

## V. WORK PRACTICES

In all workplaces where the vinyl halides are produced, handled, used, or stored, employers should supplement engineering and administrative controls with appropriate work practice programs. Work practice programs should be oriented toward methods for handling vinyl halides, procedures for cleaning up spills and responding to emergencies, and use and care of personal protective clothing and equipment. In addition, a regular program of instruction should be established to ensure that all potentially exposed employees are familiar with the specific hazards of each vinyl halide and with appropriate procedures for handling them. Employers should inform employees of any adverse effects that could be caused by inhalation of decomposition products. If contractors are employed for maintenance and repair activities or cleaning of vinyl contaminated equipment, employers should ensure that the contractor personnel are also familiar with the hazards of the compounds and with precautions to be taken when performing their duties. Employers may use the Material Safety Data Sheet presented in Appendix XVI as a guide in providing employees with the necessary information.

The vinyl halides vary in their toxicities (Chapter III) and their chemical and physical properties (see Table XVII-1). Although this chapter and the literature cited in it deal mainly with vinyl chloride, all of the vinyl halides are similarly produced, handled, stored, and transported. Similar practices and engineering controls will usually be applicable, therefore, to all vinyl halides; those specific for each halide are discussed separately. The control procedures outlined in Chapter IV for specific processes involving vinyl chloride are not a substitute for good general work practices.

Since the promulgation of the 1974 Federal occupational exposure limit of 1 ppm (2.56 mg/cu m) for vinyl chloride, many papers have been published on various ways to reduce worker exposure to this compound. Although some practices are applicable to work with vinyl chloride at any time, most controls and practices can be separated into those that apply to monomer production, those that apply during polymer production, and those that apply during polymer fabrication or processing.

Although closed loop systems may be used for quality-control sampling, the proximity of the employee to the sample cylinder connections greatly increases the likelihood of exposure in the event of leaks [280]. Therefore, caution should be used in collecting quality-control samples even where closed loops are used.

All work areas in which exposure to vinylidene chloride or vinyl bromide may occur should be posted with warnings that a potential human carcinogen is

present. For potential exposure to vinyl chloride, the area should be posted to warn that a human carcinogen is present.

Entry into regulated areas, as defined in Appendix I (29 CFR 1910.1017 (e)), or confined or enclosed spaces should be carefully controlled by a permit system or the equivalent. A confined or enclosed space is usually thought of as any reactor, autoclave, tank, chamber, vat, pit, pipe, flue, duct, bunker, or undergrade room and only properly protected personnel trained in emergency procedures should be permitted to enter such areas [305,297]. Unauthorized personnel and those not properly protected should not be permitted to enter regulated areas or confined or enclosed spaces. Records of those who enter these spaces should be kept by means of a daily log, employment records, or the equivalent. Properly fitted protective clothing and equipment should be worn by anyone entering such areas, and suitable respiratory equipment should be worn if vinyl concentrations exceed the permissible exposure limits.

Whenever airborne vinyl halide concentrations exceed the recommended environmental limits, respirators must be used in accordance with Table I-1. The current Federal standard for vinyl chloride allows the use of a chemical cartridge respirator or a gas mask, front- or back-mounted canister, at concentrations of vinyl chloride not exceeding 10 ppm or 25 ppm, respectively. Service life requirements, 1 hour for a cartridge and 4 hours for a canister, are also listed (29 CFR 1910.1017 (g)). NIOSH, however, has also required that end-of-service-life indicators be used with cartridge and canister air-purifying respirators. In December 1974, NIOSH and MSHA published the requirements for a canister or cartridge respirator with end-of-service-life indicators for use in vinyl chloride atmospheres (30 CFR 11.200-11.208). NIOSH has recently approved the 3M No. 8716 vinyl chloride cartridge respirator, which has an end-of-service-life indicator, for use in vinyl chloride at concentrations up to 10 ppm (DP Wilmes, written communication, February 1978). End-of-service-life indicators for canister gas masks for vinyl halides have yet to be developed. To prevent exposure through leakage, NIOSH recommends that each employee be provided an appropriate individually-fitted respirator in good, clean condition, and that employees be drilled in the use of these respirators and in testing them for leakage, proper fit, and proper operation.

Since vinyl chloride, vinyl bromide, vinyl fluoride, and vinylidene fluoride are gases at ambient conditions and are liquids only under pressure, a hazard from splashes rarely exists under normal working conditions. These compounds can nevertheless cause eye and skin irritation, and contact with them should be avoided. Vinylidene chloride is a liquid at ambient conditions. Because the pressurized materials evaporate rapidly on release, excessive exposure to undiluted liquid vinyls could cause a "frostbite" type of "burn" [298,299,300]. Warnings against skin irritation and burns from contact with liquid vinylidene chloride and vinyl chloride have been published [299,301]. Phenolic inhibitors of polymerization, formerly used widely, have been implicated in the causation of burns by contact with surfaces from which

the inhibited vinyl monomer had evaporated, leaving a film of the inhibitor [301]. If a vinyl halide is splashed on the skin, the affected areas should immediately be washed with soap and water. If eye exposure occurs, the affected eye should be rinsed with water for at least 15 minutes, and medical attention should be obtained as soon as possible [297]. Eyewash fountains and emergency showers should be located near all vinyl exposure areas and should be readily accessible.

