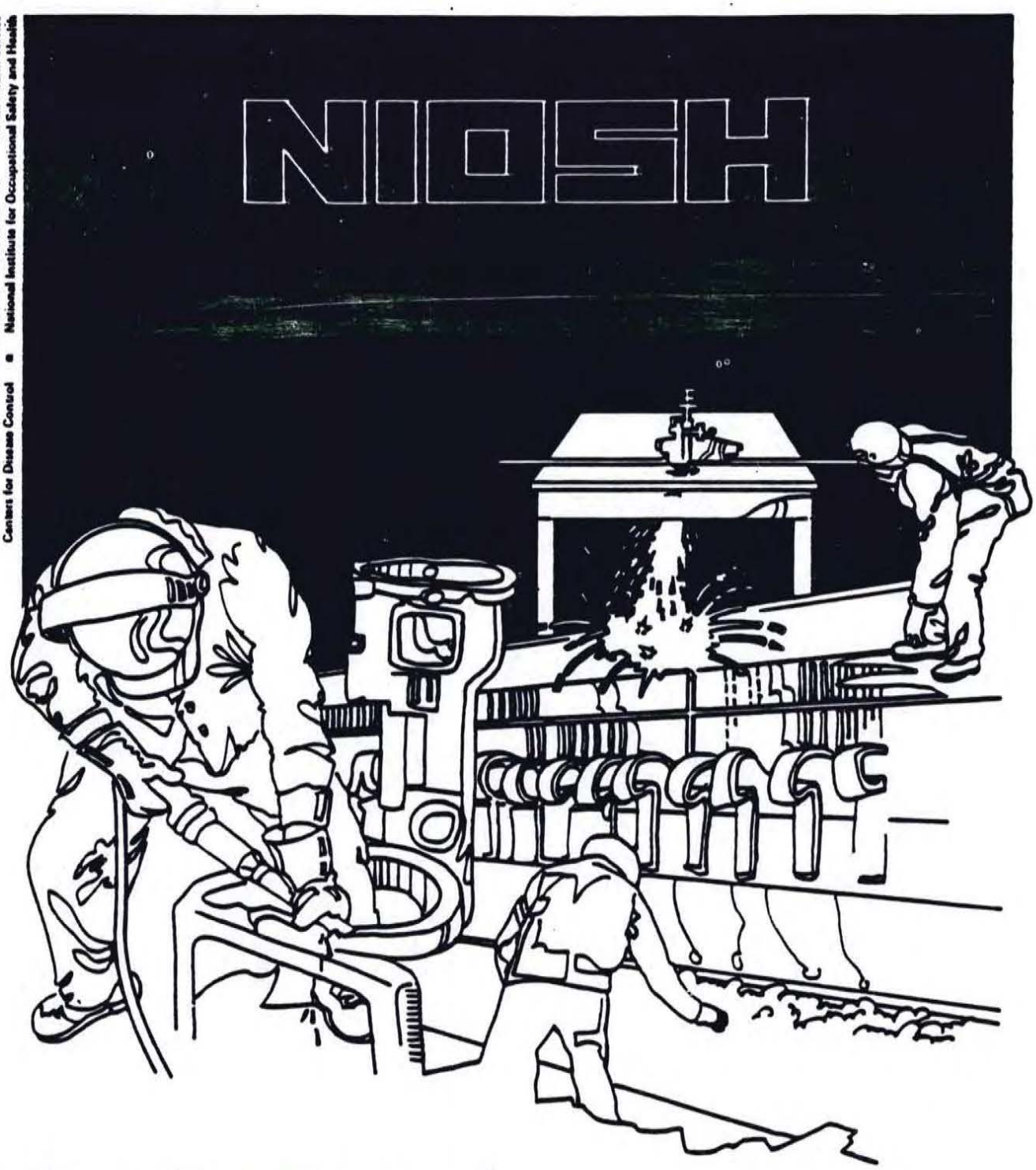
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health

NIOSH



Health Hazard Evaluation Report

HETA 84-420-1661
E.I. DUPONT SABINE RIVER WORKS
ORANGE, TEXAS

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 84-420-1661
February 1986
E.I. DUPONT SABINE RIVER WORKS
ORANGE, TEXAS

NIOSH INVESTIGATORS:
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I. SUMMARY

On June 28, 1984, the National Institute for Occupational Safety and Health (NIOSH) was requested to evaluate exposures to painters at the E.I. Dupont Sabine River Works Plant in Orange, Texas. The primary concern was to characterize employee exposures to isocyanates and to recommend the appropriate respiratory protection necessary to control these exposures.

On August 7-10, 1984, NIOSH investigators conducted an environmental survey at the Sabine Plant. Long-term personal breathing-zone and area air sampling was performed during painting operations to assess exposures to isocyanates (monomeric HDI and TDI and total reactive isocyanate groups - TRIG) and organic solvents (cellosolve acetate, ethyl acetate, methyl ethyl ketone and xylene).

