

IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

Sampling and Analysis

There are several instrumental methods suitable for the evaluation of airborne concentrations of refined petroleum solvents.

A direct reading instrument such as a combustible gas meter may be used to determine concentrations of refined petroleum solvent vapor [96]. While this type of instrument is not specific, certain calibration procedures can be used to increase the instrument's accuracy. Examples of such procedures would be: (1) calibrating the instrument with the solvent which is actually in use at the sampling site, (2) simulating temperature conditions during the calibration procedure to duplicate conditions expected to exist at the sampling site, and (3) doing the actual calibration at the sampling site.

In 1974, nine commercially available portable combustible gas meters, weight range 1.1-6.8 lb, were evaluated by NIOSH [97]. On the basis of 11 separate operation manual criteria, the total weighted scores for the tested instruments ranged from 15 to 63 out of a possible 72; the basic cost of the instruments ranged from 175 to 535 dollars.

In 1976, NIOSH [98] published the results of a study in which three types of commercial available hydrocarbon meters were evaluated: four instruments using flame ionization, one infrared analyzer, and one using photo-ionization. The test criteria were similar to those of the above study. The results of these tests were used by NIOSH to recommend construction and performance standards for these instruments.

An interferometer has been used to evaluate concentrations of solvent vapor [99]. The sensitivity of this instrument varies with the relative densities of the air and of the solvent vapor being measured: the closer the relative densities are to being equal, the less sensitive the instrument is for the particular, considered solvent.

The combustible gas meter, hydrocarbon meter, and the interferometer can be used to detect vapors of a large number of solvents, but both are subject to interferences from other chemicals, none are convenient for personal zone sampling, all require grab samples, and none are readily adaptable to TWA sampling and analysis unless many readings are taken and integrated.

Smith and Pierce [100] used nonreactive metalized polyester bags to sample for benzene, methyl alcohol, dichloromethane, and methyl isobutyl ketone. While reports of these bags being used specifically for the sampling of refined petroleum solvents have not been found, they could possibly be used successfully. This particular sampling method may be used for TWA determinations if many samples are taken at a slow sampling rate.

Ray [101] reported that petroleum distillate vapors could be collected in a midget bubbler containing chloroform or on silica gel. An unspecified lacquer thinner was injected into a polyester bag with a tared microimpinger to prepare a test concentration of 3,850 $\mu\text{g}/\text{liter}$ of the lacquer. When the sampling rate of the bubbler was 1 liter/minute, 26% of the test concentration, 1,000 $\mu\text{g}/\text{liter}$, was recovered. When the sampling rate was reduced to 100 ml/minute for two consecutive tests, the recovered solvent concentrations were 3,910 and 3,700 $\mu\text{g}/\text{liter}$ or 102 and 95%, respectively. Silica gel was tested using a known lacquer solvent vapor at

a concentration of 9,000 $\mu\text{g}/\text{liter}$. When two consecutive samples were taken at a sampling rate of 100 ml/minute, concentrations of 8,670 and 8,500 $\mu\text{g}/\text{liter}$ or 96 and 95%, respectively, were recovered. While the sampling method using chloroform can be used for solvents that can exist in both mist and vapor forms, the collection medium is a very volatile liquid which may leak or evaporate in transport without proper handling. Furthermore, the sampling rate is limited to about 100 ml/minute.

Feldstein et al [102] reported using silica gel for collecting the vapors of numerous organic substances, one of which was Stoddard solvent. Three silica gel tubes in series, each containing 20 g of silica gel, were used for sampling. Test atmospheres were described by the total amount injected rather than in terms of concentration. When 100 μl of Stoddard solvent was injected into a heated test chamber, 98 μl or 98%, was recovered, and when 210 μl was injected, 204 μl or 97%, was recovered. The air flowrate through the system, which is the same as the sampling rate in this system, was 0.25 cu ft/minute (7.1 liters/minute) for 1 hour. Several of the solvents, eg, isopropyl alcohol, butyl cellosolve, ethyl acetate, and perchloroethylene, were tested in air having a high relative humidity. Only the sampling of perchloroethylene was affected, the collection efficiency was reduced. In dry air, 95-100% of the sampled perchloroethylene was collected in the first tube. In three consecutive tests with wet air, the amount collected in the first tube was reduced to 15, 14, and 5%. Stoddard solvent was not sampled at high experimental relative humidities, however, the ambient relative humidity was 40-55% when Stoddard solvent was tested. The authors also stated that, for field studies, where sampling times may be longer than 1 hour and greater

humidity may be present, the efficiency of adsorption of organic compounds is decreased. While the three silica gel tubes in series might be cumbersome for breathing zone samples, a large single silica gel tube could possibly be adapted for this purpose.