Employees who handle vinyl or enter vinyl exposure areas should be provided with appropriate clothing. Protective clothing should be provided clean and dry for each use. To prevent contamination of other work areas, employees should not wear protective clothing outside exposure areas. In most vinyl operations, employees should use coveralls made of any nonsparking material [305]. Employees should also wear safety goggles or glasses with side shields, hardhats, respiratory protective equipment, rubber gloves, and boots whenever they enter confined or regulated areas [297]. One vinyl bromide manufacturer has recommended that neoprene gloves and boots be worn by employees opening process lines and repairing pumps and that a one-piece nylon suit, vinyl-coated on both sides, with attached neoprene boots and gloves be worn by employees entering a reactor vessel or tank [14]. Employers should warn employees that heat stroke may result from the wearing of impervious clothing.

Vinyl-contaminated work clothing should be kept separate from street clothing and should not be removed from the work area. Employers should provide shower and change rooms with locker room facilities that allow for complete separation of work and street clothing. Employers should encourage all employees working in areas where exposure to vinyls might occur to shower before changing from work clothes into street clothes. Employers should be responsible for the laundering of contaminated or soiled clothing, and no employee should be allowed to take or wear home any work clothing. All work clothing should be adequately cleaned after each wearing. Employers should inform laundry personnel of the possible hazard from vinyl contaminants on work clothing. Although the vinyl halides are at most only slightly soluble in water, clothing contaminated with liquid vinyls should be allowed to dry before being laundered. This should be done in a vacuum or other enclosed system provided with air ventilation devices in order to prevent vinyl halide release into the laundry or work area. Waste water should be handled in accordance with all applicable Federal, state, and local regulations.

The vinyl halides addressed in this document are flammable over wide ranges of concentrations in air, and contact with ignition sources should therefore be avoided. Vinyl chloride, vinylidene chloride, vinyl fluoride, and vinylidene fluoride have been reported to be explosive at concentrations of 3.6-33.0, 7-16.0, 2.6-21.7, and 5.5-21.3% by volume in air, respectively [302,303]. A producer of vinyl bromide reported that vinyl bromide at concentrations of 6.0-15% by volume in air may ignite in the presence of high-energy ignition sources and suggested that vinyl bromide be handled as a moderately flammable material [304].

Since the vinyl halides are so readily flammable, it is important to prohibit smoking, carrying of uncovered smoking materials such as matches and lighters, open flames, and use of materials that can cause sparks in areas where vinyls are present. Smoking if allowed at all on the plant site should be restricted to designated areas. Signs warning of a danger of fire or explosion should be posted in areas where vinyls are produced, handled, or stored, and transport containers should have warning labels. Warning signs should also be prominently posted in areas where spills and leaks are likely to occur. Process equipment, such as tanks, pipelines, pumps, and compressors, should be grounded to prevent the build up of static electricity [299]. Firefighting and respiratory protective equipment should be readily available for use in case of emergency. Employers should inform firefighting personnel of the possible combustion products of the vinyl halides. Vinyl chloride combustion products include phosgene, hydrogen chloride, carbon monoxide, carbon dioxide, and water. Hydrogen chloride is also a major combustion product of vinylidene chloride. Employers should therefore provide firefighters with protective equipment to prevent injury from inhalation or contact with the combustion products. Vandervort and Brooks [305] reported that the major thermal decomposition products of polyvinyl chloride films were di-2-ethylhexyl adipate and hydrogen chloride. The authors found no vinyl chloride emissions during hot-wire cutting of the film, but warned against inhalation of aerosol particles from di-2-ethylhexyl adipate and hydrogen chloride.

To ensure the effectiveness of recommended work practices in protecting the employees' health, employers should require that all employees participate in an orientation program when they are hired and in periodic information seminars led by personnel qualified by experience or training. During orientation, employees should be informed of the hazards associated with handling of the vinyl halides and of the precautions that should be taken to prevent injury or illness. Employers should also inform employees that vinyl chloride is a known human carcinogen and that the other vinyls are potential human carcinogens. Employees should be made thoroughly familiar with emergency and evacuation procedures.

Periodic training of employees should include opportunities for employees to meet with management personnel to discuss or review safety procedures and new toxicologic findings. New information on the vinyl halides should be posted in designated areas accessible to employees. It is essential to stress the importance of the employees' cooperation with management in preventing adverse effects of exposure to vinyls, and employees should be encouraged to report all circumstances that might create the potential for such exposure.

## VI. DEVELOPMENT OF STANDARD

### Basis for Previous Standards

#### (a) Vinyl Chloride

Standards for regulation of exposure to vinyl chloride in the United States were first reported in 1945 in Cook's review [306] of maximum allowable concentrations (MAC's) of industrial atmospheric contaminants. A Utah State Department of Health recommendation of 500 ppm (1,280 mg/cu m) was cited. A 1930 report by Patty et al [16] indicated that guinea pigs exposed to vinyl chloride at 5,000 or 10,000 ppm (12,800 or 25,600 mg/cu m) for as long as 500 minutes "showed no symptoms." Cook [306] recommended an MAC of 1,000 ppm for prolonged exposure. Citing the lack of long-term animal experimentation data and of data on industrial exposure at known concentrations, Cook recommended medical observation of workers exposed to vinyl chloride at concentrations near the suggested limit.

