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. 77-43-500

SHELL OIL REFINERY DEER PARK, TEXAS

JUNE 1978

I. TOXICITY DETERMINATION

Based on the NIOSH medical survey, there appears to be a possible excess of mild peripheral neuropathy among employees in the Lube B Dewaxing Unit of the Shell Oil Refinery. These neuropathies are mild and are manifested more by discomfort than by functional impairment. Adequate control data is not available at this time. The cause of the observed neuropathies is not known. Industrial hygiene data from OSHA and Shell do not reveal the presence of any known cause of peripheral neuropathies. Adequate data on past chemical exposures is not available. Animal studies to investigate the possible role of methyl ethyl ketone and toluene in the induction of neuropathy may be considered.

The prevalence of overt diabetes mellitus and elevated serum triglyceride does not appear to be excessive in the Lube B Unit. The data is suggestive, however, that the prevalence of subclincial diabetes may be excessive.

In view of the possible role of methyl ethyl ketone and toluene in causing neuropathy, exposure to these chemicals should be minimized as much as possible.

II. DISTRIBUTION & AVAILABILITY

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Service, 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, Publication Office, at the Cincinnati address. Copies of this report have been sent to:

a. Shell Oil Company, Deer Park, Texas

 Authorized Representative of Employees - Local 4-367 of OCAW

c. Oil, Chemical, and Atomic Workers Union, Washington, DC

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- d. U.S. Department of Labor Region VI
- e. NIOSH Region VI

For the purpose of informing the affected employees, the employer shall promptly post for a period of 30 calendar days, the Determination Report in a prominent place(s) near where exposed employees work.

III. INTRODUCTION/BACKGROUND

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.

NIOSH received such a request from an authorized representative of employees (Oil, Chemical and Atomic Workers International Union) at the Lube B Dewaxing Unit of the Shell Oil Refinery at Deer Park, Texas. NIOSH also received a request for assistance from the corporate medical director of Shell Oil Company.

IV. BACKGROUND DATA/STUDY DESIGN/RESULTS

A. Process Description

The Lube B Dewaxing Unit uses a conventional solvent-extraction method for removing high-melting-point hydrocarbons from petroleum in order to produce oils with adequate lubricating properties over a broad temperature range. The process involves mixing methyl ethyl ketone (MEK) and toluene with various petroleum fractions. No other chemicals are known to be used in this area of the plant.

The B Unit of the Lube Oil Plant receives several fractions of two types of crude oil for further processing. The Texas-Louisiana Straight Run residue is processed through "A" Unit, where a vacuum distillation followed by a phenol extraction process and a propane deasphalt process produces refinates which enter the B Unit to be processed into High Visocosity Index (HVI) lubricants. The Ohio-Yates/Tobarg crude Straight Run residue proceeds directly to the final stage of the B Unit process from the vacuum distillation to be hydrotreated and marketed as Low Viscosity Index (LVI) lubricants. The LVI oil has a low pour point and does not need dewaxing.

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The HVI products are stored and processed separately through the B Unit dewaxing. As a by-product, wax is collected and deoiled in B Unit and then sent to "C" Unit for further processing.

Dewaxing is accomplished by chilling a solution of HVI refinates in a solvent mixture of MEK and toluene both of which are Shell products. The ratio of solvent to refinates is about 2 or 3 to one. The percent of MEK in the MEK/toluene mixture varies from 40 percent for processing the highest boiling point fraction (Bright Stock) to 70 percent for the lowest boiling point fraction. As the product cools, wax crystals form in the mixture and are filtered out. There are 12 rotary type vacuum filters with cloth-covered cylinders approximately 16 feet long and 10 feet in diameter. Half are used in deciling the wax and half are used in dewaxing the refinates. The cylinders must be washed with hot solvent $(130-140^{\circ}F)$ periodically. (Once per shift, with good operating conditions, but several times per shift under more difficult conditions such as are frequently encountered when processing the bright stock fraction.) It is during this wash period when the vacuum is off that leakage from packing around end bearings is most likely. A nitrogen blanket is maintained in the system.

Following dewaxing, the oil receives final treatment at the lube hydrotreater where color and odor are improved by converting impurities containing sulfur, nitrogen, and oxygen to color stable oils, plus by-product gases (H_2S , NH_3 , H_2O , etc.). The oil is trickled, in the presence of hydrogen gas, through a catalyst bed at elevated temperature and pressure.

