VII. ASSESSMENT OF EFFECTS

The principal health effects due to styrene exposure involve the central nervous system. These effects include subjective complaints of headache, fatigue, dizziness, confusion, drowsiness, malaise, difficulty in concentrating, and a feeling of intoxication. Objective signs of these effects are altered equilibrium, delayed reaction times, and abnormal EEGs. Local irritation of the eyes, nose, and respiratory tract and skin irritation are also widely acknowledged as effects of styrene exposure. There have also been reports of liver injury, peripheral nervous system dysfunction, abnormal pulmonary function, chromosomal changes, reproductive effects, and carcinogenicity related to styrene exposures. Although data concerning these latter adverse effects are not well defined at this time, they do provide cause for concern.

Experimental studies have provided some of the evidence of adverse health effects related to styrene. Two human subjects experimentally exposed to styrene at 800 ppm for 4 hours experienced eye and throat irritation immediately [68]. Listlessness, drowsiness, and impaired balance occurred during exposure, and subjects were weak, unsteady, and responded poorly after the exposure [68]. During a one-hour exposure at 376 ppm, five human subjects experienced eye or respiratory tract irritation within 20 minutes, and decrements in tests of balance, coordination, and manual dexterity were measured [69]. Subjective complaints of headache, nausea, and a feeling of slight inebriation were also reported during the same study [69]. At 216 ppm, one of three subjects noted nasal irritation after 20 minutes of exposure [69]. In another experiment [71], simple psychomotor reaction times increased for the twelve subjects, but only after consecutive 30-minute exposures at 50, 150, 250, and 350 ppm styrene (i.e., an average of 200 ppm during the two-hour testing period). Eye irritation, slower reaction times, and loss of balance were found in subjects during a 90-minute exposure at 200 ppm [72].

Some of these experimental studies of human subjects have also demonstrated adverse effects of styrene exposure at concentrations as low as 100 ppm. Slower reaction times (26-28%) were found in three subjects during a 90-minute exposure at 100 ppm [72]. In the same study [72], six subjects who received a total of 13 exposures of 90-minute duration at 100 ppm styrene noted sleepiness (92% of the exposures), fatigue (77%), headache (77%), difficulty concentrating (69%), malaise (54%), nasal irritation (54%), and nausea (38%). In an experimental study that lasted 6 weeks, the investigators [70] stated that there were changes consistent with CNS depression; three of the six subjects had both visual evoked response and EEG amplitude changes after exposures at 20, 100, and 125 ppm styrene. In the same study [70], the incidence of eye, nose, and throat irritation for the ten male subjects was 13% at 0 ppm, 17% at 20 ppm, 20% at 100 ppm, 33% during exposures fluctuating between 75 and 125 ppm, and 45% at 125 ppm styrene. The incidence of eye, nose, and throat irritation for the two female subjects was 8% at 0 ppm and 32% at 100 ppm [70]. In another study [69], three of six subjects noted mild eye or throat irritation during the first 20 minutes of a 7-hour exposure to 99 ppm styrene; the irritation subsided after an additional 30 minutes. In addition, both simple visual and audiovisual choice reaction times in tests of two subjects were 22-25% slower during a 90-minute exposure at 50 ppm styrene [72]. During a total of 6 exposures each of 90-minute duration at 50 ppm in the same study, the subjects noted eye irritation, fatigue, and difficulty concentrating during 67% of the exposures, and headache during 50% of the exposures; the incidence of these complaints during exposures at 0 ppm was 10-20%.

The experimental study by Oltramare et al. [72] provides some evidence of CNS depression, manifested by subjective complaints and delayed reaction ability in human subjects exposed to styrene at 50 ppm and 100 ppm. The experimental studies by Oltramare et al. [72], Hake et al. [70], and Stewart et al. [69] indicate that styrene irritates the eyes, nose, and throat of some subjects at 100 ppm and a few subjects at concentrations as low as 50 ppm.

There are many clinical studies demonstrating these same CNS and irritation effects, as well as other health effects, among styrene-exposed workers. Subjective complaints indicative of CNS depression have been noted in numerous studies [94,101,105,106,109,110,112,113,123,138]. Although no exposure data were given, 68 of 70 workers in a Russian RP/C plant [101] complained of constant headache increasing throughout the day with fatigue and sleepiness increasing after the workshift, while 46 of the 70 workers complained of nausea, dizziness, and heart pain. In a study of 128 Czechoslovakian RP/C workers exposed to styrene at TWA concentrations of 4-195 ppm [105], 20% reported headache, 15% reported tiredness, and 13% reported symptoms of drowsiness. Similarly, higher incidences of unusual tiredness, reduced short-term memory, giddiness, and headache were reported among 33 workers from three Swedish RP/C factories with TWA styrene exposures of 5-174 ppm, than among controls with no solvent exposures [123]. Subjective complaints were also noted among 35 Czechoslovakian RP/C workers exposed at 19-130 ppm styrene [106]; these complaints included headache (51% of the workers), fatigue (41%), and drowsiness (34%). In a U.S. RP/C factory with TWA styrene exposures of 9-111 ppm, 50% of the 22 workers complained of headache and 36% of fatigue [113]. Among 22 workers in two RP/C factories in the Netherlands who were exposed at about 24-94 ppm styrene [110], 50-90% complained of drowsiness, and 30-70% noted headache and dizziness. Headache was reported by 36% and drowsiness by 24% of 55 Czechoslovakian RP/C workers exposed at 6-94 ppm styrene [109].

Among 81 Swedish RP/C workers with TWA styrene exposures of 3-312 ppm, but with 74% less than 100 ppm [112], the following subjective complaints were reported: fatigue (60% of the workers), dizziness (38%), headache (25%), poor memory (21%), and nausea (14%). Among 27 English RP/C workers exposed to styrene at about 92 ppm, 52% felt unduly tired compared to 19% of a control group comprised of workers in the same factory, but without exposure to styrene [138]. Complaints of frequent headaches were reported by 38% of the 40 workers in a Russian polystyrene production facility where styrene exposures sometimes exceeded 12 ppm [94].

