I. RECOMMENDATIONS FOR A STYRENE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to styrene in the workplace be controlled by compliance with the following sections. These recommendations are designed to protect the health and provide for the safety of workers for up to a 10-hour workshift, 40-hour workweek, over a working lifetime. Compliance with all sections of the recommended standard should prevent or greatly reduce the risk to exposed workers of adverse effects. NIOSH considers the recommended environmental limits for styrene to be upper boundaries of exposure. Thus, employers should make every effort to maintain exposure concentrations as low as possible. This recommended standard will be subject to review and revision as necessary.

Occupational injury and illness attributed to styrene results from inhalation of the vapor or from skin contact with the readily absorbed liquid. The NIOSH recommended standard is primarily based on reports of effects on the human nervous system, and on irritation of the eyes and respiratory system.

Central nervous system (CNS) effects have been observed among experimental subjects as well as workers exposed to styrene at time-weighted average (TWA) concentrations of about 100 parts per million (ppm). In addition, some investigators have reported observing these effects at concentrations less than 100 ppm, both experimentally and clinically. However, the experimental studies are of limited value in establishing a recommended exposure limit because of the small numbers of subjects studied. Similarly, the clinical studies are difficult to interpret because the exposures occurred over a wide range of concentrations, occasionally in excess of 100 ppm. The most frequently reported effects of exposures at about 100 ppm are subjective symptoms such as fatigue, dizziness, headache, nausea, poor memory, and drowsiness. These subjective symptoms of CNS depression have been substantiated experimentally in human subjects and in clinical studies of workers exposed to styrene who demonstrated slower reaction times and impaired balance; abnormal EEGs have also been noted.

It has been reported in a number of clinical studies that chromosome changes occurred with greater frequency in the lymphocytes of workers exposed to styrene at about 100 ppm than among workers not exposed to styrene. Other investigators have reported an increase in the rate of sister chromatid exchanges among styrene-exposed workers. However, the long-term significance of these effects is not clear and requires further elucidation.

Although the evidence is not strong, exposure to styrene has also been implicated with other adverse health effects such as peripheral neuropathy, abnormal pulmonary function, liver toxicity, teratogenicity, and

carcinogenicity. These health effects need further investigation, and would provide additional evidence for a reduction in the current occupational exposure standard if they were found to be styrene-related.

Although additional research is needed to clarify some of the reported effects, worker exposure to styrene should not exceed 50 ppm as a TWA concentration for up to a 10-hour workshift, 40-hour workweek. To prevent CNS depression and irritation of the eyes and respiratory tract, exposures should not exceed 100 ppm, determined as a ceiling concentration by a 15-minute sample.

The "action level" for styrene is defined as one-half the TWA concentration limit for styrene. Due to interday variability of environmental levels, a worker's single TWA exposure measurement over the workshift that is below the recommended standard does not necessarily indicate that exposures on other days would also be below the recommended standard. If a worker's TWA exposure during a workshift is at or above one-half the recommended standard, a sufficient probability exists that on other days exposures could exceed the recommended TWA standard. As such, the concept of an "action level" is needed to ensure adequate protection of the workers. Exposure to styrene below the "action level" will require adherence to all sections of the recommended standard except Sections 2(b), 8(a)(2), and the monitoring provisions of 8(b).

Section 1 - Environmental (Workplace Air)

(a) Concentration (Recommended Environmental Limits)

Exposure to styrene in the workplace shall be controlled so that workers are not exposed to styrene at concentrations greater than 50 parts per million (ppm), determined as a time-weighted average (TWA) exposure concentration for up to a 10-hour workshift, 40-hour workweek. A ceiling concentration of 100 ppm, as determined during any 15-minute sampling period, is also recommended.

(b) Sampling and Analysis

Workroom air samples shall be collected and analyzed as described in Appendix I, or by any other methods at least equivalent in accuracy, precision, and sensitivity.

Section 2 - Medical

The employer shall provide the following information to the physician performing or responsible for the medical surveillance program: the requirements of the applicable standard; an estimate of the worker's potential exposure to styrene, including any available workplace sampling results; a description of the worker's duties as they relate to the

workers's exposure; and a description of any protective equipment the worker may be required to use.

(a) Preplacement medical examinations shall include at least:

(1) Comprehensive medical and work histories with special emphasis on the nervous system, skin, respiratory tract, liver, and eyes.

(2) A physical examination giving special attention to the nervous system, skin, respiratory tract, liver, and eyes. Additional testing, such as clinical tests of liver function and enzymes, should be considered by the physician responsible for the examination.