The crude wax is then further washed in a second rotary vacuum filtration referred to as the deciling process. After the solvent is removed by distillation and steam stripping the deciled wax is sent to the wax finishing Unit "C". There, in a molten state, it is percolated through clay to improve its color and odor.

B. Toxic Properties and Medical Background

Methyl Ethyl Ketone (MEK)²

MEK is a clear, highly volatile, flammable liquid with a strong odor. The liquid and vapors are irritating to the eyes and skin in high concentrations. Absorption can take place through the skin, but animal experiments indicate low toxicity via this route. Inhalation of very high levels can cause headaches; eye, nose, and throat irritation; and eventual narcosis. The current TLV for MEK is 200 ppm. The odor threshold is about 25 ppm.

MEK has been investigated as a possible cause of peripheral neuropathy. These studies concluded that MEK alone did not cause peripheral neuropathy in the animal test systems used, but that MEK probably potentiated the effects of methyl butyl ketone (MBK) in causing peripheral neuropathy.3,4

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MEK has not been reported to alter glucose tolerance or serum triglycerides.

Toluene^{5,6}

Toluene is a clear, colorless, flammable aromatic hydrocarbon with a sweet, pungent odor. It is mildly irritating to the eyes and mucous membranes, and it can cause a defatting-type of solvent dermatitis. Absorption through the skin is slow.

Toluene has been suspected of a variety of toxic actions. It has been implicated as a bone marrow toxin, but these early results were probably due to failure to separate out the effects of benzene contamination of the toluene.

Toluene has not been reported to alter glucose tolerance or serum triglyceride levels, although there have been reports of enlarged livers in chronic toluene exposure.

Toluene's chief reported toxicity has been on the central nervous system, ranging from headaches and fatique at low concentrations, to severe narcosis, confusion, and incoordination at very high levels of exposure.

Reports of persistent damage to the nervous system have mainly come from cases of persons who have breathed very high levels of toluene in order to get a "high". Only central nervous system damage, including encephalopathy (generalized brain damage) and persistent cerebellar ataxia (loss of coordination) have been reported in humans. One study in rats has shown possible effects on the peripheral nervous system.

Peripheral Neuropathy

"Peripheral neuropathy" is a condition in which there is malfunction or destruction of peripheral nerves. "Peripheral nerves" are the nervous pathways outside the central nervous system (which consist of the brain and spinal cord). Peripheral neuropathy can have many causes, including genetic defects, infections, malnutrition, metabolic derangements (including diabetes), vascular disturbances, trauma, toxins, etc. The toxic causes of peripheral neuropathy include drugs (eg: isoniazid, thalidomide), metals (eg: lead, mercury, arsenic), organophosphate pesticides, and solvents (eg: carbon disulfide, normal hexane, methyl butyl ketone), and a variety of other agents. Hydrocarbons have been increasingly suspected as possible causes of neurpathy. Normal hexane has been clearly documented as a cause of peripheral neuropathy in humans, and related straight-chain hydrocarbons ranging from pentane to octane are suspected as possible causes. 10 There is one report of possible neuropathy caused by exposure to jet fuels, which is a mixture of small-to-moderate size hydrocarbons. 11 Mild toxic neuropathies generally improve with removal from exposure; severe cases may not return completely to normal.

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Peripheral neuropathy may involve sensory, motor, or autonomic function. Either the nerve fiber itself or the surrounding layer of insulating myelin may be involved. Many of the toxic causes of neuropathy give a "dying-back" pattern, in which the damage in the nerve first appears in the part of the nerve farthest from the central nervous system; damage thus usually appears first in the feet and hands.

The symptoms and signs of peripheral nerve damage include sensory changes (abnormal sensations such as burning, aching, tingling which may progress to numbness), motor changes (weakness with eventual wasting of muscles), and autonomic changes (loss of vascular control, changes in sweating, loss of hair, etc). In early or mild cases, these symptoms may be very vague and difficult to precisely define; physical examination may not show definite and consistent abnormalities early in this disease.

Tests for peripheral neuropathy generally include nerve conduction studies and electromyography. Damaged nerves can show a slowed conduction velocity, or a smaller electrical impulse, or both. Muscles supplied by damaged nerves can show abnormal responses to electrical stimulation. Performance and interpretation of these electrical changes requires considerable clinical skill; many factors, including the temperature of the limb, can affect the results. Many toxins can affect nerves in both the central and peripheral nervous systems; differentiating these two types of nervous system damage also requires considerable skill.