Slower reaction times [111,392] and abnormal EEGs [118,124,125] have also been reported in clinical studies. The reaction times of seven Swedish RP/C workers with TWA exposures of 3-14 ppm styrene [392] were significantly slower ($p<0.05$) than the comparison group; however, the investigators were unable to determine whether styrene was responsible. Significantly longer reaction times as compared to age-matched controls were also found in 106 workers from four Swedish RP/C plants where TWA styrene exposures were 10-120 ppm [111].

At a Finnish RP/C facility where the average styrene exposure was estimated from urinary mandelic acid measurements to be about 30 ppm, 23 of 96 workers (24%) had EEGs judged to be abnormal [124,125]. Among 35 Czechoslovakian RP/C workers with TWA styrene exposures of 19-130 ppm, only five of eighteen EEGs given were judged to be normal [106]. In a subsequent Czechoslovakian clinical study of 21 RP/C workers [108], some had abnormal EEGs after three years of styrene exposure (concentration was not specified), whereas no abnormal EEGs were found during a pre-exposure examination. In a study of Polish RP/C workers [118], abnormal EEGs were found in 31 of 43 workers (72%) with about one year of styrene exposure at 25-75 ppm, and in four of twenty-one workers (19%) with ten years of exposure at about 75 ppm.

Styrene has also been shown to cause irritation of the eyes [35,53,58,61,104,110,113,126] and respiratory tract [35,53,56,59,93,104,113, 114,115,123,126] of exposed workers. Complaints of irritation of the eyes and nasopharynx were common in a study of 17 Swedish RP/C workers whose TWA styrene exposures were 17-292 ppm [35]. In a U.S. RP/C facility where styrene exposures were 45-550 ppm [104], complaints of eye, nose, or throat irritation were made by 34 of the 35 workers (97%) examined. Among 22 workers in two RP/C facilities in the Netherlands who were exposed at 24-94 ppm styrene, 90% complained of eye irritation [110]. Complaints of irritation of the mucous membranes of the respiratory tract were reported by 44% of the workers in a Russian polystyrene production facility where styrene exposures were characterized as sometimes exceeding 12 ppm [94]. In a U.S. RP/C facility with TWA styrene exposures of 9-111 ppm, 93% of the 14 workers interviewed complained of eye irritation, 50% of nose irritation, and 29% of throat irritation [113]. The reported incidence of throat irritation was higher in 33 workers from three Swedish RP/C factories (where TWA styrene exposures ranged from 5-175 ppm) than in controls with no solvent exposures [123]. A group of 96 Finnish RP/C workers whose average styrene exposure was estimated from urinary mandelic acid measurements to be about 30 ppm, frequently experienced irritation of the eyes and nose [126].

There is some evidence of styrene-induced peripheral neuropathy. The frequencies of distal hypoesthesia of the lower extremities and hypoactive deep tendon reflexes increased with duration of exposure in styrene and polystyrene production workers [81]. The data presented did not clarify, however, whether the changes were due to age or to styrene exposures which, at the time of the study, were usually less than 20 ppm [81]. The findings of impaired radial nerve conduction in 15 of 80 workers and impaired peroneal nerve conduction in 12 of 73 workers was also reported [81]. Although the effects on the radial or peroneal nerve were not related to the magnitude of exposure, those effects on the peroneal nerve were related to the duration of exposure to styrene. However, these effects also could have been related to age; moreover, the changes were not statistically significant. In a Swedish study [123], 10 of 33 workers with TWA exposures of about 5-125 ppm had evidence of a mild sensory neuropathy with polyphasic response. Although the 10 affected RP/C workers were older, the investigators [123] concluded that age alone was not the cause. In a Finnish study [124], slightly abnormal nerve conduction velocities were found in 9 of 40 workers in a facility where the average styrene exposure was estimated from urinary mandelic acid to be about 31 ppm. In 4 of the 9 affected workers (1 with mononeuropathy, 3 with polyneuropathy) no cause other than styrene exposure could be found; however, there was no association between urinary mandelic acid concentration and nerve conduction velocity in the four workers with unexplained abnormalities. Neurological effects reported in a Czechoslovakian RP/C plant [106] included cranial nerve disturbances (in 91% of the workers), diminished reflexes (86%), and impaired balance (83%). Among 101 Polish RP/C workers with one year of exposure to 25-75 ppm of styrene, 26 had signs that the investigators [115] classified as autonomic nervous system disturbances; hypoesthesia, whitening of the fingers, trembling of the hands, weakened reactions, cat's eye pupils, excitability, and nystagmus were noted among the 26 workers. While the evidence for chronic nervous system damage (peripheral neuropathy or CNS changes) from styrene exposure is not strong, further study is warranted due to the importance of these effects.

The data on possible long-term respiratory effects of styrene is also limited. Among 35 U.S. RP/C workers exposed to styrene at 44-550 ppm, about half complained of wheezing, shortness of breath, or chest tightness [104]; exposure to an isocyanate (MDI), another respiratory system irritant, at 0.01-0.27 mg/cu m (the OSHA standard is a ceiling value of 0.2 mg/cu m) might have contributed to these effects. A possible relationship between styrene exposure and a history of wheezing or chest tightness was suggested in a study of workers making styrene and polystyrene [82]; there appeared to be some spirometric evidence of airway obstruction, but not significantly related to exposure. Conjunctival irritation related to styrene exposure was a complaint in 22% of these workers [82]. In a U.S. RP/C factory with TWA styrene exposures of 9-111 ppm [113], 54% of the workers complained of shortness of breath, 23% of chest tightness, and 18% of wheezing; however, ventilatory function was significantly changed during the shift only in those workers that smoked. Four cases of reduced FEV_1 were found among 21 RP/C workers exposed to styrene at approximately 75 ppm for about 10 years, but whether the cause was age, styrene exposure, or other factors was not clear [114]. In another clinical study [91], a significantly greater number of RP/C workers had abnormal pulmonary function (i.e., FVC less than 80% of predicted values, $FEV_1/FVC \times 100$ below 70, FEV_1 less than 80% of predicted values, and FEF(25-75) less than 70% of predicted values), when compared to unexposed workers from an electronic products plant.

Although various clinical studies [82,96,103,113,115,116,120] have suggested that styrene exposure has affected liver function, a clear relationship has not been demonstrated; clarifying research is needed. In any case, periodic screening of the liver function of styrene workers should be conducted due to the importance of this organ in the biotransformation and detoxification of toxic substances.