Three of 40 samples taken for monomeric HDI had measureable amounts: two personals at 5.9 & 23.4 ug/m^3; and one area sample at 41.5 ug/m^3. Monomeric TDI was found in only 2 of 40 samples: two personal samples at 9.3 & 33.8 ug/m^3. None of the personal air samples collected for monomeric HDI and TDI exceeded the NIOSH recommended standard of 35 ug/m^3. Results of the personal and area air samples for TRIG revealed 10 of 20 personal samples and 15 of 20 area samples had detectable concentrations: personals (59.7 - 369 ug/m^3); and areas (41.2 - 484 ug/m^3). There is no OSHA standard or NIOSH recommended standard in the United States for TRIG. Since exposures to isocyanates were measured in this study, it is prudent to utilize positive-pressure supplied-air respirators as recommended by NIOSH. Analysis of the personal and area air samples collected for cellosolve acetate revealed that 2 of 19 personal samples (31.6 mg/m^3 and 52.7 mg/m^3) and 2 of 18 area samples 43.4 mg/m^3 and 63.9 mg/m^3) exceeded the ACGIH TLV® of 27 mg/m^3. All measured concentrations of personal exposures to individual solvents were less than three percent of the respective evaluation criteria: solvent concentration ranges compared to the evaluation criteria (EC); ethyl acetate, 0.2 - 30.6 mg/m^3 (EC-1400); methyl ethyl ketone, nondetectable - 11.4 mg/m^3 (EC-590); and xylene 0.2-6.1 mg/m^3 (EC-435). However, workers were overexposed based on the additive effect of the solvent vapor mixtures: cellosolve acetate, ethyl acetate, methyl ethyl ketone and xylene, 1.2 and 1.9 mg/m (EC-1.0).

The results of this investigation indicated employees were exposed to isocyanates (detectable levels of monomeric HDI and TDI and TRIG). Also the data collected showed overexposures to cellosolve acetate and to mixtures of solvents. Measures to improve working conditions are recommended in Section VII of this report.

KEYWORDS: paints, IMRON®, spray painting, isocyanates, HDI, TDI, cellosolve acetate, organic solvents.

II. INTRODUCTION

On June 28, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a joint request from the International Painters and Allied Trades Union, Local 328, and Courtney Enterprises, Inc., Houston, Texas, to evaluate employee exposures during painting operations at the Dupont Sabine River Works Plant, Orange, Texas. As part of the plant's ongoing general maintenance schedule, Dupont Imron® paint is used to paint the processing equipment. The request's primary focus was to assess exposure to isocyanates and determine appropriate respiratory protection.

NIOSH investigators conducted an environmental investigation at the plant on August 7-10, 1984. A response letter summarizing the environmental activities conducted during the survey and outlining preliminary recommendations concerning work practices and personal protective equipment was distributed to plant management and union representatives in August 1984. A second letter regarding the general results of the isocyanate samples taken was distributed in November 1984.

III. BACKGROUND

The Dupont Sabine River Works Plant, in operation since 1946, covers about 1200 acres in Orange, Texas. It is the world's largest producer of nylon intermediates, methanol, and polyethylene resins. Three resins produced by the total workforce of nearly 2500 employees include Alathon® polyethylene resin, Elvax® vinyl resin, and Surlyn® ionomer resin.

During the NIOSH survey the painting processes operated on a one-shift, 5-day, 8-hour per day schedule. The painting contractor for Dupont's Finishes and Fabricated Products Department, Courtney Enterprises Inc., usually has an average of 15-25 painters from the Painters Union Local 328 on site at any one time, but the overall range of painters on the job has been 6 to 25. The majority of painting operations at the Sabine Plant continue all year and are done on the processing equipment located outdoors.

To prepare the surface to be painted the workers manually scrape the surface with a metal scraper and wire brush and then use sand paper to remove any excess scale. Occasionally sand blasting is performed prior to painting and the employee is equipped with a hooded supplied-air respirator for this task.

One or two coats of primer and finish paint are applied either by compressed-air spray painting, brush or roller. The spray painting equipment consists of DeVilbiss hand-held air paint atomizing guns fed from Bink's paint reservoir pressure pots of either 2 or 5 gallon capacities. Air pressure on the paint reservoir pot varies from 15-40 psi while the pressure at the spray gun tip is maintained at about 60 psi.

Various colors of Dupont's IMRON® polyurethane enamel finish paint, one color of IMRON® polyurethane enamel primer paint, two paint system activators and solvent thinners/cleaners were used at the four painting sites during the NIOSH survey: Units 3040, 552, 554, and the Tank Farm. The daily painting process varies with the amount of surface area to be covered and the weather conditions.

At the time of the NIOSH survey the workers used organic vapor/chemical cartridges along with dust/mist prefilters.

IV. EVALUATION DESIGN AND METHODS

Long-term personal and area air sampling was performed on August 7-10, 1984 during spray painting and paint rolling operations to characterize employee exposure to isocyanates (monomeric HDI and TDI and total reactive isocyanate groups) and organic solvents (cellosolve acetate ethyl acetate, methyl ethyl ketone and xylene). Bulk samples of the paint materials were obtained to aid in the analysis of the air samples. The air sampling and analytical methods for these substances, including collection device, flow-rate, and referenced analytical procedures are presented in Table I.[1]

A brief synopsis of the newly developed NIOSH air sampling/analytical method for total reactive isocyanate groups is as follows:

> A known volume of air is bubbled through a midget impinger containing a known quantity of a toluene solution of 1-(2-methoxyphenyl)-piperazine. An aliquot of the toluene solution is acetylated and then evaporated to dryness. The residue is dissolved in methanol and an aliquot is injected into a high-performance liquid chromatograph equipped with a UV detector capable of detection at 254 nm. The change in concentration of 1-(2-methoxyphenyl)-piperazine is quantitated and the number of moles of reactive isocyanate groups present determined. The isocyanate groups are quantitated regardless of the size of the molecule to which they are attached.

V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual suseptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are not usually considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and Recommendations, 2) The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV's)®, and 3) The U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Occupational Health Standards. In addition, a British isocyanate standard was included for this study to compare measured total reactive isocyanate groups (TRIG) with a referenced criteria. Further discussion regarding TRIG follows under the isocyanate evaluation.