(3) A judgment of the worker's ability to use positive and negative pressure respirators.

(b) Periodic medical examinations shall be made available at least annually to all workers occupationally exposed to styrene at airborne concentrations at or above the action level, or who have the potential for significant skin exposure (see paragraph (b)(3) of this section). These examinations shall include at least:

(1) An update of medical and work histories.

(2) A physical examination and tests as outlined in paragraph (a)(2) of this section.

(3) In those instances where there is a potential for elevated or widely varying styrene exposures through inhalation and/or skin absorption, measurement of urinary mandelic acid (a styrene metabolite) may serve as a useful adjunct for characterization of workplace styrene exposures (see Appendix II). If the measurement of a worker's urinary mandelic acid suggests possible overexposure to styrene, an effort should be made to ascertain the cause, such as failure of engineering controls, poor work practices, or nonoccupational exposures.

(c) Monitoring of urinary mandelic acid and a physical examination as outlined in paragraph (a)(2) of this section shall be made available to any worker exposed to unknown concentrations of styrene during a spill or emergency.

(d) Workers and potential workers having medical conditions, such as disorders of the nervous or respiratory systems, or a liver disease that could be directly or indirectly aggravated by exposure to styrene, shall be counseled on the possibility of increased risk of impairment to their health from working with styrene.

(e) Following completion of the examination, the physician shall give to the employer a written statement about whether the worker has any detected medical conditions which would place the worker at increased risk

of health impairment from exposure to styrene. The written statement shall include any recommended limitations upon the worker's exposure to styrene or upon the use of respirators. A copy of this written statement obtained by the employer shall not reveal specific findings or diagnoses and shall be provided to the worker.

(f) Pertinent medical records (i.e., the physician's written statement, the results of medical examinations and tests, medical complaints, etc.) for all workers subject to exposure to styrene in the workplace shall be retained for at least 30 years after termination of employment. Copies of environmental monitoring data applicable to a worker shall also be included in that worker's medical records. These records shall be made available to the designated medical representatives of the Secretary of Labor, the Secretary of Health and Human Services, the employer, and the worker or former worker.

(g) The relationship of styrene exposure to adverse reproductive effects has not been thoroughly investigated. Workers shall be made aware of the possibility of such adverse effects.

Section 3 - Labeling and Posting

All labels and warning signs shall be printed both in English and in the predominant language of non-English-reading workers. Workers unable to read the labels and posted signs shall be informed verbally regarding the hazardous areas of the plant or worksite and the instructions printed on labels and signs.

(a) Labeling

Containers of styrene used or stored in the workplace shall carry a permanently attached label that is readily visible. The label shall identify the presence of styrene and give information regarding its effects on human health. The information may be arranged as follows.

STYRENE

CAUTION!

HARMFUL IF INHALED OR IF ABSORBED THROUGH SKIN

IRRITATING TO SKIN, EYES, NOSE, THROAT, MOUTH, AND LUNGS

FLAMMABLE

In case of eye contact, immediately flush eyes with large amounts of water for 15 minutes. If irritation persists, get medical attention. Keep containers closed when not in use. Use only with adequate ventilation. Keep away from heat, sparks, and open flame.

(b) Posting

Readily visible signs containing information on the effects of styrene on human health and emergency measures shall be posted in work areas and at entrances to work areas or building enclosures where there is the likelihood of styrene concentrations above the action level or where the possibility of appreciable spills or skin contact with styrene exist. This information may be arranged as follows.

STYRENE

CAUTION!

HARMFUL IF INHALED OR IF ABSORBED THROUGH SKIN

IRRITATING TO SKIN, EYES, NOSE, THROAT, MOUTH, AND LUNGS

FLAMMABLE

Place cleaning rags and soiled clothing in fireproof containers.
Use chemical fire extinguisher.

(c) Respirators

If respirators are needed during the installation or implementation of required engineering controls, the following statement shall be added in large letters to the sign required in paragraph (b) of this section:

RESPIRATORY PROTECTION REQUIRED IN THIS AREA

(d) Emergency Situations

In any area where there is a likelihood of emergency situations arising, signs required by paragraph (b) of this section shall be supplemented with signs giving emergency and first-aid instructions and procedures, the location of first-aid supplies and emergency equipment, and the locations of emergency showers and eyewash fountains.

Section 4 - Protective Clothing and Equipment

Engineering controls and safe work practices shall be used to keep the concentration of airborne styrene at or below the limits specified in Section 1(a) and to minimize skin and eye contact. In addition, protective clothing and equipment shall be provided by the employer to the workers when necessary.