Many reviews of this subject are available. (12-14)

C. Study Design and Methods

Selection of Study Population

Because of difficulties in contracting for the neurologic and electrodiagnostic examinations and in scheduling employees for the full-day of examinations, NIOSH chose to limit this study to the following groups of Lube B employees (totaling 43):

- 1. All employees who had been in the Lube B area for several years, whether or not they had complaints or positive findings on previous studies.
- 2. All employees who had findings suggestive of peripheral neuropathy on previous examinations.
- 3. All employees who had symptoms suggestive of peripheral neuropathy, whether or not they had positive findings on previous examinations.
- 4. All employees who chose not to participate in previous medical examinations done by Shell.

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- 5. All employees who expressed a desire to be tested, whether or not they fit into the above categories.
- 6. Maintenance personnel who spend a significant portion of their time in the Lube B area.
- 7. Recent retirees who had spent many years in Lube B.

Not included in the NIOSH examinations were 18 Lube B employees who had been found by the previous Shell study to be without symptoms, signs, or electrodiagnostic findings suggestive of peripheral neuropathy, and who did not express strong interest in being retested.

NIOSH had an independent expert review the data collected by Shell*, this review agreed with the impression of the Shell neurologist that these 18 men had no evidence of a peripheral neuropathy. These men were generally younger, shorter-term employees than those restudied by NIOSH. NIOSH felt that retesting these 18 employees was unlikely to provide significant new information that would justify the inconvenience and discomfort of the employee.

Suitable age- and sex- matched controls with comparable industrial experience in non-chemically-exposed jobs were not available for this study.

Diagnostic Procedures

Peripheral Neuropathy

Because of the specialized electrodiagnostic testing required, NIOSH chose to contract with local medical facilities for the medical examinations. Laboratory support and neurologic examinations were provided by the Public Health Service Hospital in Galveston, Texas. All laboratory work was done by the same laboratory; all neurologic examinations were done by the same neurologist. All electrodiagnostic examinations were done by the same two electromyographers from the Houston area (both participated in each examination in order to assure uniformity of techniques and interpretations). The neurologic physical examinations were done without knowledge of the laboratory or electrodiagnostic results.

Attachment A shows the forms used for informed consent, medical history, and neurologic examination.

Attachment ${\tt B}$ shows the neurologic examination procedure followed by the neurologist.

Attachment C shows the electrodiagnostic protocol used.

Attachment D shows the procedures and normal values used by the electromyographers.

^{*}Dr. Herbert Schaumberg; Albert Einstein College of Medicine, Bronx, NY; Report of April 13, 1977.

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All studies on each subject were done on the same day. Electrodiagnostic studies were done with a TECA TE 44* dual amplifier electromyograph with advanced digital evoked potential averager and signal delay device. An averager was used when necessary for measuring small sensory amplitudes. Limb surface temperatures were measured by thermistor** both proximally and distally over stimulation points for nerve conduction.

On the basis of the clinical and electrodiagnostic findings, participants in the NIOSH study were classified into one of the following categories:

- 1. No clinical or electrodiagnostic evidence for periperhal neuropathy.
- 2. Probably no peripheral neuropathy present. Observed abnormalities not sufficient to make a diagnosis of peripheral neuropathy.
- 3. The data is suggestive, but not diagnostic, for a very mild peripheral neuropathy. There may be a borderline peripheral neuropathy present, but the available evidence cannot unequivocally rule in or rule out a mild neuropathy without further testing.
- 4. The data is consistent with the diagnosis of mild peripheral neuropathy. No definite cause has been established for any neuropathy present.

Based on the data available to them, the neurologist and the electromyographer each gave NIOSH their independent impressions of each individual tested. Based on these two opinions, the NIOSH medical officers in charge of the study then formed an overall impression of the probability that an individual subject had a peripheral neuropathy. Subjects with no symptoms, signs, or electrodiagnostic findings were easily classified into category 1. Subjects with isolated minimal findings, such as a decreased deep tendon reflex or a single moderately decreased nerve conduction amplitude, were classified into category 2. These subjects did not have perfectly normal exams, but the minimal findings present were not felt to be consistently suggestive of a peripheral neuropathy.