Often, the NIOSH recommendations and ACGIH TLV's® are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's® usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substance have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

The environmental evaluation criteria utilized in this study are presented in Table II. Listed for each substance are the NIOSH recommended standards, ACGIH TLVs®[2] and the OSHA[3] standards.

Isocyanates

All isocyanates contain the -N=C=O group, which reacts readily with compounds containing reactive hydrogen atoms to form urethanes. The di- and poly-isocyanates contain, respectively, two and three or more of these groups.[4] The chemical reactivity of the isocyanates makes them ideal for polymer formation. Hence, they are widely used in the manufacture of polyurethane foams, paints, adhesives, fibers, resins, and sealants.

In general, the potential respiratory hazards encountered during the use of diisocyanates in the workplace are related to their vapor pressures. The lower-molecular-weight diisocyanates tend to be more readily volatilized into the work place atmosphere than the higher-molecular-weight diisocyanates. Although the vapor pressures of the higher-molecular-weight diisocyanates are relatively low, they may generate vapor concentrations sufficient to cause respiratory and mucous membrane irritation if they are handled in poorly ventilated areas. Also, the potential for skin irritation is generally higher for the lower-molecular-weight diisocyanates, and the severity of these irritant responses is reduced with increasing molecular weight.[5]

Exposure to isocyanates can cause skin and mucous membrane irritation, nausea, vomiting and abdominal pain.[6,7] In high concentrations, isocyanates have a primary irritant effect on the respiratory tract. They can also act as respiratory sensitizers, producing asthma-like symptoms in sensitized individuals, even at very low concentrations.

Asthmatic attacks may occur immediately after exposure or at an interval of hours after cessation of exposure, presenting as nocturnal cough and breathlessness. Exposure to isocyanates may also result in chronic impairment of pulmonary function.[5] Isocyanate exposure during accidental spills is a major cause of sensitization, and there is evidence that massive exposures may produce effects on the central nervous system.[5] One recently completed animal study found dose-related statistically significant cancer exceses in mice and rats administered TDI by gavage (not the usual route of human exposure) in very high concentrations. The tumors were distant from the site of administration.[8]

In the United States, federal OSHA exposure standards for diisocyanates have been established only for toluene diisocyanate and methylene bisphenyl isocyanate. The current federal OSHA standard and ACGIH TLV® for TDI is a ceiling limit of 0.02 parts of TDI per million parts of air (ppm), (0.14 milligrams per cubic meter of air, (mg/m^3)) and an 8-hour TLV® of 0.005 ppm (0.04 mg/m^3), respectively.

The current NIOSH recommended standard for occupational exposure to HDI and TDI is 0.035 mg/m^3, for up to a 10-hour workshift 40-hour workweek, and 0.14 mg/m^3 as a ceiling concentration for any 10-minute sampling period. The NIOSH recommended standard for diisocyanates was based on three types of effects of exposure: direct irritation, sensitization, and chronic decrease in pulmonary function. This standard applies to diisocyanate monomers only, and not to higher polymers of these compounds.[5] Little is known about the toxicological effects of polymeric isocyanates. No long-term studies have been conducted on polymeric isocyanates, and furthermore, their potential for inducing pulmonary hypersensitivity, as shown for monomeric isocyanates, has not been investigated.[9] However, results of a recent NIOSH study revealed that work in an industrial setting

where polymeric isocyanate exposures were documented was associated with small mean decreases in FEV_1 and FVC which were not observed in an unexposed group. Also, the change in FEV_1 over the shift correlated with personal airborne exposure to polymeric but not monomeric MDI.[10]

Recently, in February, 1983, the United Kingdom Health and Safety Commission set a "common control limit" for workplace exposure to all isocyanates. This new control limit is an 8-hour TWA of 20 ug of isocyanate group per cubic meter of air, and a 10-minute TWA of 70 ug of isocyanate group per cubic meter of air. This new control limit, in units of ug (NCO)/m^3, requires that the analytical methods be applicable to "total isocyanate", i.e., the sum of all isocyanate species, including monomers and prepolymers.[11]

Organic Solvents
(Cellosolve acetate, ethyl acetate, methyl ethyl ketone, and xylene)

These solvents as a group have some common systemic effects. They can cause fatigue, headache, drowsiness, nausea, vomiting, dizziness, loss of coordination and other central nervous system effects. Irritation of the eye, mucous membranes and the respiratory tract can also occur. Liver damage can result, with increase in blood levels of liver enzymes such as alanine aminotransaminase, aspartate aminotransaminase and gamma glutamyl transpeptidase. Cellosolve acetate causes central nervous system depression in animals and similar effects may be expected in humans with severe exposure.[12] Animals exposed to 2-ethoxyethanol, a glycol ether, have shown significant increases in embryonic deaths, fetal abnormalities, testicular atrophy and microscopic testicular changes, altered behavioral test results, and changes in brain neuro-chemical concentrations. Test results of some compounds structurally related to glycol ethers such as cellosolve acetate (2-ethoxyethyl acetate) indicate that they have the potential for causing adverse reproductive effects similar to 2-ethoxyethanol.[13]

VI. RESULTS

Results of the personal and area air samples obtained on August 7-10, 1984, during the painting operations to determine employee exposure to isocyanates (monomeric TDI and HDI and total reactive isocyanate groups, TRIG) and organic solvents (ethyl acetate, cellosolve acetate, methyl ethyl ketone, xylene and mixtures of solvents) are presented in Tables III and IV, respectively.

Three of 40 samples taken for monomeric HDI had measurable amounts: two personal samples at 5.9 & 23.4 ug/m^3 and one area sample at 41.5 ug/m^3. Monomeric TDI was found in only 2 of 40 samples: two personal samples at 9.3 & 33.8 ug/m^3. None of the personal air samples collected for monomeric HDI and TDI exceeded the NIOSH recommended standard of 35 ug/m^3 for up to a 10-hour work shift.