(a) Eye Protection

The employer shall provide safety glasses, chemical safety goggles, or face shields (20-cm minimum) with goggles and shall ensure that workers wear the protective equipment during any operation in which splashes of liquid styrene are likely to occur. Devices for eye and face protection shall be selected, used, and maintained in accordance with 29 CFR 1910.133 (U.S. Department of Labor, Occupational Safety and Health Administration, Occupational Safety and Health Standards, Eye and Face Protection).

(b) Skin Protection

(1) Workers at risk of skin contact with styrene shall be provided with protective clothing such as gloves, boots, overshoes, and bib-type aprons (at least knee-length). The clothing shall be both impervious and resistant to styrene. Materials made of polyvinyl alcohol or polyethylene afford good protection.

(2) Clothing contaminated with styrene shall be cleaned before reuse. Anyone who handles contaminated clothing or is responsible for its cleaning shall be informed of the hazards of styrene and the proper precautions for its safe handling and use.

(3) The employer shall ensure that all personal protective clothing and equipment is inspected regularly and maintained in a clean and satisfactory working condition.

(c) Respiratory Protection

(1) The use of a respirator to achieve compliance with the recommended exposure limits is permitted only during the time necessary to install and test required engineering controls, for nonroutine operations such as maintenance or repair activities causing brief exposures at concentrations in excess of the recommended environmental limits, during work in confined spaces, or during emergencies when concentrations of airborne styrene may exceed the recommended environmental limit.

(2) Respirators shall be provided in accordance with Table I-1 by the employer when such equipment is necessary to protect the health of the worker. The worker shall use the provided respiratory protection in accordance with instructions and training received.

(3) The respiratory protective devices provided in conformance with Table I-1 shall comply with the standards jointly approved by NIOSH and the Mine Safety and Health Administration (MSHA) as specified under the provisions of the U.S. Department of the Interior, Bureau of Mines (Respiratory Protective Devices and Tests for Permissibility, 30 CFR Part 11).

(4) The employer shall ensure that respirators are properly fitted and that workers are instructed at least annually in the proper use and testing for leakage of respirators assigned to them.

(5) The employer shall be responsible for the establishment and maintenance of a respiratory protection program meeting or exceeding the requirements established by the Occupational Safety and Health Administration (Respiratory Protection, 29 CFR 1910.134) as summarized below:

(A) Written standard operating procedures governing use of respirators shall be established.

(B) The worker shall be instructed and trained in the proper use of respirators and their limitations.

(C) Where practicable, the respirators should be assigned to individual workers for their exclusive use.

(D) Respirators shall be regularly cleaned and disinfected.

(E) Respirators shall be stored in a convenient, clean, and sanitary location.

(F) Respirators used routinely shall be inspected during cleaning. Worn or deteriorated parts shall be replaced. Respirators for emergency use such as self-contained devices shall be thoroughly inspected at least once a month and after each use.

(G) Workers should not be assigned to tasks requiring use of respirators unless it has been determined that they are physically able to perform the work and use the equipment. The respirator user's medical status should be reviewed periodically (for instance, annually) as recommended by the physician responsible for the physical examination.

(H) Appropriate surveillance of work area conditions and degree of worker exposure or stress shall be maintained.

(I) There shall be regular inspection and evaluation by the employer to determine the continued effectiveness of the program.

Section 5 - Informing Workers of the Hazards of Styrene

(a) All new and current workers in areas where airborne exposures to styrene are at or above the action level, or who have the potential for significant skin exposure, shall be kept informed of the hazards, relevant prenarcotic symptoms, effects of overexposure, and proper conditions and precautions for the safe use and handling of styrene.

TABLE I-1

RESPIRATOR SELECTION GUIDE
FOR PROTECTION AGAINST STYRENE

Vapor Concentration	Respirator Type Approved Under Provisions of 30 CFR 11*
400 ppm or less	Any chemical cartridge respirator with organic vapor cartridge(s).**
	Any supplied-air respirator.**
	Any self-contained breathing apparatus.**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or front- or back-mounted organic vapor canister.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or during entry and escape from unknown concentrations.	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors.
	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.
**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

(b) The employer shall institute a continuing education program, conducted by persons qualified by experience or training in occupational safety and health, to ensure that all workers exposed to styrene above the action level have current knowledge of styrene hazards, proper maintenance, cleanup methods, and proper use of protective clothing and equipment, including respirators. The instructional program shall include oral and written descriptions of the environmental and medical surveillance programs and of the advantages to the worker of participating in these surveillance programs. The employer shall maintain a written plan of these training and surveillance programs.