In 1946, the American Conference of Governmental Industrial Hygienists (ACGIH) [307] recommended an MAC of 500 ppm (1,280 mg/cu m) for vinyl chloride. When the ACGIH changed its terminology in 1949 [308], this limit became the Threshold Limit Value (TLV) for vinyl chloride. According to the 1962 Documentation of Threshold Limit Values [309], the ACGIH TLV was also based on the study by Patty et al [16]. The 1962 documentation [309] noted that narcosis was the most important effect of exposure to vinyl chloride, and that the TLV of 500 ppm (approximately 1,300 mg/cu m) "appears to be sufficiently low to prevent significant narcosis."

In the Threshold Limit Values for 1963 [310], it was noted that a TLV in the form of a time-weighted average (TWA) concentration limit might not provide a sufficient safety factor for acutely acting substances. Consequently, a "C" or "ceiling" designation was appended to the value for vinyl chloride, indicating that the TLV, which remained at 500 ppm, was a limit that should not be exceeded.

Although the TLV had not changed, the 1966 Documentation of Threshold Limit Values [311] cited several studies that presented conflicting data. Torkelson et al [113] found liver damage in rabbits exposed repeatedly for 7 hours to vinyl chloride at 200 ppm (512 mg/cu m) and slight increases in liver weights of rats exposed at 100 ppm. Other animals were unaffected at 100 ppm. The authors suggested that worker exposure be controlled so that results for practically all analytical measurements were less than 100 ppm (256 mg/cu m) and that the TWA concentration for all exposures be limited to 50 ppm (128 mg/cu m). Lester et al [18] found some increase in the relative weights of the liver and spleen in rats exposed repeatedly to vinyl chloride at concentrations of 20,000 ppm (51,200 mg/cu m) for 92 days and 50,000 ppm (128,000 mg/cu m) for 19 days. They did not consider these changes

significantly pathologic, and they concluded that the accepted TLV for vinyl chloride of 500 ppm (1,300 mg/cu m) was adequate to protect workers. The 1966 documentation [311] concluded that, "although the available data are conflicting, the preponderance indicates a compound of relatively low toxicity with which a threshold limit of 500 ppm is consistent."

In 1970, the ACGIH [312] announced its intention to reduce the TLV for vinyl chloride to 200 ppm. In 1972, the ACGIH [313] reduced the TLV for vinyl chloride to 200 ppm (770 mg/cu m [sic], actually equivalent to 512 mg/cu m) as an 8-hour TWA concentration. Several studies supporting this action were cited in the 1971 Documentation of Threshold Limit Values for Substances in Workroom Air [314], including the 1961 study by Torkelson et al [113] and the 1963 study by Lester et al [18]. The documentation also cited a study, conducted between 1950 and 1967 and presented in 1968 by Mutchler and Kramer [315], of exposure of chemical plant workers. Workers exposed to vinyl chloride (with about 5 ppm of vinylidene chloride) at a mean concentration of 160 ppm (410 mg/cu m) did not have significant changes in blood pressure, concentration of hemoglobin in the blood, or ECG's, and acroosteolysis was not found. However, changes of possible physiologic significance were noted in serum beta-lipoprotein, icteric index, and sulfobromophthalein retention. Based on analysis of these data, the authors suggested that some liver dysfunction might result from exposure to vinyl chloride (combined with 5 ppm of vinylidene chloride) at a TWA concentration of 300 ppm (768 mg/cu m) over a working lifetime. The 1971 documentation [314] concluded that a TWA environmental limit of 200 ppm (770 mg/cu m) for vinyl chloride (with a few ppm of vinylidene chloride) "seems appropriate to prevent adverse systemic effects from long-continued daily exposure."

In 1974, the ACGIH [316] published a notice that the TLV for vinyl chloride would be reassigned as a result of its newly discovered carcinogenic potential. No specific studies were cited in support of this action. As of 1977, the TLV for vinyl chloride still awaited reassignment pending the acquisition of more definitive data [317].

According to a 1968 joint report of the International Labour Office and the World Health Organization [318], permissible limits set by foreign countries for vinyl chloride in the working environment include 30 mg/cu m for Bulgaria and 1 mg/cu m for the United Arab Republic and the Syrian Arab Republic. The German Democratic Republic has a limit of 500 mg/cu m for vinyl chloride in the work environment [319].

Limits adopted in foreign countries since 1974 reflect the accumulating evidence of the carcinogenic potential of vinyl chloride. The United Kingdom has set 25 ppm (64 mg/cu m) as a TWA limit, with a 50 ppm (128 mg/cu m) ceiling limit [305], until more definitive information is available. In 1976, the Federal Republic of Germany established Technical Guideline Concentrations for vinyl chloride of 10 ppm (26 mg/cu m) in existing polymerization plants and 5 ppm (13 mg/cu m) elsewhere until such time as an MAC value could be assigned [320]. Sweden established an 8-hour TWA limit of 1 ppm (2.5 mg/cu m)

and a ceiling limit of 5 ppm (13 mg/cu m) for exposure to vinyl chloride [321]. The Swedish document noted that vinyl chloride has carcinogenic properties and that it may be absorbed to a considerable extent through the skin.

