U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION
REPORT NO. 77-47-427

THE UNION 76 OIL COMPANY
NEDERLAND, TEXAS
SEPTEMBER 1977

I. TOXICITY DETERMINATION

A Health Hazard Evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) in the Union 76 Oil Refinery near Nederland, Texas. Environmental sampling was done on April 5-7, 1977, for benzene, toluene, xylene, cyclohexane, methyl ethyl ketone, hexane, heptane, ammonia, sulfuric acid, and sodium hydroxide. A comparison of the results of this environmental sampling with recommended maximum exposure levels presented in Section IV of this report indicates that employees at this plant were not exposed to potentially toxic concentrations of these materials during the days of this study. However, several of the samples analyzed for benzene were near the 1 part per million (ppm) level recommended by NIOSH in its "Revised Recommendation for an Occupational Exposure Standard for Benzene"[1], published in August, 1976. For this reason, continued monitoring of atmospheric contaminants, particularly benzene, is recommended.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. 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:

a) The Union 76 Oil Company
b) Oil, Chemical and Atomic Workers Local 4-228
c) Oil, Chemical and Atomic Workers International Union
d) U.S. Department of Labor - Region VI
e) NIOSH - Region VI

For the purpose of informing the approximately 700 "affected" employees, the employer will promptly "post" the Determination Report for a period of 30 calendar days, in a prominent place near where the affected employees work.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by an 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 National Institute for Occupational Safety and Health (NIOSH) received such a request from a representative of employees (Director, Citizenship and Legislative Department, Oil, Chemical and Atomic Workers International Union) to evaluate potential hazards to employees in the Union 76 Oil Refinery near Nederland, Texas. Employees in this refinery were thought to be exposed to hazards from "fumes of light hydrocarbons, mineral spirits, naptha [sic], aromatics, benzene, toluene, zylene [sic], and other chemicals." The areas of the refinery of particular concern to the requestor were the dock, the MEK unit, the phenol unit, tank car loading racks, the blending and treating area, the UDEX complex, the CRU #1, the FCC unit, and the crude tank farm.

IV. HEALTH HAZARD EVALUATION

A. Process Description

This Union Oil Refinery is involved in the conversion of crude oil into the various hydrocarbons used in the production of gasoline and other fuels, solvents, lubricating oils, asphalt and other petrochemical products. The process begins with the unloading of crude oil from ships and barges, and storage in a tank farm. This transfer is achieved, as are essentially all other transfers of materials within this refinery, by piping the oil through a closed system of tubing to its destination. The crude oil is fractionated (distilled) to obtain mixtures with various boiling point ranges. Some higher boiling mixtures are subsequently subjected to a process called "cracking" in which they are broken into simpler compounds by various physical and chemical methods. Procedures such as alkylation, desulfurization, and blending are also used to produce materials with desired characteristics. All of these processes take place in closed systems designated by names such as MEK and phenol units, UDEX, CRU and FCC, varying primarily in reaction conditions and catalysts. Products are stored in a tank farm to await blending to obtain desired mixtures and loading onto ships and barges for shipment to customers.

Since not only the transfer of material within the plant but also all process operations on those materials are conducted within closed vessels, the primary source of hydrocarbon contamination is leaks from the system. Leaks of ammonia from the refrigeration units, and acid and alkali from tank car unloading are potential sources for these contaminants. Another source of atmospheric contamination is from the storage of the various materials, although precautions such as floating

roofs on light hydrocarbon tanks minimize this source. In addition to this type of preventive system, this plant has continuous sampling for hydrogen sulfide which could be formed from the sulfur in the crude oil.

Many of the employees throughout the plant work in the various control rooms from which the refinery operations are managed and monitored. Any exposure of these people would be the result of leaks in the pipes and vessels which in some cases surround them on all four sides as well as overhead. Other employees, both maintenance and production, work on the pipes and vessels, and while on many occasions their work is in less enclosed areas, they have a potentially high exposure during a short period of time during which they have the system open.