The analytical results for the total reactive isocyanate groups are originally reported in micromoles of NCO per sample. These values are converted to micrograms per cubic meter using the molecular weight of 42 (N+C+O) for the NCO radical. These calculations were performed so that the resulting values could be compared with the United Kingdom's new standard for total isocyanate groups 20 ug/m^3 for an 8-hour TWA.[11]

Of the 40 samples collected for TRIG, (20 stationary area and 20 personal), 25 had detectable quantities. Ten of the personal samples (59.7 - 369 ug/m^3) and 15 area samples (41.2 - 484 ug/m^3) exceeded the United Kingdom's standard.

The environmental air sample values for the personal and area solvent samples collected are shown in Table IV. A total of 37 air samples were obtained for cellosolve acetate (range: nondetectable-63.9 mg/m^3). Two of 19 personal samples for cellosolve acetate (31.6 mg/m^3-Tank Farm and 52.7 mg/m^3-Unit 552) exceeded the ACGIH TLV® of 27 mg/m^3 and 2 of 18 stationary area air samples (43.4 mg/m^3 and 63.9 mg/m^3-Tank Farm) exceeded this criterion. None of the exposures exceeded the federal OSHA standard of 540 mg/m^3 for an 8-hour TWA.

Measured concentrations of individual solvents (ethyl acetate, methyl ethyl ketone, and xylene) were within 3% of the recommended evaluation criteria used for this study; NIOSH recommended standards, OSHA standards and/or ACGIH TLVs®. However, when two or more hazardous substances having similar health effects are present, measurement of exposure to the combination, in addition to the assessment of health effects should be considered. That is, the sum of the fractions, actual concentration divided by the exposure limit for each substance ($C_1/T_1 + C_2/T_2 + \ldots + C_n/T_n$) should not exceed unity (must equal 1.0 or less). Using this concept, overexposure based on the additive effect of the solvent vapor mixtures (cellosolve acetate, ethyl acetate, methyl ethyl ketone, and xylene) were found (personal samples) at Unit 552 (1.9) and at the Tank Farm (1.2).

VII. Discussion

The main purpose of the request for the NIOSH investigation was to evaluate employee exposures to isocyanates during painting operations and to recommend appropriate respiratory protection. Under conditions of this study the environmental air samples revealed worker exposures to monomeric HDI and TDI, to total reactive isocyanate groups (United Kingdom's standard), cellosolve acetate, and to mixtures of solvents. Ideally, the reduction of employee overexposures should be accomplished by the implementation of improved engineering control of workplace contaminants such as substitution of less hazardous process materials, automation, redesign or replacement of existing mechanical ventilation systems, better work practices or a combination of these measures. However, with the outdoor painting operations at the Sabine River Works Plant using engineering controls to reduce exposures may not be practical and the employer must instead rely on personal protective equipment (i.e. respirators).

The official NIOSH position on controlling respiratory exposures to isocyanates was presented in a July 12, 1985 letter[14] to Mr. Edward J. Baier, Director of Technical Support, U.S. Department of Labor, OSHA, Washington D.C., from Mr. John B. Moran, Director of the Division of Safety Research, NIOSH, Morgantown, West Virginia. This letter states:

> The NIOSH position on isocyanate containing paints remains unchanged. The lack of warning properties of isocyanates eliminates NIOSH approval for air-purifying respirators. In addition, the problem of sensitization of persons exposed to very low concentrations of isocyanates dictates use of the best available respiratory protection. Therefore, we recommend positive pressure supplied-air respirators be used for respiratory protection against isocyanate containing paints.[14]

An additional justification for the use of supplied-air respirators is that of worker comfort. The highest psychrometric measurement recorded by NIOSH personnel during the survey was 96'F dry bulb and 89'F wet bulb, corresponding to about 76% relative humidity. The painters no doubt would feel much more comfortable and have less breathing resistance using supplied-air respirators as opposed to the air-purifying type.

VIII. RECOMMENDATIONS

In view of the findings of the environmental investigation, the following recommendations are made to ameliorate existing or potential hazards and to provide a better work environment for the employees covered by this determination. (A number of the following recommendations were also made at the closing conference and in a previous letter sent to management and union representatives in August, 1984).

A. Isocyanates & Respirators

1. There should be a respirator program consistent with the guidelines found in DHEW (NIOSH) Publication No. 76-189, "A Guide to Industrial Respiratory Protection," and the requirements of the General Industry Occupational Safety and Health Standards (29CFR 1910.134). (Copies have been provided to both management and union representatives). Any respirators used, including the approved components and replacement parts should have NIOSH/MSHA approval.

   If non-certified or substituted respirator components are used, the NIOSH/MSHA approval of the entire respirator assembly is voided, and the protection offered by the respirator may be compromised.

The NIOSH criteria document for occupational exposure to diisocyanates[5] (DHEW, NIOSH, Publication No. 78-215) recommends that a worker exposed to diisocyanates should be provided with, as a minimum, a type C supplied-air respirator with full facepiece operated in pressure-demand or other positive pressure mode, or with full facepiece, helmet, or hood operated in continuous-flow mode. However, it must be realized that providing respiratory protection for individuals wearing corrective glasses is a problem. A proper seal cannot be established if the temple bars of eye glasses extend through the sealing edge of the full facepiece. Systems have been developed for mounting corrective lenses inside full facepieces. When a worker must wear corrective lenses as part of the facepiece, the facepiece and lenses should be fitted by qualified individuals to provide good vision, comfort, and a good tight seal.