There is suggestive but conflicting evidence of mutagenicity by styrene. Workers exposed to styrene in reinforced plastics applications [76,129,130,131,132] had an increased incidence of chromosomal aberrations. There were more chromosomal aberrations (16.7 vs. 1.8/100 cells in controls, $p<0.001$) among 10 Finnish RP/C workers whose average styrene exposure was estimated from urinary mandelic acid measurements to be about 30 ppm [129]. In a related study of 16 RP/C workers [130], which included 8 workers from the previous study [129], a statistically significant increase in the incidence of chromosomal aberrations was found (15.1 vs. 2.0/100 cells in the controls, $p<0.001$); this was confirmed when 10 of the 16 workers were reexamined a year later and the incidence was 16.2%. In a Swedish RP/C factory with styrene exposures of 14-73 ppm [131], an increased frequency of chromosomal aberrations was also found (10.8 vs. 5.2/100 cells, $p<0.001$). In a study of an RP/C factory where styrene exposures were 8-158 ppm [132], the 39 styrene-exposed workers studied had a significantly higher incidence of chromosomal aberrations as compared with controls (7.9 vs. 3.9/100 cells, $p<0.001$). There was also a significant increase in the average frequency of sister chromatid exchanges (8.4 vs. 7.5 SCE/cell) in 20 of the same RP/C workers [132]. In another study [76], a significant excess of chromosomal aberrations in 14 RP/C workers as compared to 20 controls was also found (9.2 vs. 5.5%); styrene concentrations ranged from 50 to 300 ppm, but urinary mandelic acid concentrations for the RP/C workers were less than 1,500 mg/l (equivalent to an 8-hour TWA styrene exposure of about 80 ppm).

Conversely, mutagenic activity has not been found in most _in vitro_ tests of styrene. This has been the case with _S. typhimurium_ [172,173,174,176], _E. coli_ [174], the yeasts _S. pombe_ and _S. cerevisiae_ [175], and cultured Chinese hamster cells [175,176]. However, a few studies [171,177,178] have found weak evidence of the mutagenicity of styrene in _S. typhimurium_.

A dose-response relationship has been shown in the induction of sister chromatid exchanges in human whole blood lymphocyte cultures treated with styrene [181]. In a study of unscheduled DNA synthesis in lymphocytes of styrene-exposed workers, styrene did not alter the efficiency of DNA repair but rather predisposed the lymphocytes to an increased risk for DNA damage from subsequent exposures to genotoxic agents [137]. Some studies in lower mammals suggest mutagenicity by styrene while others suggest otherwise. In vitro studies, such as the Ames tests, tentatively suggest that styrene is not mutagenic. Clearly, these conflicts in the data on the mutagenicity of styrene need to be resolved. These same tests, on the other hand, uniformly show styrene oxide to be mutagenic. Styrene oxide, also known as styrene epoxide, has been proposed [224,225] as an intermediate in the metabolism of styrene, but it has not been found in vivo. The ability of epoxides to react with nucleic acids, and possibly lead to germinal or somatic mutations, is a major concern in the question of intermediary metabolism of styrene. Whether styrene oxide (if formed) is present long enough to bind covalently to genetic material or other macro molecules is not known. Airborne styrene oxide is present in some workplaces, apparently those in which peroxides and styrene are mixed [233,269]. While the toxicity of styrene oxide has not been adequately studied, it is mutagenic and carcinogenic. Its health significance in these workplaces needs evaluation both in terms of its own toxicity and possible toxic interactions with styrene and other chemical substances.

There have been a few reports of defects in children born to women exposed to styrene [66], but this implication of teratogenesis has not been confirmed by experimental animal studies [190,191,192,193]. It has been demonstrated, however, that styrene can cross the rat placenta and that styrene concentrations in fetal blood are almost as high as in maternal blood [189]. Styrene can also cross the human placenta, as demonstrated by the fact that styrene was found in umbilical cords [65].

An increased incidence of spontaneous abortions among Finnish styrene workers has been reported [139]. However, the study involved only six cases, and the investigators [139] were not able to control for smoking or economic status (two variables that are risk factors in spontaneous abortions). In 1982, the same Finnish investigators [140] reported that 67 female RP/C workers, prior to the period of exposure, had no significant differences in their reproductive outcomes as compared to controls, matched for age and social class, with no solvent exposures. During styrene exposure the numbers of pregnancies were not significantly different, but there were significantly fewer births among the RP/C workers (4 vs. 14); one cause was an increased (although not significantly) number of induced abortions (8 vs. 4). The number of spontaneous abortions was identical with four in the exposed group and four in the control group. Suggestions that styrene is teratogenic and abortifacient need to be pursued, but resolution will be difficult because of the problems typically associated with attempts to relate human defects to causal factors. However, the findings presented above provide strong rationale for an investigative program, including appropriate recordkeeping and registries, to develop etiological information on birth defects and abortions associated with occupational exposures.

There seems to be little basis from experimental animal investigations or epidemiological studies to conclude at this time that styrene is carcinogenic. Two animal studies [196,197] reported an increased incidence of lung tumors, but not consistently either in one sex or in one species. Another animal study [195] reported an elevation (not statistically significant) in the combined incidence of leukemia and lymphoma. Existing mortality studies [31,78,83,84,142] have shown no relationship between styrene exposure and an excess in the incidence of deaths in the overall category, "All Malignant Neoplasms." However, excesses of deaths were reported in the specific cancer categories "Lymphatic and Hematopoietic, except Leukemia" (7 observed vs. 5.3 expected, not significantly different) and "Leukemia" (6 observed vs. 3.4 expected, not significantly different) in the study by Ott et al. [31]. While the evidence developed so far concerning the carcinogenicity of styrene is not conclusive, it does provide sufficient bases for carefully considering to what extent workers are exposed to styrene and for instituting controls to reduce those exposures. The recommendation of NCI [197] for additional animal experimentation to add more evidence because of deficiencies in present data seems the most appropriate recommendation that can be made now. Two factors warrant a high priority for investigations to help resolve this important issue: the commercial importance of styrene and the large population that is exposed to the compound.