In 1936, Cook and Coleman [99] reported using activated charcoal for sampling solvent vapors. The sampling system consisted of a tube containing 8-mesh Ascarite and 20-mesh calcium chloride to remove acid vapors and moisture, attached to an activated charcoal tube to collect solvent vapors. This system was used by the authors in sampling for trichlorethylene, dichlorethylene, benzene, carbon tetrachloride, and petroleum distillates in textile cleaning and rubber goods manufacturing plants.

Charcoal tubes without the Ascarite and calcium chloride front sections have been recommended by the Physical and Chemical Analysis Branch of NIOSH for sampling for Stoddard solvent [103] and petroleum distillates [104]. Ascarite and calcium chloride sections in front of the charcoal tubes were used by Cook and Coleman [99] in conjunction with a gravimetric analytical procedure. The NIOSH-recommended analytical procedure is gas chromatography which does not require the use of Ascarite and calcium chloride as presection to the charcoal sampling tube.

In 1971, Olkhovskaya [105] reported on a colorimetric method for collecting air samples of benzene, kerosene, and white spirits. The principle of the method involves the reaction of either benzene, kerosene, or white spirits with a solution of 0.01% potassium bichromate in concentrated sulfuric acid (specific gravity 1.84). The resultant oxidation leads to the formation of soluble substances ranging in color

from light yellow to a dark cinnamon. The intensity of the color depends on the concentration of either benzene, kerosene, or white spirits. The concentration is then determined by the degree of color change of the sample as compared with the color of standard solutions. The sensitivity of the method for benzene, kerosene, and white spirits is 0.05 mg/3 ml, 0.02 mg/3 ml, and 0.025 mg/3 ml, respectively.

Airborne samples for the above [105] method are collected in two small absorbers each containing 3 ml of 0.01% potassium bichromate in concentrated sulfuric acid. The recommended sample size is 1.5 liters collected at a sampling rate of 5-6 liters/hour. The author [105] did not state the collection efficiency of the absorbers. This method [105] might be convenient for the in-plant monitoring of air concentration of one of these three solvents, as it does not require elaborate and costly equipment.

In a report by Feldstein et al [102] on silica gel source testing, the use of infrared light for analyzing complex materials such as Stoddard solvent and varnish makers' and painters' (VM and P) naphtha was described. Carbon disulfide was used to desorb the silica gel tubes. For Stoddard-type solvents, absorption at 3.4 μm was found by the authors to be proportional to the solvent concentration. No information about the range of this analytical procedure was reported.

A commercially available portable infrared analyzer can be used for the analysis of many air contaminants [106]. It was reported that, at a wavelength of 3.4 μm , the lower detectable limit for Stoddard solvent measured with this instrument was 0.01 ppm.

Gas-chromatographic techniques have been used in the analyses of Stoddard solvent [103], petroleum distillates [104], and organic solvents [107] in air. In recent years, gas chromatography has become one of the most prevalent methods of analysis for organic solvents [108-112]. This type of analysis can be used for the qualitative and quantitative analyses of refined petroleum solvents; however, when complex mixtures, such as many types of these solvents, are analyzed, changes in the chromatographic conditions or columns may be necessary to achieve the desired separation. In conjunction with this method, mass spectrometry can be used for the qualitative determination of complex mixtures.

In 1971, Narayanaswami and Bami [108] reported on the use of gas chromatography in India for forensic studies in the detection of kerosene residues. Both the isothermal and the temperature-programmed modes of gas chromatographic-operating conditions were used. The former mode was used when the volatile constituents of kerosene were considered to be absent, eg, residue samples collected following arson. In the isothermal mode, the gas-chromatographic conditions used were: temperature of 220 C, nitrogen as the carrier gas, with an exit of 42 ml/minute; the column was a 1/8-inch x 6.4-foot Apeizon L on chromosorb 80 mesh. Adequate resolution occurred in 24 minutes with a flame ionization detector. When the more volatile components were also present, samples of kerosene were analyzed by the temperature programmed mode using an AMIL vapor phase chromatograph, a 1/4-inch x 6.4-foot Apeizon L on celite column with a flame ionization detector. The initial temperature of 120 C was increased at a rate of 5 C/minute up to 150 C, 8 C/minute up to 200 C, and 16 C/minute up to 280 C. Using nitrogen as a carrier gas, separation of the sample took 17 minutes.

With both modes, sufficient peak resolution occurred to enable the matching of the kerosene residue samples with the known kerosene bulk samples.

