer at no cost to prevent repeated or prolonged contact with formaldehyde liquids.

(B) If you are required to change into whole-body chemical protective clothing, your employer must provide a change room for your privacy and for storage of your normal clothing.

(C) If you are splashed with formaldehyde, use the emergency showers and eyewash fountains provided by your employer immediately to prevent serious injury. Report the incident to your supervisor and obtain necessary medical support.

(2) Entry into an IDLH atmosphere. Enter areas where the formaldehyde concentration might be 100 ppm or more only with complete body protection including a self-contained breathing apparatus with a full facepiece operated in a positive pressure mode or a supplied-air respirator with full facepiece and operated in a positive pressure mode. This equipment is essential to protect your life and health under such extreme conditions.

(a) Engineering controls.
(i) Ventilation is the most widely applied engineering control method for reducing the concentration of airborne substances in the breathing zones of workers. There are two distinct types of ventilation.

(ii) Local exhaust: Local exhaust ventilation is designed to capture airborne contaminants as near to the point of generation as possible. To protect you, the direction of contaminant flow must always be toward the local exhaust system inlet and away from you.

(iii) General (mechanical):

(A) General dilution ventilation involves continuous introduction of fresh air into the workroom to mix with the contaminated air and lower your breathing zone concentration of formaldehyde. Effectiveness depends on the number of air changes per hour.

(B) Where devices emitting formaldehyde are spread out over a large area, general dilution ventilation may be the only practical method of control.

(iv) Work practices: Work practices and administrative procedures are an important part of a control system. If you are asked to perform a task in a certain manner to limit your exposure to formaldehyde, it is extremely important that you follow these procedures.

(b) Medical surveillance.

(i) Medical surveillance helps to protect employees’ health. You are encouraged strongly to participate in the medical surveillance program.

(ii) Your employer must make a medical surveillance program available at no expense to you and at a reasonable time and place if you are exposed to formaldehyde at concentrations above 0.5 ppm as an 8-hour average or 2 ppm over any fifteen-minute period.

(A) You will be offered medical surveillance at the time of your initial assignment and once a year afterward as long as your exposure is at least 0.5 ppm (action level) or 2 ppm (STEL).

(B) Even if your exposure is below these levels, you should inform your employer if you have signs and symptoms that you suspect, through your training, are related to your formaldehyde exposure because you may need medical surveillance to determine if your health is being impaired by your exposure.
(iii) The surveillance plan includes:
(A) A medical disease questionnaire.
(B) A physical examination if the physician determines this is necessary.
(iv) If you are required to wear a respirator, your employer must offer you a physical examination and a pulmonary function test every year.
(v) The physician must collect all information needed to determine if you are at increased risk from your exposure to formaldehyde. At the physician's discretion, the medical examination may include other tests, such as a chest X-ray, to make this determination.
(vi) After a medical examination the physician will provide your employer with a written opinion which includes any special protective measures recommended and any restrictions on your exposure. The physician must inform you of any medical conditions you have which would be aggravated by exposure to formaldehyde. All records from your medical examinations, including disease surveys, must be retained at your employer's expense.
(c) Emergencies.
(i) If you are exposed to formaldehyde in an emergency and develop signs or symptoms associated with acute toxicity from formaldehyde exposure, your employer must provide you with a medical examination as soon as possible.
(ii) This medical examination will include all steps necessary to stabilize your health.
(iii) You may be kept in the hospital for observation if your symptoms are severe to ensure that any delayed effects are recognized and treated.