The experimental evidence [69,70,72] for styrene-induced health effects at a concentration of 100 ppm is not strong; however, there are many clinical studies showing similar, as well as other, adverse health effects in occupational settings. Although these workers also had potential exposures to other substances, their major exposure was to styrene. Additionally, in some of the studies, peak and TWA styrene exposures may sometimes have exceeded 100 ppm, but exposures for most workers were judged to be at TWA styrene concentrations at about 100 ppm [76,81,82,84,91,94,106, 109,110,111,112,113,115,118,120,124,129,130,131,132,138,392]. CNS effects noted in those workers exposed to styrene at or below 100 ppm included subjective complaints such as fatigue, dizziness, headache, nausea, poor memory, and drowsiness [106,109,110,112,113,138]; increased reaction times [111,392]; abnormal EEGs [106,118,124]; and impaired balance [106]. Chromosomal changes were also more frequent in the lymphocytes of styrene-exposed workers in several RP/C factories with TWA exposures of about 100 ppm than among controls [76,129,130,131,132].

Based on the adverse health effects demonstrated in experimental subjects and workers exposed to styrene concentrations at and below 100 ppm, a TWA exposure limit of 50 ppm is proposed over the workshift for up to a 10-hour workday and a 40-hour workweek. This recommendation is further supported by studies showing effects such as slower reactions [72], subjective complaints related to CNS depression [72], and abnormal EEGs [124] at styrene concentrations around 50 ppm.

A ceiling limit of 100 ppm based on a 15-minute sampling period is recommended to prevent acute irritation effects on the eyes and upper respiratory system. Since styrene is a defatting agent and can cause primary skin irritation [234] and dermatitis [54,56,61,91,104,113, 122,126] in workers, as well as be absorbed percutaneously [86,151,152], skin contact with styrene should be avoided through the use of good work practices and personal protective clothing.

Other toxic effects such as peripheral neuropathy, abnormal pulmonary function, liver toxicity, mutagenicity, teratogenicity, and carcinogenicity would be relevant to an occupational exposure limit if the available information established them as effects of styrene exposure or gave information on exposure-response relationships. 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.

VIII. METHODS OF WORKER PROTECTION

Informing Workers of the Hazards of Styrene

Each worker with potential exposure to styrene should be informed of (1) relevant prenarcotic symptoms, (2) effects of overexposure, including suspected but as yet unproven effects, (3) proper use and handling of styrene, (4) methods that minimize exposure, (5) proper maintenance procedures and cleanup methods, (6) correct use of protective clothing and equipment, including respiratory devices, (7) engineering controls in use or being planned to limit exposures, and (8) medical and environmental monitoring procedures in use. The advantages to the worker of participating in the monitoring procedures should be stressed. Oral as well as written instructions informing workers of proper handling methods, cleanup and emergency procedures, use of personal protective equipment, etc. should be presented by persons qualified by experience or training in occupational safety and health as part of a continuing education program. The NIOSH publication A Recommended Standard--An Identification System for Occupationally Hazardous Materials [306] should be used as a guide when preparing written material for readily available reference on the relevant physical, chemical, and toxicological properties of styrene or of mixtures or formulations containing the compound. Required information shall be recorded on the "Material Safety Data Sheet" shown in Appendix III, or on a similar form approved by OSHA, U.S. Department of Labor. Pertinent information on over 1,300 substances may be found in the Hazardous Chemicals Data Book [307] or other similar references.

Workers should also be instructed on their responsibilities for proper work practices and sanitation procedures to help protect the health and safety of themselves and their fellow workers.

Work Practices

(a) Storage, Handling, and Transportation

Because of the volatile and flammable nature of styrene (see Table III-1, p. 17), proper handling and storage should be given special attention. Good ventilation systems with explosion-proof motors are necessary in areas where styrene is handled and stored. Grounding of all equipment, tank cars and trucks, and hose connections will discharge static electricity. An inlet line that discharges at or near the bottom of the tank and makes electrical contact with the tank will eliminate uncontrolled electrical discharges [308]. If the inlet line cannot reach the tank bottom, a chain should be attached that does reach [309].

Precautions to ensure that styrene vapor does not ignite are mandatory for safe conditions, especially at elevated temperatures. Recommendations include: (1) regular inspection of equipment and storage tanks, (2) immediate repair of leaks, pumps, and lines, (3) ventilation to reduce vapor concentrations, (4) use of special nonsparking alloy tools, (5) periodic tests of pressure equipment, (6) rapid removal of spills, and (7) elimination of ignition sources [309]. Portable electric lights and power tools must conform with the National Electrical Code, Article 500 [310]. Receptacles that contain styrene monomer or hot styrene-containing resins must be tightly covered at all times except when material is removed. Safety cans can be used to hold working amounts of liquid styrene.

Styrene may polymerize if it comes in contact with oxidizing agents and catalysts such as peroxides, strong acids (e.g., sulfuric or hydrochloric), aluminum trichloride, phosphoric anhydride, and iron chloride. Storage of styrene away from oxidizing agents, catalysts, and strong acids will also help prevent explosions or fires. Centrifugal pumps will cause polymerization if allowed to run with a closed discharge line. Storage of styrene outdoors or in detached areas can be advantageous [311].

If styrene is stored more than 30 days at 90°F (about 32°C) or above, the inhibitor concentration must be checked at least bi-weekly [312]. Styrene storage containers can be installed with a temperature alarm system to signal interior temperature increases that may result in runaway polymerization, a special concern in hot climates [309,313]. 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 [313].

Catalysts, promoters, and accelerators should be stored in cool, dry, dark areas away from reducing agents, and in their original shipping containers [314]. Fuller and Jensen [314] also suggested that only a 1-day supply of peroxides be kept in laminating areas. (As was discussed in Chapter V, styrene and peroxides can possibly react to form another toxic compound, styrene oxide.)

(1) Drums

Unless drums are unloaded carefully, they may be damaged; dropping or bumping drums can lead to leaks or ruptures. Examination of each shipment for leaks can identify those drums that need special handling. If any are found, spillage can be minimized by turning the leaking part up while they are being moved to a safe place to stop the leak or by transferring the contents.

Containers that have held styrene monomer must be thoroughly cleaned with steam and then drained and dried before reuse, because small amounts of the monomer may remain and present a fire hazard. Explosions can occur if drums are not filled and emptied carefully as demonstrated in a report by the Manufacturing Chemists Association [315]. A supposedly empty drum was placed over a steam line so that the drum could be cleaned. The residual styrene ignited (probably due to a discharge of static electricity between the nozzle of the steam line and the drum) and then exploded. Drums cleaned by steam should be electrically bonded to the steam lines and the entire assembly grounded.