The International Labour Office [322] recently published the following national occupational exposure limits for vinyl chloride: Yugoslavia, 75 ppm (300 mg/cu m [sic], actually equivalent to 195 mg/cu m); Rumania, 100 mg/cu m as a TWA limit and 200 mg/cu m as a ceiling limit; Australia, 25 ppm (95 mg/cu m [sic], actually equivalent to 64 mg/cu m); Hungary, 50 mg/cu m; Poland and USSR, 30 mg/cu m; Netherlands, 10 ppm (26 mg/cu m) as a ceiling limit; Finland, 10 ppm (26 mg/cu m); and Japan, 2.5 mg/cu m. In Italy, vinyl chloride is regarded as a human carcinogen, and an exposure limit of 5 ppm (13 mg/cu m) has been recommended. However, the exposure limit is intended as a guideline, as are those of Australia, Japan, and the Netherlands, and is not legally binding. In Switzerland, vinyl chloride is regarded as a probable human carcinogen also, and a provisional exposure limit of 10 ppm (26.5 mg/cu m) has been established. Switzerland also requires that the best available technical and medical protective measures be applied to ensure maximum reduction of risk from exposure to vinyl chloride.

The 1971 US Federal standard for workplace exposure to vinyl chloride (29 CFR 1910.93) was a ceiling limit of 500 ppm (1,280 mg/cu m), based on the 1968 TLV [323]. On January 22, 1974, NIOSH informed the Occupational Safety and Health Administration (OSHA) that the BF Goodrich Chemical Company had reported the deaths of several of its employees from angiosarcoma of the liver, and that the deaths may have been occupationally related. A fact-finding hearing began on February 15, 1974 (reported in the Federal Register 39:35890, October 4, 1974), after consultation with NIOSH and a joint inspection of the BF Goodrich plant by OSHA, NIOSH, and Kentucky Department of Labor personnel. Preliminary reports of experiments conducted by Cesare Maltoni of the Instituto di Oncologia, Bologna, Italy, and other information disclosed at this hearing indicated that vinyl chloride could induce angiosarcoma in the liver of rats at exposure concentrations as low as 250 ppm (640 mg/cu m). OSHA concluded from the information presented at the hearing and in posthearing comments that occupational exposure to vinyl chloride was probably the cause of angiosarcoma of the livers observed in workers in the industry. An Emergency Temporary Standard (ETS) was promulgated on April 5, 1974 (Federal Register 39:12342), as 29 CFR 1910.93(q). This standard reduced the permissible exposure level to 50 ppm (128 mg/cu m), as a ceiling limit, and established other requirements, including monitoring and respiratory protection.

OSHA published a proposed permanent standard (Federal Register 39:16896, May 10, 1974) for the regulation of exposure to vinyl chloride. The proposed standard specified that employee exposure be limited to "no detectable level" as determined by a sampling and analytical method sensitive to 1 ppm with an accuracy of 1 ppm  $\pm$ 50%. The proposal also called for monitoring employee exposures and implementing engineering control and work practice programs when

necessary. Hearings on this proposal were conducted from June 25 through June 28 and from July 8 through July 11, 1974. The carcinogenicity of vinyl chloride in three animal species was documented in the record of this proceeding by the studies of Maltoni and of Industrial Bio-Test Laboratories (Federal Register 39:35891, October 4, 1974). These studies demonstrated the induction of angiosarcoma of the liver in rats and mice exposed to vinyl chloride at concentrations as low as 50 ppm (128 mg/cu m) and in hamsters exposed at higher concentrations. Evidence presented by these and other investigators also indicated additional tumorigenic and toxicologic properties of vinyl chloride. OSHA concluded from these findings of angiosarcoma of the liver in experimental animals and employees exposed to vinyl chloride that vinyl chloride "must be regarded as a human carcinogen, and the probable causal agent of angiosarcoma of the liver, and that exposure of employees to vinyl chloride must be controlled."

The current permanent standard for worker exposure to vinyl chloride was promulgated on October 4, 1974 (Federal Register 39:35896) and became effective January 1, 1975. The standard (29 CFR 1910.1017), presented as Appendix I of this document, includes an 8-hour TWA exposure limit of 1 ppm and a ceiling limit of 5 ppm, averaged over any period not exceeding 15 minutes. The standard specifies that no employee may be exposed to direct contact with liquid vinyl chloride. The standard also establishes requirements for monitoring employee exposure, providing respiratory protection, and instituting medical surveillance programs. A TWA action level of 0.5 ppm (1.3 mg/cu m) also is specified in the standard. Where the results of monitoring show that no employee is exposed in excess of the action level, employers are exempted from certain provisions of the standard.

(b) Vinylidene Chloride

In 1975, the ACGIH adopted a TLV of 10 ppm (40 mg/cu m) for vinylidene chloride [324]. Several studies were cited in the 1971 Documentation of Threshold Limit Values for Substances in Workroom Air [314] in support of this limit. Increased mortality in rats, rabbits, guinea pigs, and monkeys exposed to vinylidene chloride at concentrations as low as 61 mg/cu m (15.4 ppm) for 90 days was reported by Prendergast et al [122]. Gage [120] found that after vinylidene chloride inhalation 6 hours/day for 20 days at 500 ppm (1,985 mg/cu m) there was nasal irritation, retarded weight gain, and liver cell degeneration in rats. At 200 ppm (794 mg/cu m), there was only slight nasal irritation, and no liver cell abnormalities were observed. Irish [114] reported liver and kidney damage in rats, rabbits, guinea pigs, and dogs exposed to vinylidene chloride for 6 months at concentrations as low as 25 ppm (99 mg/cu m), and he suggested that concentrations in workplaces be maintained below 25 ppm.