Direct reading indicator tubes can measure hydrocarbons from 2 to 25 mg/liter (2,000 to 25,000 mg/cu m) [113]. These tubes will indicate total hydrocarbons, beginning with hexane (C6 homolog). The reaction of the hydrocarbon with the tube contents causes a brown color. The presence of aromatics such as benzene or toluene changes the color from brown to reddish. These tubes may also be used to test for kerosene vapor [113,114]. Direct reading indicator tubes may be used for worksite surveys but should not be used when precise measurements are needed. The recommended method for the sampling and analysis of the refined petroleum solvents [15,103] are presented in Appendices II and III.

The refined petroleum solvents covered in this document are primarily composed of saturated hydrocarbons, olefins, and aromatics. Many of the individual chemical components of these groups, such as benzene, naphthalene, pentane, hexane, heptane, and octane, have existing federal airborne standards or currently recommended airborne standards. The combined sampling and analytical procedure should have the capability to permit the evaluation of the air concentration of a particular refined petroleum solvent, as well as one or more of the particular substituent compounds of that particular solvent. After evaluating the above sampling and analytical procedures, the combination best suited to these criteria would be sampling with activated charcoal tubes followed by analysis of the sample using gas chromatography, possibly in combination with mass spectrometry.

The preferred and reliable sampling device consists of a glass tube with two sections, each filled with activated charcoal, separated by a section of urethane foam. These tubes are capable of collecting all of the refined petroleum solvent vapors discussed in this document. Moreover, the sampler is light, contains no liquids, and is readily adaptable to personal, TWA, and ceiling sampling. The only interference of any consequence is very high humidity, evident by the visible condensation within the charcoal tube, which will seriously reduce the collection efficiency of the sampling tube. The difficulty may be circumvented by calibration of the sampling tubes prior to field sampling, to estimate the degree to which humidity will affect the collection efficiency.

Gas-chromatographic techniques can be used in the evaluation of both the total concentration of airborne refined petroleum solvents and the concentration of certain individual constituents of the solvent, such as benzene. When using a gas chromatograph in the analysis of refined petroleum solvents, it is imperative that the analyst be supplied with a bulk sample of the solvent in question in order to prepare the standard solutions, determine desorption efficiencies, and check for interferences. The gas-chromatographic patterns of the field samples and bulk or head space samples should be compared to identify any possible interferences. Gas chromatograph-operating conditions stated in Appendix IV have been tested for Stoddard solvent [103] and varnish makers' and painters' naphtha [104] and modifications of these operating conditions may be necessary for the determination of other refined petroleum solvents.

NIOSH recommends that the sampling and analysis be performed using charcoal tubes and gas chromatography. The method has been tested by NIOSH

for Stoddard solvent [103] and varnish makers' and painter's naphtha [104] as part of the Standards Completion Project. Using a 3-liter air sample of Stoddard solvent, this method [103] was validated for concentrations of airborne Stoddard solvent from 1,417 to 5,940 mg/cu m. The probable useful range of the method, using a 3-liter air sample, was stated to be 295-8,850 mg/cu m for Stoddard solvent. Using a 4-liter air sample for varnish makers' and painters' naphtha, a similar method [104] was validated for concentrations of this refined petroleum solvent from 937 to 3,930 mg/cu m, with a probable useful range of 200 to 6,000 mg/cu m. By increasing the air sample size to 10 liters or more (depending on the suspected airborne concentrations) and using a slower sampling rate, the methods should be capable of being extended to the range of concentrations considered in this document.

The above sampling and analytical procedures do not work well for refined petroleum solvents comprised of C5-C8 hydrocarbons, such as petroleum ether which is composed of pentane and isohexane, 80 and 20% respectively, because carbon disulfide which is used as a desorbent, has a boiling point of 46.3 C, and interferes in the elution pattern of the sample. This difficulty can be resolved by the selection of a desorbent with a boiling point above that of the C5-C8 range, such as toluene. A different column packing and gas chromatograph conditions can further refine the method. These modifications however, have not yet been tested by NIOSH. An example of a sampling and analysis procedure using a combustible gas meter is given in Appendix II. A more detailed procedure for the use of charcoal tubes and gas chromatograph are presented in Appendix III and IV.

Environmental Levels

Little information has been found about the air concentrations of petroleum naphtha, mineral spirits, Stoddard solvent, and kerosene encountered in industry. Four studies [74,75,115,116] concerning Stoddard solvent illustrate contemporary uses and possible air concentrations representative of environmental levels of Stoddard solvent.