A similar accident occurred [316] when a worker who was filling drums with styrene failed to ensure that the drums were properly grounded. While the last drum was being filled, the worker moved it; a spark discharged between the filling line and the drum, causing an explosion.

Before drums are emptied they should be supported and blocked to prevent movement. When filling open containers from a drum, electrical bonding must be provided to prevent static sparks. Styrene workers should avoid striking fittings with tools or other hard objects that may cause sparks. The National Fire Protection Association (NFPA) Standard No. 77, "Static Electricity" [317], contains detailed information on the subject.

During lay-up operations in the reinforced plastics industry, it is recommended that all styrene monomer be kept in safety cans, rather than in large open containers, to prevent high local styrene concentrations.

(2) Tank Trucks and Cars

Fire hazards around tank trucks and cars can be reduced by turning off truck motors and not starting them while tank trucks are being loaded or unloaded. If tank trucks and cars are unloaded through an open dome, the unloading equipment must be electrically bonded and grounded before operations are started. Use of a rubber-type flexible hose to unload styrene is not recommended because it may not be resistant to styrene. Fluoroelastomer hoses, however, are satisfactory because they are more resistant to styrene penetration [308].

There are other hazards involved in transferring styrene from or to tanks that should be identified, so that workers can be instructed on appropriate precautions. This is exemplified in the case of one worker who, after unloading styrene from a tank car [315], disconnected a supposedly empty line that was, in fact, filled with styrene. The styrene spilled on his face and shoulders; although he was wearing safety glasses and a hard hat, the styrene ran down his forehead and into his eyes. Details regarding the extent of his injuries were not provided. After this accident, rubber gloves and goggles were worn by personnel who unloaded tank cars, and written guidelines were provided that detailed safe procedures for unloading tank cars [315].

Department of Transportation (DOT) regulations that apply to the handling, unloading, and transportation of hazardous substances are set forth in 49 CFR 100-199.

(3) Return and Disposal Precautions for Styrene Containers

Extra care in completely draining the contents and properly closing all openings before shipping containers are returned to suppliers will help prevent explosion and fire. As soon as a tank car or truck is completely unloaded, all valves must be closed tightly, the unloading connection removed, and all other closures made tight, except the heater coil inlet and outlet pipes (if any), which must be left open for drainage.

(b) Sanitation and Hygiene

In the interest of good hygiene and to prevent accidental ingestion of styrene, it is important that storing, handling, dispensing, and eating of food be prohibited in all areas where styrene is kept or used. It is also important that workers who handle styrene wash their hands thoroughly before eating, smoking, or using toilet facilities. Workers should also be provided with facilities so they can shower with soap and water at the end of each workshift, or as soon thereafter as practicable before leaving work. Facilities such as double lockers should be provided for workers so soiled clothing can be stored separately from clean clothing.

Clothing that has become saturated with styrene must be removed immediately because styrene is absorbed through the skin [151,152,153]. Because skin absorption can occur, contaminated skin must be promptly washed with soap and water. Use of acetone or other organic solvents to clean styrene from the skin can be harmful since they may be toxic themselves and contribute to the effects of styrene. In case of eye contact, flush the eyes immediately with a copious flow of water for 15 minutes to prevent corneal injury. If irritation persists, get medical attention. Eye contact can be prevented if workers wear splash-proof safety goggles or face shields that comply with 29 CFR 1910.133(a).

(c) Housekeeping

Good industrial housekeeping is imperative to prevent fires or accidental ingestion where styrene is used. Vacuuming of work areas at the end of each shift to remove particulate matter such as polymer dust, fibrous glass, and fibrous glass-reinforced plastic dust is a simple and effective measure.

Styrene spills should be cleaned up immediately after eliminating potential sources of ignition and using available ventilation. Stopping leaks and spills will also eliminate fire hazards and help conserve raw materials, keep chemicals out of the effluent system, and reduce worker exposure [32]. Vermiculite, dry sand, earth, or similar nonreactive material can be used to absorb styrene but, for best results, pretest absorbing agents for their effect on polymerization of styrene. For spills on hard surfaces, scrubbing the area with soap and water after most of the styrene has been removed is recommended. If spills occur in a confined space, pumping water into the area will prevent the ground from absorbing the styrene and may allow styrene to be recovered later [318]. Small spills can be absorbed by paper, which can be burned after evaporation in a hood or in another safe place. Only properly protected personnel should perform these procedures. Wiping rags or cloths should be placed in fireproof receptacles equipped with tight-fitting lids.

(d) Waste Disposal

Because of the exothermic nature of styrene polymerization, it is recommended that waste catalyst be disposed of separately from waste monomer. If this is not possible, the waste receptacle should be located away from any sources of heat, flame, or electrical discharge, or from any combustible material. Besides cleaning work areas at the end of each workshift, it is a good practice to determine if all wiping cloth containers, excess plastic, plastic constituents, and other refuse are removed from the building and disposed of properly. Workers should be informed of proper storage and disposal procedures and be adequately supervised in handling waste receptacles.

All waste styrene and styrene-contaminated material should be removed to a disposal area and safely burned by introducing it as a spray or mist into a suitable combustion chamber; incineration will be more complete if styrene is mixed with a more flammable solvent [314]. Water contaminated by styrene can be safely treated by removing the mixture to a safe location and blowing it with air. The outlet air stream can then be burned to remove the styrene [308]. Waste effluent gases can also be burned to remove styrene [319]. Liquid styrene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion, at least in warm or hot areas.

(e) Fire Control

Styrene poses a significant fire hazard. As shown in Table III-1 (see p. 17), styrene has a boiling point of 145.2°C (293.4°F), a flashpoint of 34° to 37°C (94° to 98°F), and flammable (explosive) limits of 1.1-6.1% by volume in air. Thus, according to the criteria of OSHA, styrene would be classified as a Class 1C flammable liquid (29 CFR 1910.106) and a Class B fire hazard (29 CFR 1910.156).