2. The medical recommendations for current and future painting employees exposed to isocyanates, as outlined in the NIOSH diisocyanate criteria document,[5] should be followed. These recommendations include the need for pre-placement examinations and periodic medical surveillance:

   a. Preplacement examinations should include at least comprehensive medical and work histories, with special emphasis on pre-existing respiratory conditions such as asthma. A smoking history should also be compiled.

      Physical examination giving particular attention to the respiratory tract and baseline measurements of forced vital capacity (FVC) and forced expiratory volume at 1 second (FEV_1) should be done. The worker's ability to use negative and positive pressure respirators should be assessed.

   b. Periodic examinations should be made available at least annually, or as determined by the responsible physician. This should include, interim medical and work histories, and clinical examination giving particular attention to the respiratory tract and measurements of FEV_1 and FVC.

   c. During examinations, applicants or employees found to have medical conditions that could be directly or indirectly aggravated by exposure to diisocyanates, e.g.; respiratory allergy, chronic upper or lower respiratory irritation, chronic obstructive pulmonary disease, or evidence of sensitization to diisocyanates, should be counseled on their risk from working with these substances. Chronic bronchitis, emphysema, disabling pneumoconiosis, or cardiopulmonary disease with significantly impaired ventilatory capacity similarly suggest an increased risk from exposure to diisocyanates. If a history of allergy is elicited, applicants should be counseled that they may be at increased risk of adverse health effects from exposure to diisocyanates. Employees should also be advised that exposure to diisocyanates may result in delayed effects, such as coughing or difficulty in breathing during the night.

B. Miscellaneous Recommendations

3. Gloves impervious to the paints and solvents used should be provided for and worn by the painters during clean-up operations. It should be ascertained that the gloves provided are of sufficient length and are flexible enough to be used for clean-up tasks.

4. Hand washing facilities should be made available at all painting sites. In lieu of wash basins with running water and soap, waterless hand cleaners and paper towels would suffice.

5. Current Material Safety Data Sheets and information concerning products used (including descriptions of potential adverse health effects) should be on file at the Sabine River Works Plant and made available to all affected personnel. Furthermore, a continuing education program conducted by a person or persons qualified by experience or special training, should be instituted to ensure that all employees have current knowledge and understanding of job safety and health hazards, proper work practices and maintenance procedures, and that they know how to use respirators correctly.

6. The painters' work clothes may become contaminated with organic solvents and paint particulates. Occasionally paints containing leaded pigments are used. Based on the fact that lead-based paints are sometimes used (and more generally that it is good hygiene practice), the following recommendations are advised:

   a. All painters should shower at the end of the workday before going home. Adequate shower and changing room facilities should be made available. You may wish to provide some time at the end of the workday for their use.

   b. Workclothes and shoes used by the painters at work should not be worn outside the plant and certainly should not be worn home. You should institute a system of changing from street clothes to workclothes and shoes before work, and changing back after work.

   c. The painters' workclothes should be laundered by the employer and not at home with other family clothing.

7. Periodic environmental evaluations of employee exposures to isocyanates and cellosolve acetate should be conducted to assure that the above recommendations are adequate to protect the affected employees.

IX. REFERENCES

1. National Institute for Occupational Safety and Health. NIOSH Manual of Analytical Methods: Vol 2, Publication no. 77-157-B, 1977; Analytical Method, 5505 Total Isocyanates, Third Edition, Publication no. 84-100, 1984; Vol 1, Publication no. 77-157-A, 1977.

2. American Conference of Governmental Industrial Hygienists. Threshold limit values for chemical substances and physical agents in the workroom environment and biological exposure indices with intended changes for 1984-85. Cincinnati, Ohio: ACGIH, 1984.

3. Occupational Safety and Health Administration. OSHA safety and health standards. 29 CFR 1910.1000. Occupational Safety and Health Administration, revised 1983.

4. Woolrich, Paul F. Toxicology, Industrial Hygiene and Medical Control of TDI, MDI, AND PMPPI. AIHA Journal, Vol. 43, February, 1982.

5. National Institute for Occupational Safety and Health. Criteria for a recommended standard: occupational exposure to diisocyanates. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1978. (DHEW publication no. (NIOSH) 78-215).

6. National Institute for Occupational Safety and Health. Occupational diseases: a guide to their recognition. Revised ed. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1977. (DHEW (NIOSH) publication no. 77-181).

7. International Labour Office. Encyclopedia of occupational Health and safety. Vol I/a-k. Geneva: International Labour Office, 1971 Third (Revised) Edition, 1983.

8. Dieter, M. P., NTP, Technical Report on the Carcingogenesis Bioassay of Toluene Diisocyanate. NIH Publication No. 82-2507, National Toxicology Program, Research Triangle Park, North Carolina, August, 1982.

9. Weyel, D. A., Rodney, B.S., and Alaire Y. Sensory Irritation, Pulmonary Irritation, and Acute Lethality of Polymeric Isocyanate and Acute Lethality of 2, 6 - Toluene Diisocyanate. Toxicology Appl. Pharmacol, 1982; 64:423-430.

10. National Institute for Occupational Safety and Health. Health Hazard Evaluation Report No. HETA 80-073-1589. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1985.

11. Silk, S. J., Hardy, H. L. Control Limits for Isocyanates. Ann. Occupational Hygiene. Vol. 27, No. 4, pp. 333-339, 1983.

12. Proctor NH, Hughes JP. Chemical hazards of the workplace. Philadelphia: J.B. Lippencott Company, 1978.

13. National Institute for Occupational Safety and Health. Current intelligence bulletin 39--glycol ethers. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1983. (DHHS (NIOSH) publication no. 83-112).