In 1976, the ACGIH [325] adopted a tentative Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) of 20 ppm (79 mg/cu m) for vinylidene chloride. The TLV-STEL was described as the maximum concentration at which employees could be exposed continuously for up to 15 minutes without suffering



from intolerable irritation, chronic or irreversible tissue change, or narcosis sufficient to increase accident proneness, impair self-rescue, or reduce work efficiency. It should be noted that the 1976 STEL's were not determined on the basis of occupational or experimental data; rather, they were set empirically. A provision limiting the number of 20-ppm excursions to no more than four each day, with at least 60 minutes between exposure periods, was also included.

According to the 1968 joint report of the International Labour Office and the World Health Organization [318], national permissible limits for vinylidene chloride in the working environment include the following: Yugoslavia, 200 ppm (794 mg/cu m), listed as "dichloroethylene," and Bulgaria and Hungary, 50 mg/cu m, listed as "dichloroethylene." A 1977 publication of the International Labour Office [322] lists the following occupational exposure limits for vinylidene chloride in foreign countries: Rumania, 500 mg/cu m as a TWA limit and 700 mg/cu m as a ceiling limit; Poland and USSR, 50 mg/cu m as a ceiling limit; and Belgium, Federal Republic of Germany, Netherlands, and Switzerland, 10 ppm (40 mg/cu m). Australia has established a provisional exposure limit of 10 ppm (40 mg/cu m) for vinylidene chloride. The exposure limits shown for Australia and the Netherlands are intended as guidelines and are not legally binding.

No US Federal standard for workplace exposure to vinylidene chloride currently exists.

(c) Vinyl Bromide

In 1971, the ACGIH [326] recommended a TLV for vinyl bromide of 250 ppm (1,095 mg/cu m). This TLV was adopted in 1972 [313].

Two studies were included in the 1971 Documentation of Threshold Limit Values for Substances in Workroom Air [314] as bases for this TLV. In an unpublished study cited by ACGIH, Torkelson determined an oral LD50 of 500 mg/kg in male rats. In acute inhalation studies, Torkelson observed no tissue changes in rats exposed to vinyl bromide at concentrations as high as 25,000 ppm (109,500 mg/cu m). Leong and Torkelson [127] reported no significant pathologic changes in rats exposed for 20 days to vinyl bromide at 10,000 ppm (43,800 mg/cu m). In a chronic inhalation study, they found no significant changes in growth rate, hematology, organ-to-body weight ratio, or gross and microscopic tissue findings as a result of exposure to vinyl bromide at 250 or 500 ppm (1,095 or 2,190 mg/cu m). The ACGIH concluded that "a TLV of 250 ppm should protect against bromide intoxication and organic injury, and...excursions even to 500 ppm would be acceptable provided the time-weighted average does not exceed 250 ppm."

In 1976, in addition to the TWA exposure limit of 250 ppm (1,095 mg/cu m) for vinyl bromide, the ACGIH [325] adopted a tentative TLV-STEL of 250 ppm (1,100 mg/cu m). In 1977, the ACGIH [317] proposed a reduction of the TLV to 5 ppm (22 mg/cu m).

According to a 1977 publication of the International Labour Office [322], exposure limits of 250 ppm (1,095 mg/cu m) for vinyl bromide have been set by Australia, Belgium, Finland, and the Netherlands. The Australian and Dutch limits are intended as guidelines and are not legally binding.

No US Federal standard for workplace exposure to vinyl bromide currently exists.

(d) Vinyl Fluoride

The ACGIH has not adopted a TLV for vinyl fluoride. No US Federal standard for exposure to vinyl fluoride currently exists. No foreign standards have been located.

(e) Vinylidene Fluoride

The ACGIH has not adopted a TLV for vinylidene fluoride. No US Federal standard for exposure to vinylidene fluoride currently exists. No foreign standards have been located.

Basis for the Recommended Standard

(a) Permissible Exposure Limits

Among the vinyl halides discussed in this document, only vinyl chloride is regarded as a known human carcinogen that can induce a characteristic tumor, angiosarcoma of the liver [31,32,34,36,37,40,41]. Animal studies have shown that vinyl chloride [134,135,140], vinyl bromide [327], and vinylidene chloride [140] are capable of inducing angiosarcoma of the liver and other tumors. In these experiments, exposure to vinyl chloride at 50 ppm for 4 hours/day, 5 days/week, for 52 weeks induced angiosarcoma of the liver in 1/59 rats after 135 weeks [135]; vinyl bromide at 250 ppm caused angiosarcoma of the liver in 2/30 rats after 52 weeks [327]; vinylidene chloride at 55 ppm for 6 hours/day, 5 days/week, for up to 12 months caused angiosarcoma of the liver in 3/72 mice [140]. Exposure at higher concentrations induced a greater incidence of tumors and shortened the latency for their development, indicating that there was a dose-response relationship for tumor induction.

No reports in regard to the carcinogenicity of vinyl fluoride or vinylidene fluoride have been located. However, this lack of information cannot be construed as an indication that these compounds have no carcinogenic potential. Each of the vinyl halides may form reactive intermediates that can bind to cellular macromolecules [1-3,210]. Putative metabolic pathways and reactive intermediates are shown in Figure XVII-3. The metabolic studies referenced with the figure, along with information from reports on structure-activity relationships [229, RL Schowen, written communication, September 1977], indicate that both vinyl fluoride and vinylidene fluoride may have the capacity to form intermediates capable of alkylating DNA, RNA, or proteins.