If ventilation is adequate to maintain the concentration of styrene at recommended levels, the potential for fire and explosion will be greatly reduced. However, elevated styrene concentrations may occur if the vapor accumulates, for example, above the liquid surface, in depressions, at container openings, at vent openings, or in areas having poor ventilation. Thus, all ignition sources, such as fire, sparks, and smoking materials, must be prohibited in those areas where styrene is made, used, or stored. NFPA Standard No. 77, "Static Electricity" [317], lists precautions designed to prevent the accumulation of static electricity, a potential ignition source. Fifty feet from open flames or other possible ignition sources, such as sparks, hot surfaces, or arcs, has been suggested as the minimum safe distance for location of processes that involve styrene [314]. Fire hazards can also be reduced by isolating mixing and formulating operations from other operations (particularly laminating areas) in a well-ventilated area equipped with an automatic sprinkler system; mixing, formulating and laminating operations should also be separated from finishing areas by at least 2-hour fire partitions to slow the spread of a fire [314].

Some processes do not lend themselves to control by physical separation. This is especially true when the contaminant permeates an entire work area. In those cases, either isolation or enclosure of the operation will limit the amount of contaminant dispersed in the workplace [90].

Fires involving styrene can be safely extinguished with the proper use of foam, dry powder, or carbon dioxide. Water is not an effective extinguishing agent but can be used to keep fire-exposed containers cool. Regulations governing the use of electrical equipment where styrene is present can be found in the National Electrical Code NFPA 70-1971, ANSI CI-1971 (Rev. of C1-1968) which was adopted as a national concensus standard by OSHA in 29 CFR 1910.308.

Incomplete combustion of styrene-containing materials may result in the formation of a toxic gas such as carbon monoxide; the breathing of fumes, smoke, and gas liberated by styrene, polystyrene, or other styrene-containing materials [309,318] can be avoided by using the appropriate respiratory protection.

Fuller and Jensen [314] suggested that sprinkler systems be installed in new factories where reinforced plastics are laminated. They recommended that these systems deliver a minimum of 0.3 gallons of water/min/sq ft (3.7 liters/min/sq m) applied over an area of 5,000 sq ft (464 sq m), that the sprinkler system be provided with hand hose connections, and that portable Class B fire extinguishers also be available [314].

To help control potential fires, Fuller and Jensen [314] suggested that smoke and heat vents be installed with about 100 feet (30.5 m) between their centers. They also suggested that curtain boards be installed at 100-foot intervals so that curtained areas are no greater than 10,000 square feet (929 sq m).

(f) Entry into Confined Spaces

Entry into confined spaces (tanks, pits, tank cars, barges, process vessels, and tunnels) should be controlled by a permit system or other program offering equal protection. These spaces need to be tested for oxygen deficiency, styrene concentration, and the presence of any other harmful gas or vapor. Only supplied-air hoods or suits impervious to styrene are recommended for entering a confined space unless sampling data indicate that the area is safe for entry with other equipment. Air- or oxygen-supplied masks equipped with full facepieces are recommended to be worn when the oxygen content of the air is less than 16% or when the styrene vapor concentration is over 5,000 ppm.

It is imperative that confined spaces be thoroughly ventilated and cleaned before workers enter without respiratory protection. It is a good practice to flush the confined space with steam or water to remove styrene vapor. When a worker enters a confined space, use of a safety line is recommended with another properly protected worker on standby outside to maintain communication by voice and sight with the worker inside. The safety line must never be abandoned while the worker is in a confined space. An additional safety measure is to have the workers in or near to the confined space close to others who can be quickly contacted in an emergency [308]. The NIOSH document Working in Confined Spaces [320] contains a more thorough discussion on the subject of confined spaces.

A number of effective work procedures and housekeeping practices in the RP/C industry were noted during a 1981 NIOSH-sponsored study on worker education, training, and motivation [321].

Engineering Controls

Engineering controls for production and use of styrene are designed in consideration of its volatility, flammability, and toxicity. Styrene undergoes rapid, exothermic polymerization. If unchecked, this reaction can become violent and ignite or explode [322]. Fuller and Jensen [314] reported that one such incident occurred in 1971 in a plastics manufacturing plant in Ohio. To avoid this problem, continuous monitoring of the temperature and pressure of liquid styrene storage tanks can be used to alert workers of any temperature or pressure increase that would indicate polymerization.

The following control principles and methods are pertinent to all processes used for the production of styrene, polystyrene, reinforced plastics, synthetic rubber, and other styrene-based plastics. The methods of control include process isolation, process containment, and ventilation.

(a) Isolation of Incompatible Processes

The physical isolation of incompatible processes is sometimes required to achieve a safe work environment. For example, styrene readily reacts with low concentrations of halogens in the presence of ultraviolet light to form a potent lacrimator [323], a problem that can be prevented by isolating processes that generate halogens from processes that use or make styrene. In the reinforced plastics industry, the separation of grinding and sanding operations and fibrous glass cloth cutting areas from areas where styrene is being used has been recommended to reduce dermatitis [324].

(b) Containment

Closed process systems are the best way of preventing worker exposure to styrene; where practical, closed systems with negative pressure inside are preferred. Even with the use of closed systems, contact with styrene may still occur at pump seals and sampling ports, during draining, filling, and cleaning processes, and at spills. Unreacted styrene may be recycled to separate it from the polymerized product by vacuum devices. Closed loop sampling devices help minimize worker exposure [32]. For these systems to be effective, proper operation, maintenance, and frequent testing for leaks or other malfunctions are necessary. Use of remote control and automated processes can also reduce exposure to styrene.

(c) Ventilation

When closed process systems are not possible, exhaust ventilation, preferably local exhaust ventilation, may be needed to limit exposures to styrene. Because of fire hazards, ventilation systems need nonsparking fans and ducts. In addition, ventilation systems should prevent the recirculation of contaminated air. The ease of periodic inspection and cleaning are necessary considerations in proper design and location of valves, vents, gauges, pressure-relief devices, and other engineering controls. This is very important because styrene can easily polymerize and block vents or prevent valves, gauges, and pressure-relief devices from functioning properly [308].

(1) Local Exhaust Ventilation

Well-designed local exhaust systems can be used to effectively control styrene vapor, particularly during such work as spray-up, lay-up, and open molding operations where high concentrations of styrene are often encountered. Intensive local ventilation has been recommended as the only practical method of reducing styrene vapor concentrations during the construction of large reinforced plastic objects [324].