14. Letter of July 12, 1985 from John B. Moran, Director of the Division of Safety Research, NIOSH, Morgantwon, West Virginia to Edward J. Baier, Director Directorate of Technical Support, U.S. Dept. of Labor, OSHA Washington, D.C.

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Publications Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. E.I. Dupont DeNemours & Company Inc.
2. Courtney Enterprises Inc.
3. Painters Union, Local 328
4. International Painters and Allied Trades Union
5. NIOSH, Region VI
6. OSHA, Region VI

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE I
Air Sampling and Analysis Methodology
E.I. Dupont Sabine River Works
Orange, Texas
HETA 84-420

Substance	Collection Device	Flow Rate (liters per minute)	Analysis	References[1]
Cellosolve Acetate	Charcoal Tube	0.2	Gas Chromatography	NIOSH P & CAM 541 with modifications*
Ethyl Acetate	Charcoal Tube	0.2	Gas Chromatography	NIOSH P & CAM 549 with modifications*
Methyl Ethyl Ketone	Silica Gel	0.05 & 0.2	Gas Chromatography	OSHA METHOD #16 with modifications*
Monomeric Hexamethylene Diisocyanate (HDI)	Midget Impinger with 15 ml of 1-(2-methoxyphenyl)-piperazine in toluene	1.0	High Performance Liquid Chromatography	NIOSH METHOD 5505 Total Isocyanates
Monomeric Toluene Diisocyanate (TDI)	Midget Impinger with 15 ml of 1-(2-methoxyphenyl)-piperazine in toluene	1.0	High Performance Liquid Chromatography	NIOSH METHOD 5505 Total Isocyanates
Total Reactive Isocyanate Groups (TRIG) (monomer & polymer)	Midget Impinger with 15 ml of 1-(2-methoxyphenyl)-piperazine in toluene	1.0	High Performance Liquid Chromatography	NIOSH METHOD 5505 Total Isocyanates
Xylene	Charcoal Tube	0.2	Gas Chromatography	NIOSH P & CAM 127 with modifications*

*The modifications included sample preparation, instrument condition settings, and/or column selection.

TABLE II

Environmental Evaluation Criteria
E.I. Dupont Sabine River Works
Orange Texas
HETA 84-420

Substance	(mg/m^3)* NIOSH Recommended Standard	ACGIH TLV®	OSHA Standard
Cellosolve Acetate	-	27	540
Ethyl Acetate	-	1400	1400
Hexamethylene Diisocyanate	0.035	-	-
Methyl Ethyl Ketone	590	590	590
Toluene Diisocyanate	0.035	0.04	0.14**
Total Reactive Isocyanate Groups (Monomer & Polymer)	--***	-	-
Xylene	435	435	435

All values given are time-weighted average exposures for a normal workday, 40-hour workweek unless other wise designated.

*mg/m^3 = milligrams per cubic meter of air
**The federal OSHA standard for TDI is a ceiling limit (0.14 mg/m^3).
***There is no available evaluation criteria in the United States for total reactive isocyanate groups. The United Kingdom's standard for TRIG is 20/ug/m^3 for an 8-hour TWA and 70 ug/m^3 for a 10-minute TWA.

Table III
Results of Environmental Air Samples for Isocyanates[1]
E.I. Dupont Sabine River Works
Orange, Texas
HETA 84-420
August 7, 1984

Time	Sample Location	Personal Sample(P) or Area Sample (A)	Sample Volume (Liters)	Total Reactive Isocyanate Groups (ug/m^3/umoles NCO per sample)[3]	(ug/m^3)[2] Monomeric TDI	Monomeric HDI
0954-1555	Unit 552 Adipic Acid On lighting Panel C 2nd Floor	A	230	248/1.36	ND[4]	ND
1004-1556	Unit 552 Adipic Across from Eyewash Above Cabinet Opposite End of Painting Area	A	282	171/1.15	ND	ND
0947-1600	Unit 552 Adipic Acid	P	302	369/2.65	ND	23.4
0925-1545	Unit 554 Cooling Tower	P	337	96/0.77	ND	5.9
0927-1545	Unit 554 Cooling Tower	P	333	ND/ND	33.8	ND
0940-1540	Unit 554 Cooling Tower In AM Sample Placed on Stairs/Side Wall-In PM Sample Mounted on Worker's Platform/Bucket Lift	A	320	86.7/0.66	ND	ND
0817-1545	Unit 3040	P	399	95.8/0.91	ND	ND
0827-1548	Unit 3040	P	391	93.3/0.87	ND	ND
1015-1552	Unit 3040 North-East Corner	A	294	ND/ND	ND	41.5

(continued)

Table III (continued)
Results of Environmental Air Samples for Isocyanates[1]
E. I. Dupont Sabine River Works
Orange, Texas
HETA 84-420
August 8, 1984

Time	Sample Location	Personal Sample(P) or Area Sample (A)	Sample Volume (Liters)	Total Reactive Isocyanate Groups (ug/m³/umoles NCO per sample)[3]	(ug/m³)[2] Monomeric TDI	Monomeric HDI
0818-1535	Unit 552 Adipic Acid	P	359	216/1.85	ND[4]	ND
0826-1541	Unit 552 Adipic Acid On Lighting Panel C	A	383	216/1.97	ND	ND
0834-1546	Unit 552 Adipic Acid Across From Eyewash Station Opposite End of Painting Area	A	377	189/1.70	ND	ND
0842-1550	Unit 552 2nd Floor Along Wall East End Between Two Steel Doors	A	335	198/1.58	ND	ND
0830-1547	Unit 554 Cooling Tower	P	353	ND/ND	ND	ND
0825-1549	Unit 554 Cooling Tower	P	421	59.7/0.60	ND	ND
0820-1553	Unit 554 Cooling Tower Mounted on Workers' Lift Bucket	A	352	98.7/0.83	ND	ND
0830-1547	Unit 3040	P	398	93.8/0.89	ND	ND
0849-1105	Unit 3040	P	136	ND/ND	ND	ND
0953-1545	Unit 3040	P	322	ND/ND	0.3	ND
0924-1556	Unit 3040 North-East Corner	A	392	61.8/0.58	ND	ND