Category 3 includes subjects with some findings on clinical and/or electrodiagnostic examination that were suspicious for some peripheral nerve abnormality, but were not severe or consistent enough to warrant a definite diagnosis. This is a category of possible borderline or subclinical neuropathy. For example, subjects with minimal sensory changes, but without nerve conduction changes, would fall into this category. Also, subjects whose only finding was one or two isolated minimal decreases in nerve conduction amplitude would fall in this category.

^{*} NIOSH does not recommend any particular brand name products.

** Surface thermocouple manufactured by Yellow Springs Instrument Company.

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Category 4 includes subjects with fairly definite evidence of some peripheral nerve abnormality, usually on both clinical and electrodiagnostic examination. Some subjects with fairly definite electrodiagnostic findings were included, even if there were no definite clinical findings.

For the physical exam and electromyography there are no definite numerical standards; the examining physician must call on his clinical experience in deciding if significant abnormality is present. For nerve conduction velocity and latency, the electromyographers used normal values derived from training and experience at Ohio State University. Attachment D shows these normal values. The clinical series from which these values were derived comes from work by Melvin, Johnson, et al. 20,21 The group of normal subjects used in this series was derived from a university area, so it was probably somewhat younger and less blue collar than the group of employees studied at Shell by NIOSH. 22

Normal nerve conduction amplitude values are less well defined because of the many factors of physiology and technique that can affect amplitude. Limb temperature can affect both nerve conduction velocity and amplitude; limb surface temperature should be above 30°C (preferably between 31.5-33.5°C for best results).

Surface temperatures in the NIOSH study were measured proximally and distally over stimulation sites, and temperature was taken into account by the electromyographer in interpreting his results.

Amplitudes are very sensitive to technique; the recording electrode must be directly over the nerve to obtain a maximal amplitude reading. Amplitudes as measured in this study were generally peak-to-peak values. The electromyographers used the following normal ranges based on their experience:

Sensory amplitude in median and ulnar nerves should be 20-50 uv. Below 15 uv is generally abnormal.

Sural nerve sensory amplitude is normal if above 10 uv, possibly abnormal in the 7.5 to 10 uv range, and probably abnormal if less than 7.5 uv.

Motor evoked amplitudes are usually normally above 10 mv, and is usually abnormal below 5 mv. These values generally apply to median, ulnar, and peroneal nerves.

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2. Diabetes

Glucose tolerance tests were done after a 12-hour overnight fast. A 100g glucose load was given orally; venous blood was drawn fasting and at 1,2, and 3 hours post-ingestion.

Because of logistic difficulties in scheduling, glucose tolerance tests were only requested on employees who had not had a recent oral glucose tolerance test done elsewhere. Known diabetics were not subjected to a glucose tolerance test; the repeated confirmation of diabetes was not considered to be worth the risk to the employee.

Glucose tolerance tests were categorized as follows:

- 1. Normal
- 2. Slightly abnormal, possibly indicating a diabetic tendency.
- 3. Abnormal, probably indicating a diabetic tendency.

Criteria for categorizing glucose tolerance tests were derived from the Report of the National Commission on Diabetes. 15 These criteria were primarily derived from work by Fajans 16 , 17 and Andres. 18

Attachment E shows relevant tables and graphs from the National Commission on Diabetes report.

3. Triglycerides

Triglyceride levels were to have been drawn on all 43 employees studied by NIOSH.

Serum triglyceride levels were drawn after a 12-hour overnight fast.

Triglyceride levels were categorized as normal or elevated by the laboratory normal range (30-175 mg/dl serum).

D. Results

I. Medical Results

A. Peripheral neuropathy

A total of 62 persons from the Lube B area had neurologic testing at one time or another during this study. Of the 49 Lube B operators and supervisors tested, 18 were tested by Shell only, 8 were tested by NIOSH only, and 21 were tested by both NIOSH and Shell; 10 of the

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49 also had testing by a private physician in addition to testing by NIOSH and/or Shell. Operators and supervisors are grouped together because the number of supervisors is small, and most had worked as operators before becoming supervisors. The 13 maintenance personnel were tested only by NIOSH.

Table 1 shows the distribution of peripheral nerve abnormalities in the operators/supervisors and maintenance groups. A chi-square test was done to compare these two groups. There is a difference in overall rates of neuropathy (significant at p=0.05 level) between operators and maintenance personnel when potential confounding factors, such as diabetes, are not taken into account; but this difference disappears when looking at rates of neuropathy only among persons with no abnormality in glucose tolerance.