(c) Workers shall also be instructed on their responsibilities for following proper work practices and sanitation procedures to help protect the health and provide for the safety of themselves and their fellow workers.

(d) All new and current workers in areas where exposure to styrene may reasonably be expected to occur during spills or emergencies shall be trained in proper emergency and/or evacuation procedures.

(e) Required information shall be recorded on the "Material Safety Data Sheet" shown in Appendix III, or on a similar form specified by the Occupational Safety and Health Administration (OSHA) describing the relevant toxic, physical, and chemical properties of styrene and of mixtures of styrene that are used or otherwise handled in the workplace. This information shall be kept on file and shall be readily available to workers for examination and copying.

Section 6 - Work Practices

(a) Handling and General Work Practices

(1) Operating instructions for all equipment shall be developed and posted where styrene is handled or used.

(2) Transportation and use of styrene shall comply with all applicable local, State, and Federal regulations.

(3) Styrene shall be stored in tightly closed containers in well-ventilated areas.

(4) Containers shall be moved only with the proper equipment and shall be secured to prevent loss of control or dropping during transport.

(5) Storage facilities shall be designed to contain spills completely within surrounding dikes and to prevent contamination of workroom air.

(6) Ventilation switches and emergency respiratory equipment shall be located outside storage areas in readily accessible locations that will remain only minimally contaminated with styrene in an emergency.

(7) Process valves and pumps shall be readily accessible and shall not be located in pits or congested areas.

(8) Styrene containers and systems shall be handled and opened with care. Approved protective clothing and equipment as specified in Section 4 shall be worn by workers who open, connect, and disconnect styrene containers and systems. Adequate ventilation shall be provided to minimize exposures of such workers to airborne styrene.

(9) Styrene storage equipment and systems shall be inspected daily for signs of leakage. All equipment, including valves, fittings, and connections, shall be checked for leaks immediately after styrene is introduced therein.

(10) When a leak is found, it shall be repaired promptly. Work shall resume normally only after necessary repair or replacement has been completed, and the area has been well ventilated.

(b) Engineering Controls

(1) Engineering controls shall be used when needed to maintain exposure to airborne styrene within the limits prescribed in Section 1(a). Complete containment of the vapor is the recommended method for control of styrene exposure. Local exhaust ventilation may also be effective when used alone or in combination with process enclosure. When a local exhaust ventilation system is used, it shall be designed and operated so as to prevent accumulation or recirculation of airborne styrene into the workplace environment and to effectively maintain safe levels of styrene in the breathing zones of workers. Exhaust ventilation systems discharging to outside air shall conform with applicable local, State, and Federal air pollution regulations and shall not constitute a hazard to workers or to the general population. Before maintenance work on control equipment begins, the generation of airborne styrene shall be eliminated to the extent feasible.

Enclosures, exhaust hoods, and ductwork shall be kept in good repair so that designed airflows are maintained. Measurements such as capture velocity, duct velocity, or static pressure shall be made at least semiannually, and preferably monthly, to demonstrate the effectiveness of the mechanical ventilation system. The use of continuous airflow indicators, such as water or oil manometers marked to indicate acceptable airflow, is recommended. A log shall be kept showing design airflow and the results of all airflow measurements. Measurements of the effectiveness of the system to control exposures shall also be made as soon as possible after any change in production, process, or control which may result in any increase in airborne concentrations of styrene.

(2) Forced-draft ventilation systems shall be equipped with remote manual controls and should be designed to shut off automatically in the event of a fire in the styrene work area.

(c) Confined or Enclosed Spaces

(1) Entry into confined or enclosed spaces, such as tanks, pits, tank cars, and process vessels, where there is limited egress, shall be controlled by a permit system. Permits shall be signed by an authorized employer representative and shall certify that preparation of the confined space, precautionary measures, and personal protective equipment are adequate and that precautions have been taken to ensure that prescribed procedures will be followed.

(2) Confined spaces that have contained styrene shall be thoroughly ventilated, inspected, and tested for oxygen deficiency and for the presence of styrene and any other known or suspected contaminants. Every effort shall be made to prevent inadvertent release of hazardous amounts of styrene into confined spaces in which work is in progress. Styrene supply lines shall be disconnected or blocked off before and while such work is in progress.

(3) No worker shall enter any confined space that does not have an entryway large enough to admit a worker wearing safety harness, lifeline, and appropriate respiratory equipment as specified in Section 4(c).