(continued)

Table III (continued)
Results of Environmental Air Samples for Isocyanates[1]
E.I. Dupont Sabine River Works
Orange, Texas
HETA 84-420
August 9, 1984

Time	Sample Location	Personal Sample(P) or Area Sample (A)	Sample Volume (Liters)	Total Reactive Isocyanate Groups (ug/m^3/umoles NCO per sample)[3]	(ug/m^3)[2] Monomeric TDI	Monomeric HDI
0815-0924	Unit 554 Cooling Tower	P	69	ND/ND	ND[4]	ND
0850-0950	Unit 554 Cooling Tower Sample Mounted on Stairway to Roof	A	60	ND/ND	ND	ND
0819-0950	Unit 554 Cooling Tower Sample on Workers' Lift Bucket	A	91	108/0.23	ND	ND
0834-0942	Tank Farm	P	68	ND/ND	ND	ND
0838-0940	Tank Farm	P	62	ND/ND	ND	ND
0845-0942	Tank Farm	P	57	ND/ND	ND	ND
0845-0943	Tank Farm South Side Center of Tank on Vertical Pipe	A	58	ND/ND	ND	ND
0845-0943	Tank Farm North Side Between Tanks #1 and #2 Center I-Beam	A	58	ND/ND	ND	ND

(continued)

Table III (continued)
Results of Environmental Air Samples for Isocyanates[1]
E.I. Dupont Saline River Works
Orange, Texas
HETA 84-420
August 10, 1984

Time	Sample Location	Personal Sample(P) or Area Sample (A)	Sample Volume (Liters)	Total Reactive Isocyanate Groups (ug/m³[2]/umoles NCO per sample)[3]	(ug/m³)[2] Monomeric TDI	(ug/m³)[2] Monomeric HDI
0841-0951	South Side of Tank Farm Tank Adjacent to Railroad Track Center of Tank on Vertical Pipe	A	70	ND/ND	ND	ND
0910-0952	North Side of Tank Farm Between Tanks #1 and #2 Center I-Beam	A	47	484/0.48	ND	ND
0840-0949	Tank Farm	P	60	240/0.40	ND	ND
0841-0945	Tank Farm	P	64	245/0.37	ND	ND
0840-0948	Tank Farm	P	68	ND/ND	ND	ND
0822-1410	Unit 554 Cooling Tower	P	260	ND/ND	ND	ND
0825-1400	Unit 554 Cooling Tower Sample Mounted on Workers' Lift Bucket	A	275	41.2/0.27	ND	ND
0840-1413	Unit 554 Cooling Tower Sample Placed on Stairway Along Side Wall	A	263	65.6/0.41	ND	ND
0935-1323	North-East Side Unit 3040	A	228	66.1/0.40	ND	ND
0935-1535	Unit 3040 North Side	A	360	66.1/0.57	ND	ND
0922-1515	Unit 3040	P	321	118/0.91	ND	ND
0927-1533	Unit 3040 North Side	A	366	172/1.5	ND	ND
Evaluation Criteria Normal workday, 40 hr/wk, time weighted average:					35	35
Laboratory analytical limit of detection (LOD) in micrograms/sample				8.4	1.3	1.7
Laboratory analytical limit of quantitation (LOQ) in micrograms/sample of NCO				16.8	2.2	2.8
LOD/LOQ in micromoles of NCO/sample		0.2/0.4				

1. All concentrations are time-weighted averages for the period sampled
2. ug/m³ = micrograms per cubic meter of air
3. The conversion from micromoles of NCO per sample to micrograms per cubic meter of air is made using the NCO radical and the molecular weight of 42 (N+C+O) and dividing by the air volume
4. ND = nondetectable concentration

Table IV
Results of Environmental Air Samples For Solvents[1]
E.I. Dupont Sabine River Works
Orange, Texas
HETA 84-420
August 7, 1984

Time	Sample Location	Personal Sample(P) Or Area Sample(A)	Sample Volume (liters)	(mg/m³)[2] Ethyl Acetate	Cellosolve Acetate	Methyl Ethyl Ketone	Xylene	Additive Effect
0830-1548	Unit 3040	P	75.9	3.3	3.9	-	0.7	0.1
1023-1552	Unit 3040 North-East Corner	A	52.8	0.5	2.8	-	0.6	0.1
0947-1600	Unit 552 Adipic Acid	P	59.2	30.6	52.7	-	6.1	1.9
0954-1555	Unit 552 Adipic Acid 2nd Floor Lighting Panel C	A	49.9	4.3	14.4	-	1.4	0.5
1004-1556	Unit 552 Adipic Acid Across From Eyewash Area Above Cabinet Opposite End Of Painting Area	A	51.5	0.7	1.7	-	0.2	0.1
0925-1545	Unit 554 Cooling Tower	P	62.1	0.6	1.4	-	0.2	0.1
0927-1545	Unit 554 Cooling Tower	P	59.7	1.1	2.9	-	0.4	0.1
0940-1540	Unit 554 Cooling Tower-Sample On Lift Platform/Bucket	A	55.2	0.2	0.8	-	0.1	0.03

(continued)