The hazard potential of these compounds in a biologic system is difficult to determine, however, because of detoxication mechanisms (reduction, hydrolysis, and conjugation) that compete with alkylation, as well as repair, mechanisms.

Each of the vinyl halides has been found to be mutagenic in some test system. Vinyl chloride has been shown to have a direct mutagenic effect on Salmonella [146,149,150,162,163]; metabolic activation by microsomal enzyme systems has been shown to increase its mutagenic activity [146,145]. Vinylidene chloride [151,162,173], vinyl bromide (VF Simmon and R Nangham, written communication, August 1977), and vinyl and vinylidene fluorides [174] have also been shown to be mutagenic in bacterial test systems. Since many mutagenic compounds are known to also be carcinogenic, these findings suggest that all the vinyl halides might be potential carcinogens.

No studies have demonstrated teratogenic or other effects on human reproduction from exposure to any of the vinyl halides. Structural abnormalities, including increased numbers of unfused sternebrae, delayed ossification of skull bones, and an increase in the number of lumbar spurs in mice whose dams were exposed to vinyl chloride at 500 ppm during days 6-15 of gestation [132] and in rats exposed in utero to vinylidene chloride at 80 ppm during the same period [133], have been observed. Other reproductive effects included increased resorptions/implants, decreased numbers of live fetuses/litter, and increased fetal crown-rump length [132,133]. The authors of these studies suggested that the abnormalities observed were secondary to the maternal toxicity of the compounds. Although these changes are not generally considered to be evidence of teratogenicity, they do indicate fetotoxic effects from maternal exposure to vinyl chloride.

Other adverse health effects attributed to exposure to vinyl halides include CNS [18-20,33,78,114,127,129], cardiovascular [19,20,32,33,78,107,110,121], respiratory [19,32,106,120,122,140], skin [19-21,32,111,112], and skeletal effects [20,21,32,35,74,78,111,112], as well as liver and spleen abnormalities [18-20,30-32,36-39,78,113].

The risk to the health of employees exposed to the vinyl halides is a combination of the risks of neoplastic and other systemic effects from their inhalation or ingestion and of their subsequent metabolism to reactive intermediates.

The observation of neoplasms in humans and animals exposed to vinyl chloride and in animals exposed to vinylidene chloride and vinyl bromide, the similarities in the excreted metabolic products of the vinyl halides, and the calculations of relative reactivity of these compounds on the basis of their physical and chemical properties suggest that each of the five may have a neoplastic potential.

Concern for employee health requires that risk of carcinogenesis as a result of workplace exposure to these compounds be minimized. NIOSH believes that sufficient information does not exist to warrant changing the present Federal Standard for vinyl chloride as stated in 29 CFR 1910.1017. Further,

NIOSH believes that the available information on vinylidene chloride and vinyl bromide indicates that they are at least as toxic as vinyl chloride. Although sufficient biologic information is not available concerning vinyl fluoride and vinylidene fluoride, chemical information suggests that these compounds may also exhibit toxicities similar to that of vinyl chloride, ie, until better animal toxicity and metabolism data are available, there appears to be no reason to treat the fluorides differently from the other vinyl halides. Therefore, NIOSH recommends that workplace exposure to each of the five vinyl halides be controlled by adherence to the provisions of 29 CFR 1910.1017, and on the basis of animal carcinogenicity data, NIOSH suggests that employers make every effort to limit employee exposures to the lowest feasible levels with an eventual goal of zero exposure. As pointed out in Chapter IV there has been a steady decline in workplace environmental concentrations of vinyl chloride since 1974. The lower limits of reliable detectability (see Appendices II-III) are 0.003 ppm for vinyl chloride and 0.5 ppm for vinylidene chloride. Workplace concentrations of vinyl bromide have been measured as low as 0.01 ppm [249]. Vinyl fluoride and vinylidene fluoride in air samples have been measured at concentrations as low as 1 ppm and 2 ppm respectively (see Appendices V-VI).

Since the promulgation of the vinyl chloride standard in 29 CFR 1910.1017 in October, 1974, several advances in respirator technology have taken place. Table I-1 reflects the latest developments in respiratory protection, and NIOSH recommends the substitution of these provisions and requirements for those contained in 29 CFR 1910.1017, paragraph (g).

## VII. COMPATIBILITY WITH OTHER STANDARDS

The Environmental Protection Agency (EPA), the Department of Transportation (DOT), the Food and Drug Administration (FDA), and other Federal agencies have proposed or enacted standards regulating the use or release of several vinyl compounds. The standard recommended by NIOSH in this document for the vinyl halides is compatible with the standards promulgated and proposed by other Federal agencies. Standards proposed by other government agencies that are directly applicable to the standard proposed by NIOSH are reviewed below.