In 1968, Oberg [115] reported a survey of 30 of 140 randomly selected drycleaning plants in Detroit, Michigan. Twelve plants used Stoddard 105, a Stoddard solvent with a closed-cup flashpoint of 41 C (105 F); nine used 120, a solvent with a closed-cup flashpoint of 49 C (120 F); and nine used Stoddard 140, a solvent with a closed-cup flashpoint of 60 C (140 F). Air concentrations were measured with a Davis Model 6 Vapo Tester, Davis Model 11-650 Flame Ionization Meters, and a J and W Model SS Aromatic Hydrocarbon Indicator. TWA exposures were calculated for each of the three solvents for the entire drycleaning cycle. The actual drycleaning operation was observed by the author to be about one-half of the total 8-hour work shift. The following are 4- and 8-hour time-weighted exposures for each of the three solvents: Stoddard 105, 65 and 35 ppm; Stoddard 120, 47 and 25 ppm; and Stoddard 140, 25 and 15 ppm. Two plants, one using Stoddard 105 and the other using Stoddard 140, had air samples taken at 1-minute intervals during the entire drycleaning cycle, approximately 40 minutes. Higher than average airborne solvent concentrations were found during the washing and extraction cycles. The author gave the following reasons for these above-average air concentrations: (1) the improper placement of air inlets and exhaust ventilation, (2) interruptions in the washing cycle to add additional clothes released high concentrations of the solvents into the

workroom environment, and (3) the placement of extractors at long distances from the washing equipment permitted clothes wet with Stoddard solvent to remain in contact with the atmosphere for longer than normal periods of time.

In 1974, Larsen and Shmunnes [75] reported a hazard evaluation in a metals-manufacturing plant. Nine machines, five with a 2-inch belt and four with a 3-inch belt, were used to polish aircraft engine blades. Each polisher had six heads and five polishing stations composed of aluminum oxide and silicon carbide. The blades passed automatically from one polishing station to the next. The only operator who changed the blades was located at the sixth head. About 500 large blades were changed each day; a greater number of smaller blades were polished. Coolant oil was automatically fed in a small stream at the top and bottom of the blades. No visible mist was produced, and, if the blades were adequately cooled, no visible "smoke" was produced. Stoddard solvent was used to clean the machines about once a week.

About 10 workers were involved in this operation; however, Larsen and Shmunnes [75] did not specify whether all 10 workers were involved in the operation at the same time. Workers complained of eye, nose, and throat irritation, sinus problems, headache, and nausea. There was no warning label on the storage container of the coolant. The employees also indicated that a coolant which had been used for about 2 years was causing more problems than the one used previously, although analysis of samples from the old and new coolants showed that they were essentially the same. Stoddard solvent was the only component that would have been volatile at room temperature.

On March 25, 1972, breathing-zone sample findings showed concentrations of oil mist that ranged from 0 to 0.55 mg/cu m [75]. The oil mist was generated during the polishing operation when the coolant was placed on the blades and came in contact with the polishers. Oil mist samples were collected on 37-mm vinyl metrical filters [75]. The oil mist was analyzed by an undescribed fluorescence procedure. No Stoddard solvent was found in breathing-zone samples taken using charcoal tubes. No analytical procedure for Stoddard solvent was reported by the authors. On May 8, 1972, sampling was performed again, and airborne concentrations of Stoddard solvent were found to be less than 20 ppm. The sampling performed on March 25 occurred several days after the machines were cleaned with Stoddard solvent, and the May 8 sampling occurred immediately after the machines had been cleaned with Stoddard solvent and put back into operation. The authors concluded that concentrations of airborne Stoddard solvent could at certain times, eg, during startup after cleaning, be higher than those found during the survey unless the Stoddard solvent was thoroughly removed from the system after it was cleaned.

In 1974, Markel and Shmunis [74] reported a health hazard evaluation by NIOSH at a greeting card company in Cincinnati, Ohio, where six people were involved in a flocking operation. The evaluated operation involved insertion of flattened greeting cards under silk screens containing a preselected pattern mesh. An appropriate colored glue was squeezed through the silk screen onto the card which was then dipped into the matching color flocking compound (dyed rayon tow). The glues contained a type of Stoddard solvent. No specific information, such as boiling range or flashpoint, about the Stoddard-type solvent component of the glue was given by the

authors. The persons involved in the flocking operation also cleaned the silk screens with a mineral spirits solution for about 5 minutes/day. The Stoddard-type solvent was sampled with a charcoal tube at a sampling rate of 1 liter/minute. The analysis was with gas chromatography at a sensitivity of 0.05 mg/tube. Twelve general area samples were taken, one of which became contaminated and was discarded. For the remaining 11 samples, the minimum, average, and maximum air concentrations were 99, 438, and 1,906 mg/cu m, respectively.