B. Evaluation Design and Methods

On April 5, 1977 a walk-through survey was conducted in this plant with representatives of union and management to determine sampling strategy. During this walk-through, total hydrocarbon measurements were made using a flame ionization analyzer. Ammonia and toluene concentrations were measured using certified "length of stain" detector tubes. Pertinent data was obtained from company and union representatives regarding materials and processes.

On April 6 and 7, personal environmental samples were taken in the following areas: dock, MEK unit, phenol unit, tank car loading racks, blending facility, UDEX, CRU #1, FCC, and alkylation. An attempt was made to get as close as possible to a full shift (8-hour) sample, but due to the size of the refinery, its physical layout and the nature of the jobs, most samples ranged from six to seven hours duration. In addition to the personal samples, one area sample for ammonia was taken near the ammonia loading rack to determine ambient concentration there. This sample is not intended to be indicative of any personal exposure.

Sampling for hydrocarbons was done with low flow (100-200 cc/minute) battery powered personal pumps and tubes containing activated charcoal which adsorbed the contaminants. Subsequent analysis was done by gas chromatography for benzene, toluene, xylene, cyclohexane, methyl ethyl ketone (MEK), hexane and heptane following desorption with carbon disulfide.

Samples were also taken for ammonia, sulfuric acid and sodium hydroxide using battery powered sampling pumps. Sulfuric acid was sampled at 1.5 liters per minute (lpm) on 37 mm cellulose acetate ester filters. Analysis was done by extraction and titration. Ammonia and sodium hydroxide were sampled at 1 lpm in midget impingers containing 0.1 N H_2SO_4 and 7.5×10^{-3} N HCl respectively. Analysis for ammonia was colorimetric using Nessler's reagent. Analysis for sodium hydroxide was by atomic emission spectrophotometry for sodium.

On April 7, samples were collected in the tank farm near tanks 103, 114, and 115. These samples were for hydrogen sulfide using certified detector tubes and for total hydrocarbons using detector tubes and flame ionization analyzer.

In addition to environmental sampling, several employees were interviewed regarding health problems and work histories.

C. Evaluation Criteria

Listed below are maximum exposure levels recommended by NIOSH and by the American Conference of Governmental Industrial Hygienists (ACGIH) for occupational exposure to the various contaminants measured at Union Oil:

Substance	NIOSH Recommendation[1-7]	ACGIH TLV[8]
Benzene	1 ppm	10 ppm
Toluene	100 ppm	100 ppm
Xylene	100 ppm	100 ppm
Cyclohexane	NA*	300 ppm
MEK	NA	200 ppm
Hexane	NA	100 ppm
Heptane	NA	400 ppm
Ammonia	50 ppm ceiling	25 ppm
Sulfuric Acid	1 mg/M^3	1 mg/M^3
Sodium Hydroxide	2 mg/M^3 ceiling	2 mg/M^3
Hydrogen Sulfide	10 ppm	10 ppm

* Indicates no recommendation available for this substance.

The NIOSH exposure recommendations for ammonia and sodium hydroxide are designated "ceiling" limits since the recommendations are for 5 and 15 minute maximum exposures to those compounds respectively. Other recommended exposure levels are for 8-hour time weighted average exposures.

Since there are data suggesting a relationship between exposure to benzene and the occurrence of leukemia and other malignant diseases, NIOSH recommends that benzene be considered carcinogenic. "Because it is not possible at present to establish a safe exposure level for a carcinogen, the NIOSH recommendation is to restrict exposure to very low levels that can still be reliably measured in the workplace. The NIOSH recommendation can be expected, at a minimum, to materially reduce the risk of benzene induced leukemia."[1] The recommended level has been set at 1 ppm since the reliability of analytical techniques at that level has been established by the NIOSH Standards Completion Program. This does not, however, preclude the ability to make valid measurements at lower concentrations.

Since each employee is potentially exposed to a combination of the seven hydrocarbons, the effects of these materials must be considered as additive since they have similar toxicologic effects. Therefore, if the sum of the fractions of exposure over standard for each substance is greater than unity, there is a probability that continued exposure at those levels will result in adverse health effects.