### (a) Vinyl Chloride

In 1976, EPA established a national emission standard for vinyl chloride (40 CFR 61.60-71) because vinyl chloride had been implicated in the development of angiosarcoma and other serious disorders in occupationally exposed persons and in experimentally exposed animals. Vinyl chloride emissions from ethylene dichloride and vinyl chloride production and purification processes were thereby limited to 10 ppm. For the oxychlorination process, vinyl chloride emissions were restricted to 0.2 g/kg of ethylene dichloride product. Vinyl chloride emissions from polymerization plants were limited to 10 ppm through the stripping stage and to 0.02 g/kg of polyvinyl chloride product when reactors were opened. Emissions of vinyl chloride were required to be controlled after stripping operations by reduction of residual monomer in the polymer to below 400 ppm (2,000 ppm for dispersion resins). Where control devices rather than stripping technology were used to limit emissions, dispersion resins were required to be controlled to 2 g/kg of polyvinyl chloride product and all other resins to 0.1 g/kg of polyvinyl chloride product. EPA assumed that adherence to these limits would reduce hazards to the health of the estimated 4.6 million people who live within 5 miles of controlled plants so that the incidence of new primary cancers as a result of exposure to vinyl chloride in this group of people would not exceed 1/year of exposure (Federal Register 41:46560, October 21, 1976). EPA stated that a complete ban on vinyl chloride emissions was not desirable because (1) vinyl chloride has beneficial uses for which substitutes are not available, (2) potential substitutes may have unknown health effects, (3) unemployment would result, and (4) control technology is available to greatly reduce vinyl chloride emissions.

On June 2, 1977, EPA proposed amendments to the national emission standard (Federal Register 42:28154-28159). Sources currently subject to a 10-ppm emission limit and new sources of this type would be required to limit emissions to 5 ppm. Emissions from oxychlorination reactors in ethylene dichloride-vinyl chloride plants would also be limited to 5 ppm. The amendments would direct that residual monomer in the polymer after stripping be limited to 500 ppm in new dispersion resins and 100 ppm in all other new resins. Where control devices rather than stripping technology would be used

to limit emissions, new dispersion resins would have to be controlled to 0.5 g/kg of polyvinyl chloride product and all other new resins to 0.1 g/kg of polyvinyl chloride product. The proposed amendments also would prohibit any increase in emissions due to the construction of new sources within 8 km of existing sources. EPA proposed these amendments in an effort to continue to approach the zero-emissions level for vinyl chloride with available technology because of its determination that this is the only level absolutely protective of health. These limits and proposed amendments are not directly comparable with those proposed by NIOSH, since they do not specify breathing zone sampling. They do, however, reflect the same philosophy espoused by NIOSH; that is, that the final goal is zero exposure.

Aerosol drug products containing vinyl chloride as an ingredient or propellant are considered to be new drugs by FDA and are regulated as such (21 CFR 310.506). EPA (Federal Register 39:14753, April 26, 1974), FDA (21 CFR 700.14), and the Consumer Product Safety Commission (16 CFR 1500.17(a)(10)) have banned the use of vinyl chloride as an ingredient or propellant in aerosol products, including pesticides, cosmetics, and foods, intended for consumer use. These standards are more conservative than that proposed by NIOSH; however, they relate primarily to use of the product and only secondarily to occupational exposure.

FDA proposed rules for regulating the use of vinyl chloride polymers in contact with food on September 3, 1975 (Federal Register 40:40529-37). FDA stated that the use of vinyl chloride polymers and copolymers should be prohibited where there was a reasonable expectation of migration of vinyl chloride monomer into food. FDA proposed a ban on the use of vinyl chloride polymers and copolymers in food-contact articles except where specifically permitted in the FDA regulations. Exceptions to this ban included coatings, gaskets, cap liners, flexible tubing, and plasticized films. Use of polyvinyl chloride in water pipe was also permitted on an interim basis pending the outcome of studies to determine whether vinyl chloride could be extracted by water passing through such pipes. FDA has subsequently published regulations concerning the formulations and amounts of extractable monomer allowable in vinyl chloride copolymer components of paper and paperboard in contact with foods (21 CFR 176). Similar regulations for vinyl chloride copolymers used as basic components of single and repeated use food contact surfaces have also been promulgated (21 CFR 177). These are compatible, although not directly comparable, with the provisions of the NIOSH standard specifying that no food shall be stored, dispensed, prepared, or consumed in vinyl halide exposure areas.

The Materials Transportation Bureau of DOT has designated vinyl chloride as a hazardous material for purposes of transportation in commerce and has established requirements pertaining to its labeling, packaging, and transportation (49 CFR 172.101). Regulations for the bulk transport of vinyl chloride by water have been established by the US Coast Guard (46 CFR 40.15-1, 46 CFR 151.50-34). These regulations also set an exposure limit of 1 ppm (3 mg/cu m), averaged over any 8-hour period, or 5 ppm (13 mg/cu m), averaged

over any 8-hour period, or 5 ppm (13 mg/cu m), averaged over any period not exceeding 15 minutes, for personnel involved in vinyl chloride transfer operations. Continuous monitoring must be conducted during such operations, using a method with an accuracy of not less than  $\pm 50\%$  from 0.25 through 0.5 ppm,  $\pm 35\%$  from 0.5 ppm through 1 ppm, and  $\pm 25\%$  over 1.0 ppm. The US Coast Guard [328] has also developed a cargo compatibility guide for bulk liquid chemicals indicating combinations of chemicals that result in dangerous chemical reactions when accidentally mixed inside a cargo tank or pipe. Vinyl chloride is listed as incompatible with nitric acid and caprolactam solution. Regulations for unmanned barges carrying certain dangerous bulk cargoes, including vinyl chloride, also have been established by the US Coast Guard (46 CFR 151). The Coast Guard standard for occupational exposure is less stringent than that proposed by NIOSH.