(4) Confined spaces shall be ventilated while work is in progress to keep the concentration of styrene at or below the recommended limits, to keep the concentration of other contaminants below dangerous levels, and to prevent oxygen deficiency.

(5) If the concentration of styrene in the confined space exceeds the recommended environmental limit, respiratory protective equipment is required for entry.

(6) Anyone entering a confined space shall be kept under observation from the outside by another properly trained and protected worker. An additional supplied-air or self-contained breathing apparatus with safety harness and lifeline shall be located outside the confined space for emergency use. The person entering the confined space shall maintain continuous communication with the standby worker.

(d) Emergency Procedures

Emergency plans and procedures shall be developed for all work areas where there is a potential for exposure to styrene. They shall include those procedures specified below as well as any others considered appropriate for a specific operation or process. Workers shall be instructed in the effective implementation of these plans and procedures.

(1) If styrene leaks or spills, the following steps shall be taken:

(A) All nonessential personnel shall be evacuated from the leak or spill area.

(B) The area where the leak or spill occurs shall be adequately ventilated to prevent the accumulation of vapor.

(C) The styrene shall be collected for reclamation or be absorbed on vermiculite, dry sand, earth, or similar nonreactive material and be disposed of properly.

(2) Only personnel trained in the emergency procedures and protected against the attendant hazards shall clean up spills, control and repair leaks, and fight fires in areas where styrene is present.

(3) Personnel entering the spill or leak area shall be furnished with appropriate personal protective clothing and equipment. Other personnel shall be prohibited from entering the area.

(4) Safety showers, eyewash fountains, and washroom facilities shall be provided, maintained in working condition, and located so as to be readily accessible to workers in all areas where skin or eye contact with styrene is likely. If styrene is splashed or spilled on a worker, contaminated clothing shall be removed promptly and the skin washed thoroughly with soap and water. Eyes splashed by styrene shall be irrigated immediately with a copious flow of water for 15 minutes. If irritation persists, get medical attention.

(e) Storage

Styrene shall be stored in well-ventilated areas and kept away from ignition sources such as heat or sparks and from oxidizing agents, catalysts, and strong acids. If styrene is stored more than 30 days at 32°C (about 90°F) or above, the inhibitor concentration shall be checked periodically. Large styrene storage containers should be installed with a temperature alarm system to signal interior temperature increases that may result in runaway polymerization, a special concern in hot climates. The rate of polymer formation in storage tanks can be reduced by cooling the tank by means of a water spray, refrigeration, insulation, or reflective painting. In a laboratory, samples of styrene may be stored in refrigerators or cold boxes.

Section 7 - Sanitation

(a) The preparation, storage, dispensing (including vending machines), or consumption of food shall be prohibited in areas where styrene is manufactured, formulated, processed, stored, or otherwise used.

(b) Smoking shall be prohibited in areas where styrene is manufactured, formulated, processed, stored, or otherwise used.

(c) Workers who handle styrene or equipment contaminated with styrene shall be instructed to wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

(d) Facilities such as double lockers should be provided for workers so soiled clothing can be stored separately from clean clothing.

Section 8 - Exposure Monitoring and Recordkeeping Requirements

(a) Exposure Monitoring

(1) The employer shall conduct an industrial hygiene survey to determine whether exposures to airborne concentrations of styrene are in excess of the action level (i.e., 25 ppm determined as a TWA over the workshift). The employer shall keep records of these surveys. If the employer concludes that exposures are below the action level, the records must show the basis for this conclusion. Surveys shall be repeated at least annually and within 30 days of any process change likely to result in an increased concentration of airborne styrene.

(2) If there is exposure to styrene at or above the action level, a program of personal monitoring shall be instituted to identify and measure, or to permit calculation of, the exposure of each worker occupationally exposed to airborne styrene. Source and area monitoring may be a useful supplement to personal monitoring. In all personal monitoring, samples representative of the TWA and ceiling exposures to airborne styrene shall be collected in the breathing zone of the worker. Procedures for sampling and analysis shall be in accordance with Section 1(b). For each determination of an occupational exposure concentration, a sufficient number of samples shall be collected to characterize each worker's exposure during each workshift. While all workers do not have to be monitored, sufficient samples should be collected to characterize the exposure of all workers. Variations in work and production schedules, as well as worker locations and job functions, shall be considered in decisions on sampling locations, times, and frequencies.