During the production of synthetic rubber, a large amount of styrene may be vaporized and released during drying operations, which are usually performed at elevated temperatures and are open to the atmosphere. Mallette [54] recommended that dryers be operated with a slight negative pressure or, if this was not feasible, that exhaust hoods be installed at the dryer outlets to regulate the escape of styrene vapor. When local exhaust systems are not feasible, area fans may have to be used to direct vapors away from the workers.

(2) Dilution Ventilation

When the concentration of the contaminant cannot be reduced at its source, other methods are necessary. One method controls the concentration in the general work environment by using general dilution ventilation, a method which is not usually as satisfactory as local exhaust ventilation.

Data such as the evaporation rate, temperature, and the surface area of the source of the contaminant, together with information on the toxicity of the contaminant, are needed to design an efficient dilution ventilation system [325]. To help reduce the risk of fires in the reinforced plastics industry, Fuller and Jensen [314] recommended use of a general ventilation system with an air flow of 1 cu ft/min/sq ft of floor space.

When ventilation is used to control exposure, it is desirable to have trained personnel make measurements that demonstrate system efficiency (i.e., velocity pressure, static pressure, or total pressure) on a periodic schedule as determined by a qualified industrial hygienist. It is also a good practice to measure system efficiency when there is any change in production, process, or control method. This necessitates maintenance of records that demonstrate the effectiveness of such changes; information needed includes date, type, and location of test, and results of the measurements taken.

(d) Other Control Methods

The difficulties in limiting exposures of workers to styrene and other materials in RP/C operations by conventional methods such as local exhaust ventilation or closed processes have motivated development of other approaches. Several of those attempts are described below.

In 1971, Maisonneuve and Lardeux [326] described a ventilation scheme that could be used in the construction of reinforced plastic boats. They suggested that the boat form should be mounted on wheels and be made so that it could rotate on its axis to facilitate work on both sides from one position. They also suggested that the boats (6.5 m long in this case) be constructed in a room that was 8 m long and had a fresh air stream with a flow of 0.5 m/s (about 100 ft/min). This air stream should be supplied across the entire length of the room, particularly at worker breathing zones. The investigators [326] also described various ventilation systems designed to reduce a worker's exposure to styrene during production of boats made from reinforced plastics.

In 1980, Willis [327] described some of the problems in trying to reduce styrene emissions during the curing process in boat building. An attempt to reduce styrene emissions by decreasing gel time was unsuccessful because the method used to decrease gel time involved increasing the workshop temperature to a high level. This halved the cure time but increased the amount of styrene evaporated to three times normal. Low-styrene emission (LSE) resins (also known as environmental resins) were tried several years ago, but there were disadvantages with the first resins tried. At first, addition of paraffin wax to the resin was thought likely to produce a screen between the resin and the air; however, the wax did not rise to the surface soon enough, and the wax impaired interlaminar adhesion. Other resins have subsequently been developed, but their nature, other than that some act to increase surface tension, was not described; apparently, their formulation or exact nature is proprietary.

LSE resins are now available, according to undocumented statements by Willis [327], that do not inhibit interlaminar adhesion, and claims for reduction of emissions of as much as 95% have been made. It was emphasized that use of these resins did not preclude the necessity for proper ventilation, but it was said that their use reduced the amount of ventilation needed, and assisted in reducing airborne concentrations of styrene.

In 1980, a group of representatives from the RP/C industry in the U.S. visited Sweden to assess Swedish technology in reducing styrene emissions and its applicability to U.S. operations. Their unpublished report [328] was furnished to NIOSH by The Society of the Plastics Industry, Inc. Only plants manufacturing small boats (up to 30 feet in length) were visited; these shops utilized hand lay-up/spray-up operations. The visiting group concluded that, in these small boat plants, engineering controls alone were not sufficient to achieve the occupational environmental limit in force at the time (i.e., 40 ppm), but that compliance could be achieved through a combination of high volume, low velocity air movement, use of personal protective equipment, different plant layouts, proper work practices, and environmental resins. Moreover, plant layouts needed to help achieve these reduced emissions were judged to result in productivity lower than that found in U.S. plants. It seemed doubtful to the study team that the 60 ppm ceiling limit was being met. (Verification of such a ceiling limit has not been found in other sources, including an official Swedish listing [329].) It was noted that there were no styrene emission standards in Sweden, so styrene could be exhausted directly outside the plant.

Other Swedish control systems found useful, in addition to ventilation, were the use of airless spray guns, and the bulk storage of resins underground which were piped directly to the spray guns. Specially designed cutting and grinding tools reduced dust exposure. In one boat plant, the spray booths had movable curtain walls that could completely surround the object being fabricated. In all cases, the inlet to the booths was constricted in some manner. Swedish experiments had indicated that an air velocity of 0.5 m/s was necessary to achieve 40 ppm, and 0.8 m/s to achieve 25 ppm. This air was introduced through diffusion filters. Elephant trunk hoses were placed at strategic locations around styrene sources for the purpose of exhausting the air. Dust emissions were exhausted through tool-mounted vacuum systems [328].

The Swedish workers were well trained, and followed proper practices well; work practices were reinforced by management attitudes. Workers were rotated so that only about half of their time was spent on spraying or rolling. During spraying, workers wore full head coverings, charcoal respirators, ear protection, and full-face plastic shields. Management of the Swedish boat plants felt that these protective items were not needed [328].

Initial LSE (environmental) resins, put into use in Sweden in early 1977, posed delamination problems, but these were eliminated in the second generation resins introduced about a year later. In addition to resulting in reduced styrene emissions, these resins result in a surface that is less tacky, thereby reducing the potential for dust accumulation with consequent lamination problems [328]. One Swedish firm installed strips of fibrous glass screen in areas where further lamination to stringers or bulkheads was expected. It was installed in the final application of wet resin, then peeled off just before the stringer or bulkhead was installed, revealing a clean surface for lamination.

The nature of the environmental resins was not described in the Swedish report [328], although several European purchase sources were listed; this reinforces the inference made earlier that these resins are proprietary in nature.

A 1980 report [330] gave drawings and some specifications for a number of types of hoods, canopies, and ducts, with exhaust air quantities and velocities and other general information, recommended for use in various RP/C operations. These were described as hardware either currently in use or available for use to control styrene emissions in RP/C operations. Efficacy data, for example, data regarding what the airborne emissions were, or how much of a reduction in air emissions could be or was achieved, were not reported.