(b) Vinylidene Chloride

FDA has published regulations concerning the formulations and amounts of extractable monomer allowable in vinylidene chloride copolymer components of paper and paperboard that come into contact with foods (21 CFR 176). Similar regulations for vinylidene chloride copolymers used as basic components of single and repeated use food contact surfaces have also been established (21 CFR 177).

The Materials Transportation Bureau of DOT has designated vinylidene chloride as a hazardous material for purposes of transportation in commerce and has established requirements pertaining to its labeling, packaging, and transportation (49 CFR 172.101). In its cargo compatibility guide for bulk liquid chemicals, the US Coast Guard [328] has listed vinylidene chloride as incompatible with nitric acid and caprolactam solution. Regulations for unmanned barges carrying certain dangerous bulk cargoes, including vinylidene chloride, have been established by the US Coast Guard (46 CFR 151).

NFPA [329] provides a compilation of information on the hazardous properties and firefighting aspects of vinylidene chloride. This compound is very flammable and readily forms explosive mixtures in air. Polymerization may occur at elevated temperatures, possibly rupturing containers. A readily explosive peroxide may be formed during long-term storage. In the 1975 Manual of Hazardous Reactions [330], NFPA notes that vinylidene chloride polymer is self-reactive and may explode under appropriate conditions. It also reports that mixtures of vinylidene chloride and chlorosulfonic acid, nitric acid, or oleum (fuming sulfuric acid) in closed containers cause increased temperature and pressure. In firefighting operations, NFPA recommended that the gas flow be stopped and that dry chemical, foam, or carbon dioxide be used to extinguish flames. Water may be ineffective in putting out fires, but it should be used to cool containers, protect personnel in the area, flush spills away from flames, and disperse vapors if appropriate. The provisions of the National Electrical Code [331] and those of the Sections of the National Fire Codes dealing with flammable and combustible liquids [335] and static electricity [333] should be complied with where applicable.

(c) Vinyl Fluoride

The Materials Transportation Bureau of DOT has designated vinyl fluoride as a hazardous material for purposes of transportation in commerce and has established requirements pertaining to its labeling, packaging, and transportation (49 CFR 172.101).

(d) Vinylidene Fluoride

FDA has published regulations concerning the formulations and amount of extractable monomer allowable in polyvinylidene fluoride resin components of articles intended for repeated food-contact use (21 CFR 177.2510).

(e) Vinyl Bromide

No other standards were located for this compound.



## VIII. RESEARCH NEEDS

The current information on biologic effects of exposure to the vinyl halides is incomplete. Vinyl chloride has been studied more extensively than the other vinyl halides; however, the exact mechanism of its toxic action is not known. Further studies are needed to obtain additional information.

### (a) Epidemiology

Since one study [101] has suggested that vinyl chloride causes increased fetal mortality in the wives of exposed workers, studies should be performed to investigate this potential for each of the vinyl halides.

Epidemiologic studies should be conducted to compare cohorts from the same plant having various magnitudes of exposure. This can be done relatively easily for the vinyl halides since these compounds are generally produced and used in specific units of large chemical plants. The epidemiologic studies should include precautions to minimize the "healthy worker" and "survivor" effects usually apparent in any worker population.

### (b) Toxic Effects

Exposure to vinyl chloride has been shown to induce a wide variety of toxic effects including central nervous, respiratory, cardiovascular, digestive, skin, and skeletal system effects. Studies should be designed to determine which of these systems are affected directly by vinyl chloride or its metabolites and which effects if any are secondary to the primary systemic effects. Studies should also be conducted to determine the range of toxic effects of exposure to the other vinyl halides. These studies should be designed so that comparison of primary toxic effects can be made between the compounds, ie, the same species, strains, and protocols should be used for each study.

Studies should be conducted to determine the long-term effects of inhaled and ingested vinyl fluorides. Because of the increasing latency of tumor induction with decreasing exposure concentrations reported in studies of animals exposed to vinyl chloride [135], future experiments should not be terminated until the animals become moribund or die.

### (c) Sampling and Analysis

Experiments are needed to validate the lower range of the sampling and analytical methods proposed for vinyl bromide, vinyl fluoride and vinylidene fluoride. Procedures and equipment should be improved to further minimize interferences and standardize the measurement of these compounds.

Although continuous monitoring devices are commercially available for vinyl chloride and vinylidene chloride, such devices are needed for the other

vinyl halides. Research should also be conducted to increase the sensitivity and accuracy of the existing equipment so that reliable, continuous records of exposure for all work areas can be obtained.

Research is also necessary to develop techniques for biologic monitoring. At present, because of the rapid metabolism of the vinyl halides, blood analyses have only indicated adverse effects rather than determining exposures, and urinalysis has not been developed to the extent necessary to define exposures. Further studies of metabolism and excretion may develop the information necessary to calculate the body burden from the excretion products, so that an accurate assessment of the total accumulated dose can be made.

In addition, resources should be expended to assess the current state of control technology and the feasibility of implementing advances in this area. Thought should be given to the feasibility of using less toxic substitutes. Finally, respirators with end-of-service-life indicators should be developed for the vinyl halides for which they are not available.