If a worker is found to be exposed to styrene at or above the action level but below the recommended environmental limits, the exposure of that worker shall be monitored at least once every 6 months or as otherwise indicated by a professional industrial hygienist. If a worker is found to be exposed to styrene in excess of the recommended environmental limits, controls shall be initiated, the worker shall be notified of the exposure and of the control measures being implemented, and the exposure of that worker shall be evaluated at least once a week. Such monitoring shall continue until two consecutive determinations, at least 1 week apart, indicate that the worker's exposure no longer exceeds the recommended limits. At that point, semiannual monitoring shall then be resumed.

(b) Recordkeeping

Records of the monitoring used to characterize the environmental exposures for each worker shall be retained for at least 30 years after the individual's employment has ended. These records shall include the name of the worker being monitored; Social Security number; duties performed and job locations within the worksite; dates and times of measurements; sampling and analytical methods used; number, duration, and results of samples taken; and the type of personal protection used, if any. Workers shall be able to obtain information on their own environmental exposures. Workplace environmental monitoring records shall be made available to designated representatives of the Secretary of Labor, the Secretary of Health and Human Services, and the worker or former worker.

Pertinent medical records (i.e., results of medical examination results, the physician's written opinion, medical complaints, medical and work histories, etc.) for all workers subject to exposure to styrene in the workplace shall be retained by the employer for at least 30 years after termination of employment. Copies of environmental monitoring data applicable to a worker shall be included in that worker's medical records. These medical records shall be made available to the designated medical representatives of the Secretary of Labor, the Secretary of Health and Human Services, the employer, and the worker or former worker.

II. INTRODUCTION

This report presents the criteria and recommended standards that have been prepared to meet the need for preventing impairment of health arising from exposure to styrene. The criteria document is developed by the Secretary of Health and Human Services, in response to Section 20(a)(3) of the Occupational Safety and Health Act of 1970, to "develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no worker will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

NIOSH has formalized a system for the development of criteria on which standards could be established to protect the health and provide for the safety of workers from exposure to hazardous chemical and physical agents. The criteria and recommended standard are intended to enable management and labor to develop better engineering controls and more healthful work practices, and to comply with the recommended environmental limits should not be the final goal.

These criteria for a recommended standard for styrene are part of a continuing series of recommendations developed by NIOSH. The proposed standard applies only to workplace exposure arising from the processing, manufacturing, handling, and use of styrene. The standard is not designed for the population-at-large, and any extrapolation beyond the occupational environment is not warranted. It is intended to: (1) provide protection against the development of systemic effects and local effects on the skin and eyes of workers, and (2) be measurable by techniques that are valid, reproducible, and available to industry and government agencies.

Styrene is used extensively in the manufacture of plastics and rubber. The principal acute hazards from worker exposure to styrene are central nervous system (CNS) depression and irritation of the skin, eyes, and upper respiratory tract. The possibility of styrene-related adverse health effects such as damage to the central and peripheral nervous systems, birth defects, chromosomal aberrations, sister chromatid exchanges, unscheduled DNA synthesis, impaired pulmonary function, liver injury, and carcinogenicity has also been suggested. Further study of these latter effects will help to elucidate their etiology.

III. SCOPE OF THE DOCUMENT

This document assesses the hazards of occupational exposure to styrene, a commercially important compound. This chapter gives information on the physical and chemical properties of styrene, its production methods and uses, and the extent of worker exposure. Chapter IV discusses and summarizes the effects of styrene exposure on humans and animals. Subsequent chapters describe environmental sampling and analytical methods for styrene, biological monitoring techniques, existing occupational health standards, and a correlation of exposure and effect. In addition, methods for worker protection are discussed and include suggested work practices, engineering controls, personal protective clothing and equipment, and monitoring and recordkeeping.

Most of the clinical studies cited in Chapter IV. Effects of Exposure are based on the evaluation of workers in the reinforced plastics industry, along with a number of studies of workers who produce styrene and polystyrene. Since the formulation of styrene-butadiene rubber (SBR) involves numerous substances besides styrene and butadiene, and also since many other substances are emitted during vulcanization and curing, the likelihood of any effects being due to styrene alone are quite small, although styrene could be a contributing factor. For example, among workers who produce SBR, adrenocortical insufficiency [1], enlarged liver and spleen [2], inflammation of the gall bladder [2,3], and degeneration of the capillaries [4], have been reported. These effects are different from those reported to have occurred among workers in other occupational settings where styrene is made or used. A detailed discussion of the SBR industry is beyond the scope of this document.