Table IV (continued)
Results of Environmental Air Samples For Solvents[1]
E.I. Dupont Sabine River Works
Orange, Texas
HETA 84-420
August 8, 1984

Time	Sample Location	Personal Sample(P) Or Area Sample(A)	Sample Volume (liters)	(mg/m^3)[2] Ethyl Acetate	Cellosolve Acetate	Methyl Ethyl Ketone*	Xylene	Additive Effect
0924-1556	Unit 3040 North-East Corner	A	71.1	0.9	4.2	ND (19)	0.3	0.2
0830-1547	Unit 3040	P	73.4	3.1	8.1	ND (74.9)	0.7	0.3
0849-1148	Unit 3040	P	33.9	2.5	7.3	ND (9.3)	0.8	0.3
0953-1545	Unit 3040	P	70.9	5.7	6.0	3.9(18.1)	1.5	0.2
0818-1535	Unit 552 Adipic Acid	P	67.1	7.6	19.4	0.3(66.2)	1.9	0.7
0826-1541	Unit 552 Adipic Acid On Lighting Panel C	A	70.4	0.6	2.4	ND(18.3)	0.2	0.1
0834-1546	Unit 552 Adipic Acid East End by Cabinet Across from Eyewash	A	73.3	1.7	5.3	ND(17.2)	0.6	0.2
0830-1547	Unit 554 Cooling Tower	P	62.2	0.2	0.8	4.9 (1.3)	0.4	0.04
0825-1549	Unit 554 Cooling Tower	P	62.4	1.7	3.4	6.1(18.1)	0.5	0.1
1035-1553	Unit 554 Cooling Tower	A	50.3	1.0	1.3	ND(17.7)	0.2	0.05

(continued)

Table IV (continued)
Results of Environmental Air Samples For Solvents[1]
E.I. Dupont Sabine River Works
Orange, Texas
HETA 84-420
August 9, 1984

Time	Sample Location	Personal Sample(P) Or Area Sample(A)	Sample Volume (liters)	(mg/m^3)[2] Ethyl Acetate	Cellosolve Acetate	Methyl Ethyl Ketone*	Xylene	Additive Effect
0815-0924	Unit 554 Cooling Tower	P	12.6	3.3	3.8	ND(3.5)	0.8	0.1
0834-0942	Tank Farm	P	12.8	1.4	3.2	ND(12.4)	0.6	0.1
0838-0940	Tank Farm	P	11.7	8.2	17.2	ND(11.8)	2.5	0.6
0845-0942	Tank Farm	P	10.9	1.5	4.5	6.9(2.9)	0.7	0.2
0845-0943	Tank Farm South Side Center Vertical Pipe	A	10.9	ND	ND	ND(2.9)	ND	-
0845-0943	Tank Farm North Side Between Tanks #1 & #2 Center I beam	A	10.2	30	63.9	ND(2.9)	9.9	2.4
0819-0950	Unit 554 Cooling Tower	A	17.2	4.9	3.6	-	0.9	0.1

(continued)

Table IV (continued)
Results of Environmental Air Samples For Solvents[1]
E.I. Dupont Sabine River Works
Orange, Texas
HETA 84-420
August 10, 1984

Time	Sample Location	Personal Sample(P) Or Area Sample(A)	Sample Volume (liters)	(mg/m³)[2] Ethyl Acetate	Cellosolve Acetate	Methyl Ethyl Ketone*	Xylene	Additive Effect
0935-1323	Unit 3040 North-East End	A	41.5	0.5	2.0	0.7(41.8)	0.3	0.1
0935-1535	Unit 3040 Along North Side	A	64.7	0.8	6.8	1.8(16.9)	0.3	0.3
0922-1515	Unit 3040	P	59.8	1.5	8.3	3.2(15.6)	0.4	0.3
0927-1533	Unit 3040	A	63.7	1.1	6.3	ND(17.6)	0.5	0.2
0822-1410	Unit 554 Cooling Tower	P	48.1	2.7	6.0	ND(12.1)	0.8	0.2
0825-1400	Unit 554 Cooling Tower Sample on Lift Platform/Bucket	A	55	8.1	9.7	ND(56.2)	1.4	0.4
0840-1413	Unit 554 Cooling Tower Sample on Stairs	A	50	1.1	4.0	1.4(14.1)	0.4	0.2
0841-0951	Tank Farm R.R. Track Side (South) Center of Tank on Vertical Pipe	A	12	4.5	15.3	2.3(13)	1.7	0.6
0840-0952	Tank Farm Between Tanks #1 & #2 Center I Beam North Side	A	13.4	12.5	43.4	2.9(13.8)	4.3	1.6
0840-0949	Tank Farm	P	13	13.9	31.6	11.4(3.5)	3.8	1.2
0841-0945	Tank Farm	P	12.2	3.6	8.8	ND(2.8)	1.3	0.3

(continued)

Table IV (cont.)
August 10, 1985

Time	Sample Location	Personal Sample(P) Or Area Sample(A)	Sample Volume (liters)	$(mg/m^3)^2$ Ethyl Acetate	Cellosolve Acetate	Methyl Ethyl Ketone*	Xylene	Additive Effect
0840-0948	Tank Farm	P	13	3.5	9.2	ND(3.4)	0.9	0.3
Evaluation Criteria				1400	27	590	435	1.0
Laboratory analytical limit of detection (LOD) in micrograms/sample				4.2	12	10	2.3	
Laboratory analytical limit of quantitation (LOQ) in micrograms/sample				14	41	50	7.6	

1. All concentrations are time-weighted averages for the period sampled
2. mg/m^3=milligrams per cubic meter of air
*3. Air sample volumes for the Methyl Ethyl Ketone samples are indicated in brackets ().

ND=nondetectable concentration

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