In 1976, the Research and Development Committee of the Institute of Industrial Launderers [116] conducted a survey to determine the concentrations of petroleum solvents vapors in laundering plants with petroleum solvent cleaning systems. In this survey, concentrations of airborne Stoddard solvent were determined at two representative industrial laundry plants. Air samples were taken by a consultant industrial hygienist to determine an 8-hour average worker exposure and excursion spot tests. The excursion spot tests were taken when the concentrations of airborne Stoddard solvent were believed to be the greatest.

At the first plant [116], a drycleaning machine was used an average of 4 hours/day. Two-hour samples were taken from the breathing zones of the two workers operating the machine. During this period, four loads of clothes were cleaned. The Stoddard solvent concentration in the breathing zone of one worker (designated as a cleaner) was reported to be 50.3 ppm, and, for another worker (designated as a helper), the reported breathing zone concentration was 65.3 ppm. These two concentrations were reported by the consultant industrial hygienist to be an 8-hour average exposure to Stoddard solvent. However, what the two workers did during the remaining 4

hours of their work shift was not mentioned. The excursion spot tests were collected at the breathing level of the two workers while they were (1) removing cotton work gloves and trousers from the machine, (2) removing fender covers from the machine, and (3) removing cotton work gloves from the machine. The concentrations of airborne Stoddard solvent found during these operations were reported as: 67, 68, and 60 ppm, respectively.

At the second plant, similar sampling was performed. However, in addition to breathing zone and excursion spot-test samples, area samples were taken. A breathing-zone sample of approximately 3.5 hours' duration was taken on one worker who operated a drycleaning machine. An area sample was also taken in the immediate vicinity. The drycleaning machine was used on an average of 10 hours/day. The results of the breathing-zone and area samples were 242 and 66 ppm of Stoddard solvent, respectively, and were considered to be representative of an 8-hour exposure. Three excursion spot tests were performed. Two were conducted at the breathing zone level while the worker removed shirts first, and then coveralls from the cleaning machine. The third sample was taken near the extractor, 5 feet above the floor. The Stoddard solvent concentrations during these three spot tests were 60, 57, and 70 ppm, respectively. The 242-ppm value for the breathing-zone sample is higher than the ACGIH recommended level of 100 ppm for Stoddard solvent [117]. The author did not explain the disparity between the TWA breathing-zone sample and the excursion samples. It was recommended that other sampling be performed. Approximately 2 months later, the breathing-zone and area samples were repeated for the same worker and the airborne Stoddard solvent concentrations were reported to be 20.0 and 28.0 ppm. Excursion spot tests were performed for operations

similar to those checked earlier and Stoddard solvent concentrations of 68, 63, and 62 ppm were reported.

Engineering Controls

Engineering controls and work practices for operations using petroleum solvents should have as their objectives: control of vapor concentrations, minimizing of skin contact, prevention of eye contact, and the prevention of fire and explosion.

Where practicable, closed systems should be designed, properly operated, and maintained to achieve these major objectives and should be periodically checked for performance. Where closed systems are not feasible, other control measures, such as local exhaust systems and temperature control, may be used to control petroleum solvent exposures. Specific operations such as spray painting and metal degreasing may require additional precautions such as the placement and design of specialized exhaust hoods, an increase in the capture velocity of the hood, and installation of air movers with designed capabilities to produce a negative pressure relative to the surroundings.

Where mechanical ventilation is used to control concentrations of airborne petroleum solvents, it should be designed and maintained to prevent the accumulation or recirculation of the solvent vapors into the workroom. Exhaust systems discharging into outside air must conform with applicable local, state, and federal air pollution regulations. Measurements to determine the efficiency of ventilation systems used to control exposure should be taken at least every 3 months, and within 5 working days of any change in production, process, or control that might

result in any increase in air concentrations. Air velocity, static pressure, and air volume [118] can be used in the evaluation.

When a fan is located in duct work and the solvent may exceed an air concentration of one-fourth of the lower flammable limit, the rotating element should be nonsparking material or the casting should be coated with or consist of a nonsparking material. The ventilation system should contain devices along its length intended to prevent the propagation of possible flashbacks. Additional information regarding ventilation systems can be found in Industrial Ventilation--A Manual of Recommended Practice [119], Fundamentals Governing the Design and Operation of Local Exhaust Systems 29.2-1971 [120], and Recommended Industrial Ventilation Guidelines [121].