Physical and Chemical Properties

Styrene, also known as vinylbenzene or phenylethylene, is an aromatic organic compound with the chemical formula $C_6H_5CH=CH_2$. Styrene is a volatile liquid with a low vapor pressure [5]. The odor threshold is below 1 ppm [6,7,8]. Identifiers for styrene include the Chemical Abstracts Service Registry No. 100-42-5 and the Registry of Toxic Effects of Chemical Substances No. WL3675000. Standard specifications for styrene have been issued by the American Society for Testing and Materials [9]. Styrene is soluble in many organic solvents, but only slightly soluble in water [10,11]. Other information about styrene, including some of its chemical and physical properties is given in Table III-1.

TABLE III-1

STYRENE PROPERTIES

Synonyms	Cinnamene, cinnamenol, cinnamol, ethenylbenzene, monostyrene, phenethylene, phenylethene, phenylethylene, stirolo (Italian), styreen (Dutch), styren (Czech), styrol(German), styrole, styrolene, styron, styropol, styropor, vinylbenzen (Czech), vinylbenzene, vinylbenzol
Molecular formula	$C_6H_5CH=CH_2$
Formula weight	104.16
Boiling point (760 mm Hg)	145.2°C (293.4°F)
Freezing point	-30.6°C (-23.1°F)
Density	0.9018 g/cu cm (25°C)
Solubility	Soluble in ethyl ether, benzene, methanol, toluene, ethanol, acetone, n-heptane, carbon tetrachloride, carbon disulfide; slightly soluble in water (about 25 mg/100 g water at 25°C)
Flammable (explosive) limits	1.1-6.1% by volume in air
Flashpoint	34.4°C (94°F) Tag closed cup 36.7°C (98°F) Tag open cup
Autoignition temperature	490°C (914°F)
Vapor Pressure	Temperature

°F	°C	mm Hg	kPa
50	10	2.34	0.31
68	20	4.50	0.60
77	25	6.45	0.86
86	30	8.21	1.09
104	40	14.30	1.91

Concentration in saturated air	8,500 ppm (25°C)
Conversion factors (25°C, 760 mm Hg)	1 ppm = 4.26 mg/cu m 1 mg/cu m = 0.235 ppm

Adapted from references [5,10,12,13,14,15]

Discovery of Styrene, Production Methods, and Uses

Styrene was isolated and described in 1831 by Bonastre who distilled a fragrant natural balsamic resin called liquid amber [16]; the reaction forming styrene was later shown to be the decarboxylation of cinnamic acid, a constituent of the natural resin [17]. Mention of a similar investigation by Neumann was made in 1795 by Nicholson [18]. A procedure for the synthesis of styrene was published in 1866 by Berthelot et al. [19], in which benzene and ethylene mixtures were passed through a heated porcelain tube.

Although styrene was known for many years to polymerize, the first successful production of high purity styrene was begun in 1925 by I.G. Farbenindustrie of Germany [20]. The first successful production of styrene in the United States (U.S.) was begun in 1930 by the Dow Chemical Company [17]. Today, most styrene continues to be produced by the catalytic dehydrogenation of ethylbenzene [21,22,23]. Recently, styrene has also been produced as a coproduct with propylene oxide. In this latter process, ethylbenzene is first oxidized to its peroxide and is then reacted with propylene to yield propylene oxide and alpha-methylphenyl carbinol; the carbinol is dehydrated to styrene [21,22,23]. Almost all of the ethylbenzene used in styrene production in the U.S. is obtained by on-site alkylation of benzene with ethylene [23]. A small amount (10-15 ppm) of p-tert-butylcatechol is added to the styrene monomer to prevent spontaneous polymerization [21].

The U.S. production of styrene grew from 2.4 million pounds in 1940 to 1,745 million pounds in 1960, to a peak of 7,473 million pounds in 1979 [23]. U.S. styrene production was 6,612 million pounds in 1981 [24]; in 1984, 62% is expected to be consumed in polystyrene production, 22% in copolymers such as styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS), 7% in styrene-butadiene rubber (SBR), 7% in unsaturated polyester resins, and 2% in miscellaneous uses [23]. Many consumer products are made from styrene-containing compounds including packaging and insulation from polystyrene, pipes and automotive components such as instrument panels and consoles from ABS, drinking tumblers and battery cases from SAN, carpet backcoatings from styrene-butadiene latexes, passenger car tires and industrial hoses from SBR, and boats and open storage tanks from unsaturated polyester resins. Some other end-uses of styrene are shown in Table XIII-1.