D. Evaluation Results

Tables I and II list the results of hydrocarbon samples taken April 6 and 7, respectively. It can be seen from these tables that, with the exception of benzene, exposure to the various organic compounds sampled was generally three orders of magnatude less than the recommended maximum concentration. Of the 40 samples taken for benzene, 33 were less than half of the most stringent (NIOSH) recommendation, and all but two were below that concentration. Of those two, the one sample indicating a high benzene exposure is of questionable validity in view of the other measurements (including benzene) in the same area.

The second sample, which indicated that the exposure of the FCC compressor house operator was equal to the recommended criteria, is difficult to evaluate. This benzene exposure is above the mean benzene concentration, yet is consistent with the other hydrocarbon samples taken on this employee. However, one sample out of 40, by itself, is in this case not cause to justify the conclusion that a hazard exists from this source.

In addition to the samples listed in these tables, five others were taken. One for sodium hydroxide indicated approximately 0.7 mg/M^3 on the tank car loading rack man. One for sulfuric acid failed to detect that compound in the alkylation unit. Three for ammonia indicated 2.5 ppm, 0.3 ppm, and 2.0 ppm respectively on the MEK refrigeration man, in the area of the ammonia loading rack, and on the MEK refrigeration man again. These samples ranged from four to six hours duration during mid-shift. Short duration breathing zone samples for ammonia and sodium hydroxide were impractical to obtain, especially since personal exposures were expected to be low.

Direct reading instruments were also used to measure short term contaminant concentration. Detector tube measurements indicated approximately 20 ppm ammonia in the refrigeration area of the MEK unit, but did not detect ammonia or toluene in other areas. A flame ionization hydrocarbon analyzer indicated total hydrocarbon concentrations as follows:

Docks	- 15-30 ppm with peaks of 50-70 ppm
MEK Unit	- 15-30 ppm with peaks over 100 ppm in areas with strong ammonia odor
Loading Rack	- approximately 20 ppm
UDEX	- 10-20 ppm with peak of 45 ppm
Alkylation	- approximately 40 ppm

The primary purpose of determining total hydrocarbon concentration was for the development of sampling strategy. There is no criteria with which to compare these results, although by comparison to any of the individual hydrocarbon criteria (except benzene) it can be seen that concentrations of a few parts per million are relatively low.

Discussions with employees indicated that, while there was occasional irritation due to a transient high exposure, there were no serious health complaints due to exposure to the materials handled in this plant.

E. Summary and Conclusions

From a comparison of the information collected in this evaluation with recommended criteria, it is concluded that employees of the Union Oil Company's Nederland Refinery are not exposed to toxic concentrations of the contaminants measured during this study. Concentrations of separate compounds were generally a thousand fold below recommended criteria. Calculations indicate that, excluding two benzene samples, the additive concentrations of these contaminants are also far below the hazardous level. Since most solvent concentrations (including benzene) were very low, the two highest benzene samples are not believed typical exposures.

It is recommended that Union Oil continue periodic testing for atmospheric contaminants to assure the concentration of benzene and other substances stays at levels which are considered safe.

V. REFERENCES

1. Revised Recommendation for an Occupational Exposure Standard for Benzene, August, 1976, NIOSH.

2. Criteria for a Recommended Standard, Occupational Exposure to Toluene, 1973, NIOSH.

3. Criteria for a Recommended Standard, Occupational Exposure to Xylene, 1975, NIOSH.

4. Criteria for a Recommended Standard, Occupational Exposure to Ammonia, 1974, NIOSH.

5. Criteria for a Recommended Standard, Occupational Exposure to Sulfuric Acid, 1974, NIOSH.

6. Criteria for a Recommended Standard, Occupational Exposure to Sodium Hydroxide, 1975, NIOSH.

7. Criteria for a Recommended Standard, Occupational Exposure to Hydrogen Sulfide, 1977, NIOSH.

8. Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976, American Conference of Governmental Industrial Hygienists.