Drycleaning operations should be provided with general ventilation systems. The system should be designed so that exhaust air is replaced with clean, tempered, makeup air. All connections of this system should be well-sealed and periodically checked for leakage. Drycleaning equipment should be operated at negative pressure so that, when the loading door is opened, air from the room will be drawn into the machine, preventing the escape of contaminants into the workroom [122]. Although respiratory protective equipment is not an acceptable substitute for proper engineering controls, it should be available for emergencies and for nonroutine maintenance and repair.

For additional information on specific operations, pertinent federal regulations should be followed. For example, the design of open surface tank ventilation is dealt with in 29 CFR 1910.94(d). Open surface tanks are used in operations involving the immersion of materials in liquids or

in the vapors of such liquids to clean or impart a finish to a material. There are 16 classes of open surface tanks. The class into which a particular tank operation would be categorized is determined by two factors: specific toxicity and the rate at which gas, vapor, or mist is given off by the system. Dip-tank operations are considered in 29 CFR 1910.108 and in 1910.94(d), and 29 CFR 1910.107 and 1910.94(c) deal with spray finishing.

Emission control of solvent vapors into the atmosphere can be accomplished by several methods. These methods include direct or catalytic combustion, activated carbon adsorption, and condensation [123].

V. WORK PRACTICES

Engineering controls and work practices should be designed and implemented primarily to maintain airborne solvent concentrations below prescribed limits, minimize excursions, prevent skin and eye contact, and reduce fire and explosion hazards. Since the types of solvents discussed in this document have many different industrial uses, the work practices recommended are applicable to many solvents.

Table XIV-1 [1,3-14,17-19,21,27,56,67,82,124-129] gives the chemical and physical properties for six refined petroleum solvents. These solvents are designated as combustible and flammable liquids of Classes IA, IB, IC, II, and IIIA based on the criteria in 29 CFR 1910.106 (a)(18)(i), (a)(18)(ii), (a)(19)(i), (a)(19)(ii), and (a)(19)(iii). These classifications for these refined petroleum solvents are determined primarily on the basis of boiling point and flashpoint or flashpoint range. A particular solvent may belong to different OSHA classifications depending on the properties of the product in use. Petroleum ether is designated as a Class IA flammable liquid if its boiling point is below 37.8 C (100 F) (29 CFR 1910.106 (a)(19)(i)) and as Class IB flammable liquid if its boiling point is at or above 37.8 C (100 F) (29 CFR 1910.106 (a)(19)(ii)). Rubber solvent and varnish makers' and painters' naphtha are flammable liquids of Class IB (29 CFR 1910.106 (a)(19)(ii)). Mineral spirits is handled as a Class IC flammable liquid if its flashpoint is below 37.8 C (100 F) (29 CFR 1910.106 (a)(19)(iii)) and as a Class II combustible liquid if its flashpoint is at or above 37.8 C (100 F) (29 CFR 1910.106 (a)(18)(i)). Stoddard solvents and kerosene are designated as Class II

combustible liquids if their flashpoints are below 60 C (140 F) (29 CFR 1910.106 (a)(18)(i)) and as Class IIIA combustible liquids if their flashpoints are at or above 60 C (140 F) (29 CFR 1910.106 (a)(18)(ii)). When a combustible liquid is heated for use to within 16.7 C (30 F) of its flashpoint, it should be handled in accordance with the requirements for the next lower class of liquids (29 CFR 1910.106 (a)(18)(iii)). The National Fire Protection Association NFPA No. 30 Flammable and Combustible Liquids Code [130] should be strictly adhered to when handling refined petroleum solvents; NFPA No. 70 Electrical Code [131] NFPA No. 36 Solvent Extraction Plants Code [132], and NFPA No. 32 standard for drycleaning plants [26] should be complied with where applicable.

Two articles have been reported in the literature concerning the flashpoint of a redistilled Stoddard solvent [133,134]. The National Association of Dyeing and Cleaning, Inc [133] reported that, when new (unused) Stoddard solvent was continuously distilled from 3 to 8 hours at a time for a total of 50 hours, the distillate had the same flashpoint as the original Stoddard solvent. In the second article, Howanitz [134], reported that, when used Stoddard solvent was redistilled, the flashpoint of the distillate was lower than that of the original material. The reduction in flashpoint after the first recovery was 5-10 F. The actual test data were not reported. In a written communication to NIOSH from the International Fabricare Institute (AC Lloyd, January 1977), data were presented regarding changes in the flashpoint of redistilled (used) regular 100 flash Stoddard solvent. In plant I, the mean and standard deviations for the flashpoint were 104.32 and 1.20 F, respectively, for 20 consecutive flashpoint determinations after the redistillation of used regular Stoddard solvent.