Worker Exposure

The number of workers in the U.S. potentially exposed to styrene is difficult to estimate. Currently, there are 13 facilities producing styrene monomer [23] which is mainly used as a constituent in a variety of different plastic and rubber items. Polystyrene is made at over 40 locations; other styrene-containing polymer resins such as ABS and SAN are also produced at about 40 locations with some facilities producing both types of resins [25,26,27]. About 20 facilities produce SBR and SBR latexes with 66% utilized in the tire and tire products industry [26,28]. Many plants are involved with the fabrication of reinforced plastics/composites, including hundreds of boat producers [26,29]. There are also hundreds of plastic fabrication facilities where polystyrene, ABS, SAN, etc., are custom molded, extruded, formed, or cast into thousands of finished products [26]. In these operations, styrene exposure is due to the unreacted residual monomer or the thermal degradation of the plastics. In addition, exposures to styrene may occur during the use of miscellaneous products containing styrene such as floor waxes and polishes, paints, adhesives, putty, metal cleaners, autobody fillers, and varnishes. NIOSH estimates that at least 30,000 workers in 1,000 plants are potentially exposed in the U.S. on a

full-time basis to styrene [30]. It is also estimated that compounds containing styrene are utilized in over 20,000 facilities with more than 300,000 workers potentially exposed [30]. In most of these latter facilities, the potentially exposed workers may not work directly with styrene or may only periodically come in contact with it. Tables XIII-2 and XIII-3 summarize styrene exposure levels found during industrial hygiene surveys in various industries.

In the past, workers involved in the production of styrene and polystyrene may have been significantly exposed to styrene and other toxic chemicals such as benzene and ethylbenzene [31]. The current use of closed systems in styrene monomer and copolymer resin production (i.e., polystyrene, ABS, SAN, SBR, etc.) limits exposures (for the most part) to spills, sample collections, the cleaning of vessels, and fugitive emissions from valves, pump seals, etc. [32,33]; full-shift TWA styrene exposures are generally less than 10 ppm. Usually, styrene exposures are also less than 10 ppm during the fabrication (i.e., molding, extruding, casting, etc.) of items from polystyrene or styrene copolymers which contain low residual levels of styrene monomer. The most substantial exposures to styrene occur when it is used as a solvent-reactant for unsaturated polyester products that have been reinforced with fibrous glass. For these reinforced plastic items such as boats, open storage tanks, wall panels, tub and shower units, and truck camper tops, The Society of the Plastics Industry, Inc. has given the formal designation of "reinforced plastics/composites" (RP/C) [34]. The very nature of many of these operations subjects workers to intimate contact with materials used in the process; workers may be exposed to high concentrations of styrene vapor and have skin contact with liquid styrene or resin. Average styrene exposures in RP/C plants can range from 40-100 ppm with individual TWA exposures often found as high as 150-300 ppm (see Table XIII-3). Short-term exposures (i.e., 5-15 minutes) of styrene in the 1,000-1,500 ppm range have also been reported in some RP/C plants [35,36].

In the fabrication of RP/C, after the surface of the mold is treated with a release agent (usually a wax) and the initial layer of resin (gel coat) is applied, hand lay-up or spray-up is done which consists of putting a layer of chopped fibers or woven mats of fibrous glass in place and then applying resin. Following disposition of fiber reinforcement and resin, it is necessary to roll-out or squeegee-out by hand the structure to saturate the fibrous glass with resin and to remove entrapped air. Other layers of glass fiber and resin are added and rolled out until the desired thickness is obtained. The styrene content in the resin is approximately 40 percent by weight [37,38]. High exposure levels of styrene (especially in building large items such as boats) occur during the manual spray-up or lay-up operations, since about 10 percent of the styrene evaporates into the workplace air as the resin cures [37,38]; the remainder of the styrene is consumed in the chemical reaction with the unsaturated polyester. The amount of styrene evolved is dependent on the surface area being fabricated, thickness of the laminate, ratio of resin to reinforcement, workshop temperature, and duration of each step in the process [39].

Workers exposed to styrene are usually also exposed to other chemicals as well. These potential exposures are to substances utilized as raw materials, solvents, catalysts, accelerators, or inhibitors; exposures are also possible to chemical intermediates, thermal degradation products, and resin-curing emissions. Table XIII-4 lists other substances that have been found (usually at low levels) in processes utilizing styrene or styrene-derivatives.

The Standard Industrial Classifications (SICs) of some of the industries with potential exposures to styrene are listed in Table XIII-5. In addition to occupational exposure to styrene, exposure may occur from styrene in community air [40,41,42], drinking water [43,44,45], fermented grains [46], food [47,48], toys [49], building panels, and floor coverings [50], and in the domestic usage of certain floor polishes, metal cleaners, or adhesives containing styrene.