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RESULTS OF PERSONAL BREATHING ZONE SAMPLES FOR HYDROCARBONS

April 6, 1977
Union 76 Refinery
Nederland, Texas
RHE 77-47

Location	Benzene (PPM)	Toluene (PPM)	Xylene (PPM)	Cyclohexane (PPM)	MEK (PPM)	Hexane (PPM)	Heptane (PPM)
Dock Helper	< 0.03	0.06	0.05	0.6	< 0.04	0.6	< 0.2
Dock Helper	0.1	0.03	0.03	0.2	< 0.04	< 0.08	< 0.07
Dockman	0.2	< 0.1	< 0.1	< 0.1	< 0.2	0.5	< 0.03
MEK Operator	0.07	0.5	0.03	0.2	0.1	-	-
MEK Assistant	0.08	0.3	0.06	0.3	< 0.08	-	-
MEK Control Board Operator	0.06	0.5	< 0.02	0.2	0.07	-	-
MEK Filter Man	0.06	0.7	< 0.02	0.2	0.4	-	-
MEK Refrigeration Man	0.07	0.6	< 0.03	0.1	0.2	-	-
Blender, North Gauger	0.5	0.4	0.08	0.4	< 0.1	< 0.1	< 0.1
Blender	0.4	0.2	0.1	0.4	< 0.04	< 0.2	< 0.1
Blender, South Gauger	-	-	-	-	-	< 0.03	< 0.2
UDEX Operator	0.8	0.3	0.1	0.5	< 0.07	< 0.1	< 0.1
UDEX Control Board Operator	0.6	0.3	0.09	0.4	< 0.06	0.08	< 0.02
UDEX Outside Asst. B	12.	0.9	0.2	1.2	< 0.04	0.07	0.06
UDEX Outside Asst. A	0.8	0.3	0.1	2.1	< 0.04	0.07	< 0.03
CRU Outside Asst.	0.03	< 0.03	< 0.03	0.06	< 0.04	< 0.04	< 0.03
CRU Outside Asst.	0.07	< 0.03	< 0.03	0.1	< 0.04	-	-
CRU Control Board Operator	0.04	< 0.03	0.05	0.07	< 0.04	< 0.03	< 0.03
Alkylation, Control Board Oper.	< 0.07	0.1	0.05	0.2	< 0.08	-	-
Alkylation, Operator	< 0.1	0.1	< 0.09	0.2	< 0.1	-	-
Alkylation, Contact Man	< 0.09	0.3	0.07	0.3	< 0.1	-	-
Alkylation, Acid Man	< 0.09	0.07	< 0.06	0.7	< 0.1	-	-
Alkylation, Helper	< 0.1	0.2	0.1	0.3	< 0.1	-	-

TABLE II

RESULTS OF PERSONAL BREATHING ZONE SAMPLES FOR HYDROCARBONS

April 7, 1977
Union 76 Refinery
Nederland, Texas
RHE 77-47

Location	Benzene (PPM)	Toluene (PPM)	Xylene (PPM)	Cyclohexane (PPM)	MEK (PPM)
Dock Helper	0.04	0.03	0.03	0.1	<0.04
Dockman	0.04	<0.03	<0.03	0.3	<0.04
Dock Helper	<0.2	<0.2	<0.2	0.6	<0.02
MEK Control Board Operator	<0.03	0.1	0.02	0.2	<0.04
MEK Recrystallization Man	<0.03	0.2	0.02	0.1	<0.03
MEK Operator	0.04	0.1	<0.09	0.1	<0.04
MEK Refrigeration Man	0.04	0.06	<0.03	0.07	<0.04
Phenol Operator	0.07	0.09	0.07	0.06	<0.04
Phenol Control Room Operator	0.07	0.09	0.08	0.1	<0.04
Phenol Outside Asst. Operator	<0.2	<0.1	<0.1	0.3	<0.2
FCC Control Board Operator	0.04	0.03	0.06	0.2	<0.04
FCC Control Board Operator	<0.1	<0.08	<0.07	<0.09	<0.1
FCC Operator	<0.1	<0.1	<0.1	0.4	<0.1
FCC Compressor House Operator	1.0	0.9	1.0	<0.03	<0.4
FCC Outside Asst. Operator	<0.1	<0.1	0.08	<0.1	<0.1
FCC Operator	0.2	<0.1	<0.1	<0.1	<0.2
FCC Outside Asst. Operator	0.04	0.03	0.05	0.1	<0.04
Tank Car Loading Rack Man	0.8	2.4	0.4	0.7	<0.04