The mean and standard deviations for the flashpoint after 7-14 consecutive distillations in plants II-IV were similar. In plant IV, however, the flashpoint dropped from 105 to 101 F in one distillation. This may have been the result of an error in the testing method, but the Stoddard solvent was not retested because of insufficient sample size. The flashpoint changes presented in this article (AC Lloyd, written communication, January 1977) were not of the magnitude of those reported by Howanitz [134].

The discrepancy in the magnitude of flashpoint changes after the redistillation of used Stoddard solvent reported by Howanitz [134] and the data presented by the International Fabricare Institute (AC Lloyd, written communication, January 1977) could be because of the type of contaminant found in the used Stoddard solvent. The Stoddard solvent tested by Howanitz had been used to clean electric motors, whereas the other Stoddard solvent had been used to clean garments. The different contaminants could have an effect on the flashpoint of redistilled (used Stoddard solvent); however, the magnitude of this effect is not readily apparent. Consequently, whenever Stoddard solvent is redistilled, the flashpoint of the distillate should be checked.

Special precautions are necessary for entering tanks, extractors, or vessels which may contain refined petroleum solvents, for performing flame- or spark-generating operations such as welding and cutting, and for transferring refined petroleum solvents. Before any employee enters a vessel, all pipelines leading into or out of the vessel must be blanked to prevent the entry of refined petroleum solvent liquid or vapors [135]. The vessel interior should then be washed with water and then purged with air or with nitrogen followed by air. After the purging, the vessel atmosphere

should be tested with a combustible gas meter or other suitable instruments [135]. No one should enter a tank, vessel, or extractor without first being equipped with an appropriate respirator (if necessary) and a secured lifeline and harness. At least two other workers should watch at all times from outside the vessel. These workers should be equipped with respiratory protection (at least one being the positive pressure type) and secured lifelines and harnesses. One additional employee should be able to assist in the event of an emergency. The use of portable lights to illuminate the interior of tanks, vessels, or extractors when they are undergoing cleaning or repairs should be prohibited. Such interiors should be illuminated by reflected light [135]. Only nonferrous (sparkproof) tools should be used for scraping away clinging residues or accumulated deposits. Rags and other materials used to wipe up and absorb refined petroleum solvents should be placed in standard safety containers for subsequent disposal. Cutting or welding must be performed only when an authorized representative of the employer signs a permit indicating that all necessary safety precautions have been taken [135].

In 1945, Lawrence [33] reported an incident in which a worker was overcome by aviation spirit vapor while wearing an oxygen-breathing apparatus. The worker was not, however, wearing a harness and lifeline. Within 10 minutes after descending into a hole drilled near a large aviation fuel storage tank the worker was seen holding onto a crossbar and reeling drunkenly. At this point a second worker (totally unprotected) descended into the hole to assist the first worker. Both workers were subsequently overcome by the aviation spirit vapors. Both workers were eventually rescued and recovered following treatment. This particular

report is an example of an operation in which the proper safety equipment and proper emergency procedures were not used. The use of a harness and lifeline alone would probably have prevented the necessity of the second worker entering the hole and would have expedited the removal of the first worker.

The transfer of refined petroleum solvents by gravity flow or compressed air should be avoided. Where feasible, transfer from tank to process use should be through rigid pipe systems operated by remote control. When performed indoors, liquid transfers from portable containers should be through readily attached approved pumps and continuous armored hose lines [135]. If safety cans are used, they should be of the approved type, with a spring-closing lid and spout cover and designed to release internal pressure when they are subjected to heat [136]. When refined petroleum solvents are transferred from one container to another, the containers should be bonded or electrically grounded [118].

Containers of refined petroleum solvents should not be stored in direct sunlight, because of the possible generation of high pressure within the containers. Where tarpaulins or similar covering are used, they should be positioned to allow for air circulation [137]. Heating of an area should be by direct means. Open-flame devices must be prohibited in any area where refined petroleum solvents are used, stored, or handled [135].

Appropriate types of protective fire-resistant clothing, such as gloves, boots, aprons, and face shields (8-inch minimum), impervious to refined petroleum solvents should be provided and worn where needed to prevent repeated or prolonged skin contact [118]. In addition, whenever employees are required to handle solvent-saturated materials, such as when

removing clothes from a drycleaning operation, the materials should be kept as far from the breathing zone of the worker as possible [122]. Personal sampling should be performed during this operation to determine the need for respiratory protection. Additional information concerning work practices for drycleaning operations is given in Health and Safety Guide for Laundries and Dry Cleaners [122].