As was indicated in Chapter V, airborne styrene oxide may be found in reinforced plastics operations. While the concentrations reported in limited studies [233,269] have been low, they may nevertheless be toxicologically significant.

When worker exposure cannot be adequately controlled by engineering controls, protective clothing and equipment, including respirators, may be needed. These are controls of last choice because of the difficulty of program management, which includes selecting and maintaining equipment and instructing workers on proper use and fitting, and worker acceptance and efficiency. Thus, neither respiratory protective equipment nor personal protective clothing is an acceptable substitute for proper engineering controls.

More detailed information on industrial ventilation can be found in publications of the American National Standards Institute (ANSI) [331], the American Conference of Governmental Industrial Hygienists (ACGIH) [325], and NIOSH [332]. Other NIOSH publications [333,334] give details of engineering control technology in use in the plastics and resins industry.

Personal Protective Clothing and Equipment

There have been several reports of skin irritation caused by styrene [2,54,56,61,91,104,113,122,126]. Blistering of the skin with loss of hair occurred when liquid styrene was applied repeatedly to the ear of a rabbit, and marked irritation with necrosis was found with two applications of liquid styrene to the shaved abdomens of rabbits [53,162]. Liquid styrene has been shown to be absorbed through the skin of both humans [151] and animals [165]. It was estimated that exposure of the palms of both hands to liquid styrene for 90 seconds would result in an absorption of styrene equivalent to the inhalation dose during a day of work at about 12 ppm [151].

Where workers may come in contact with liquid styrene, the use of appropriate equipment such as impervious gloves, boots, overshoes, bib-type aprons (at least knee length), face shields with goggles, and appropriate protective clothing is recommended. Proper selection of protective equipment is also necessary. For example, neoprene gloves and boots deteriorate rapidly and give protection for only a short time [32]. Leather shoes also do not provide adequate protection against liquid styrene [308,318]. Polyvinyl alcohol and polyethylene are reported to provide good protection against styrene [335].

Dermal contact may be a particular problem in those shops where styrene is poured, spread by hand, and sprayed. It is during the use of these techniques that the greatest airborne concentrations of styrene should also be expected. Thus, any worker who performs these operations or is near them while they are being performed should be provided with protective clothing and eye protection that will prevent skin and eye contact with styrene. These precautions should also be taken when workers enter an area where a leak or spill has occurred. Suitable pre-tested respiratory protective devices should also be made available to the worker.

Although barrier creams have been suggested as a beneficial method of preventing skin irritation [102], it has not been demonstrated that barrier creams are sufficiently impermeable to prevent absorption of styrene and dermal irritation. It is also possible that barrier creams may hold styrene in contact with skin and thereby increase irritation and penetration.

Styrene vapor can also penetrate the skin [154]. Thus, when work is being performed in areas where there are high concentrations of styrene, such as some confined space work, protective clothing as well as respiratory protection may be needed to prevent undue absorption.

In 1971, Bagdinov [336] reported that styrene vapor does not diffuse through certain protective textiles until the vapor concentration is greater than 5 ppm. In a comparison of the protective properties of various textiles, the least diffusion was through a mixture of wool and polyacrylonitrile . The effects of body movements that might force air through the fabric faster than it could diffuse were not considered.

While inside protective gloves, the hands may perspire. This problem can be minimized by wearing white cotton inner liners and making replacement liners available [337].

Workers exposed to styrene have experienced eye or nasal irritation or, usually, both [35,53,56,58,59,61,93,104,110,113,114,115,126]. To prevent eye irritation at moderately low concentrations, full-facepiece rather than half-facepiece respirators are recommended whenever work must proceed in areas where styrene concentrations are excessive.

If a worker complains of eye irritation from styrene while wearing an approved full-facepiece respirator, poor fit or sorbent exhaustion may be the cause [338]. Chemical cartridge respirators provide respiratory protection for relatively short periods. Respirators currently available do not contain an end-of-service-life indicator for styrene; therefore, the user must follow the manufacturer's recommendations for changing canisters or cartridges.

Although many workers may become accustomed to the irritancy of styrene vapor, systemic effects may still occur. Therefore, it is important that the employer follow the manufacturer's directions for changing canisters or cartridges on a regular schedule and not rely on worker complaints of irritation as an end-of-service-life indicator for respirators.

The type and class of respiratory device to use (see Table I-1, p. 8) is determined by taking atmospheric samples in the work areas and then selecting the appropriate device according to guidance on respirator selection. Routine sampling, as well as sampling after control, process, or climatic changes is recommended. Approved full-facepiece respiratory protection is desirable if the worker is exposed concurrently to styrene and benzene, toluene, or ethylbenzene, because simultaneous exposures to styrene and one or more of these other solvents may cause a decrease in the rate of metabolism of styrene, according to an experimental study [218]. Such exposure should be avoided whenever possible.

Regulations concerning personal protective equipment and respiratory protection can be found in 29 CFR 1910.133, 29 CFR 1910.134, and 30 CFR 11. NIOSH test data and recommendations for eye protection, which comply with ANSI Z87.1, can be found in two NIOSH publications [339,340].

Exposure Monitoring and Recordkeeping

To characterize worker exposures, the employer should conduct personal sampling and analysis for styrene. Estimates of the exposure of each worker should be made, whether or not each worker's exposure is measured by a personal sampler. Thus, a sampling strategy that allows reasonable estimates of each worker's exposure should be used. Records of such monitoring should include sampling and analytical methods, times and locations of samples, whether protective devices (especially respiratory protective devices) were in use, and the concentrations found or estimated. It is important, in the case of estimated concentrations, that information on which the estimates were based be included.

It is also important that pertinent medical records (i.e., results of medical examinations, the physician's written opinion, medical complaints, medical and work histories, etc.) be established and maintained for all workers, and that copies of any environmental monitoring data applicable to the worker be included in these records. To ensure that they will be available for future reference and correlation, they should be maintained for the duration of employment plus a period of 30 years. Copies of these medical and environmental records should be made available to the worker, former worker, or to his or her designated representative following specific written consent of the worker. In addition, the designated representatives of the Secretary of Health and Human Services and the Secretary of Labor should have access to the records or to copies of them.