The employer should provide soap and water for washing skin contaminated with these solvents [118]. Handwashing with solvents such as Stoddard solvents, mineral spirits, and kerosene, or other refined petroleum solvents should be prohibited. If soap and water are not effective, the employer should provide an alternate cleanser. For additional skin protection, skin creams can be used during and after work. One such skin cream consists of 5% lanolin, 5% glycerol, 5% castor oil, 10% toilet soap, 23% kaolin, 1% carboxymethyl-cellulose, 0.5% antiseptic, and water to 100% [138]. For kerosene, a skin cream composed of 50% water, 25% glycerin, 10-15% cellulose-methasol gum, and 2-3% preservative, has been experimentally shown to protect human skin in contact with this solvent for up to 90 minutes [139].

Unless clothing is impervious to refined petroleum solvents, a change of clothing should be made available to any employee whose clothes become wetted with solvents. Contaminated clothing should be stored in closed containers until it is either removed by drying or laundering, or discarded. The employer should inform the persons laundering or otherwise handling the contaminated clothing of the hazardous properties of these solvents [118].

Chemical safety goggles (splashproof) and fullface shields (8-inch minimum) meeting the requirements of 29 CFR 1910.133 and ANSI Z87.1-1968 should be provided and worn in any operation where there is a reasonable probability that refined petroleum solvents could be splashed into the eyes. If these solvents are accidentally splashed into the eyes, copious amounts of water should be used to flush the eyes while the eyelids are lifted, and a physician should be contacted.

Whether employees should be allowed to wear contact lenses when working around eye irritants such as refined petroleum solvents is not readily answered. Under some circumstances, contact lenses may act as a barrier to eye contact from a splash, but under other circumstances they may act to retain the solvent in contact with the eye. The preferability of wearing contact lenses instead of conventional glasses with respirators is an obvious advantage, but at other times contact lenses may pose an overall disadvantage, since conventional glasses should also be somewhat effective as a barrier to splashes. As a minimum, supervisors should know of those employees wearing contact lenses so that appropriate decisions can be made in the event of splashes. Soft contact lenses should not be worn around irritant atmospheres because they can absorb the irritant materials.

When the concentrations of airborne refined petroleum solvents cannot be kept at or below prescribed limits by engineering controls, eg, during spills, equipment failure, maintenance, or vessel entry, special respiratory protection is required. The selection of proper respiratory devices is presented in Chapter I, Tables I-1, I-2, and I-3.

Protective clothing and equipment, including respirators, should be kept clean and maintained in good condition. This equipment should be

cleaned and inspected by trained personnel after each use. Worn equipment should be replaced when necessary. The employer must ensure that all equipment is in working order and that it is stored properly when not in use.

During emergency operations, fire and explosion may be the primary hazards involved. A program for the rapid evacuation of the work area should be implemented. In addition, all potentially exposed employees should be aware of escape procedures, of the proper use and location of respirators designated for emergency situations, and of firefighting methods. Instructions should be given for transporting injured employees to areas where emergency medical care can be given.

Safety showers, eyewash fountains, and fire extinguishers should be located in or near areas where refined petroleum solvents splashes are likely to occur and must be properly maintained. Washing facilities, soap, and water, or an alternate cleanser should be available to employees. As a good hygienic practice, it is recommended that employees wash their hands before eating, smoking, or using toilet facilities.

The consumption or storage of food or beverages in exposure areas should be prohibited in accordance with provisions of 29 CFR 1910.141 (g)(2) and (g)(4).

In summary, precautions must be taken to guard against exposure of personnel to toxic concentrations of refined petroleum solvents and to the fire and explosion hazards associated with them. It is also important that employees be informed prior to job placement of any hazards associated with one or more of the refined petroleum solvents that they may come in contact with. The employees should also be informed whenever process changes could

alter their exposure. The safe handling of refined petroleum solvents is dependent on the employees' knowledge and proficiency in handling these materials. Proper initial training and periodic retraining of the employees concerning the correct use of equipment and protective devices required for the safe handling of these solvents is the responsibility of the employer. During these training programs, emergency procedures should be stressed. Recommended labels and posters should be displayed. The US Department of Labor "Material Safety Data Sheet" shown in Appendix V or a similar approved form must be filled out and filed in a location readily accessible to all employees who may be exposed to refined petroleum solvents. If the recommended work practices are observed and good engineering controls are installed, employees working with refined petroleum solvents should be adequately protected from various hazards associated with refined petroleum solvents, including overexposure, fire, and explosion.