Tables 2, 3, 4 show the grouped data from the Shell and NIOSH studies, displaying peripheral nerve abnormality vs. age and work history. These tables show that the group of 19 operators with possible peripheral nerve abnormality is almost exclusively in the 50-59 year age group (mean 53.6 years old). They have spent much of their working life at Shell (mean of 28.5 years at Shell, mean of 21.8 years at Lube B).

The group of 30 operators without neuropathy is generally younger (mean of 40.7 years old), and has spent less time at Shell (mean of 14.6 years at Shell; mean of 9.8 years at Lube B).

The 13 maintenance personnel tested did not show the same pattern as the operators. The 6 with possible neuropathy had a mean age of 58 years, a mean time at Shell of 31.0 years, and a mean time at Lube B of 14.2 years. The 7 without evidence of neuropathy had a mean age of 54.4 years, a mean time at Shell of 29.3 years, and a mean time at Lube B of 19.6 years. This maintenance group is small and has a narrow age range between 49 and 61 years; also, work time in Lube B is difficult to estimate from available records. For these reasons, analysis of correlations between age, neuropathy, and exposure history in this group would probably not be very useful.

Essentially all subjects in this study were white males, except for one female.

Table 5 shows the distribution of ages in the group studied by NIOSH and Shell in the Lube B area. There is a bimodal distribution with peaks around ages 30 and 55, reflecting past trends in hiring and economic conditions in the petroleum industry.

Table 6 shows the close relationship between age of employees and the time spent working for Shell. There is little job turnover

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among these employees; individuals tend to stay at Shell for long periods of time.

Table 7 shows that there is also a fairly close relationship between age and years spent working in the Lube B area. There is usually some movement from job to job in the refinery during the early years of employment at Shell, but most employees spend a long period of time in Lube B once they reach that location.

The very asymmetric distribution of ages in the Lube B area, and the close relationships between age and time spent at Shell and Lube B cause problems in separating out the effects of age from the effects of working in a chemical environment.

Correlation coefficients were calculated for the relationship between exposure time working in Lube B versus various parameters of nerve function from the grouped NIOSH and Shell data, including ulnar motor conduction, velocity and amplitude, ulnar sensory latency and amplitude, median sensory latency and amplitude, posterior tibial conduction velocity and amplitude, and sural latency and amplitude. No significant correlations were noted. Age was used as a covariate in this analysis because of the close relationship between age and exposure history.

Comparison of NIOSH results with other medical testing

On 22 of the 43 employees tested by NIOSH there had been previous neurologic and electrodiagnostic evaluation done by Shell or by other private physicians. Seven individuals had had evaluation done by NIOSH, Shell, and private physicians.

Both NIOSH and Shell examinations were done with similar advanced equipment (TECA TE4). Surface limb temperatures were not measured in the Shell study; this could make a difference if adequate time were not allowed for equilibration with the laboratory environmental temperature, since Shell's study was in wintertime and NIOSH's study was in summertime.

The Shell protocol did not include routine testing of the ulnar nerves, paraspinal muscles, and "H" reflex, all of which were usually done in the NIOSH study. These protocol differences probably make the NIOSH study somewhat more sensitive in differentiating radiculopathy from peripheral neuropathy. In two of the 20 cases tested by both NIOSH and Shell, NIOSH indicated the presence of radiculopathy, Shell's study did not identify radiculopathy in any of these 20 cases.

Of the 21 employees tested by both NIOSH and Shell, there were 7 cases in which NIOSH differed from the Shell data (4 cases in which NIOSH

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indicated a higher probability of peripheral neuropathy; 3 cases in which NIOSH indicated a lower probability of peripheral neuropathy).

Most of these differences were between calling a case a borderline neuropathy vs. calling the case a definite neuropathy or non-neuropathy; in only two cases did Shell's evaluation fail to indicate the presence of a possible neuropathy when NIOSH thought there was probably a neuropathy present.

The testing of individual nerves by NIOSH and Shell was compared. When the same nerves on the same side of the body were tested, the following differences were found where one electromyographer called the nerve normal and the other called the nerve abnormal:

- 1. 12 median nerves compared, with 3 differences in motor conduction velocity and amplitude, and 4 differences in sensory latency and and amplitude;
- 2. 12 peroneal nerves compared, with 1 difference in motor conduction velocity and amplitude;
- 3. Il posterior tibial nerves compared, with 2 differences in conduction velocity and 5 differences in amplitude.
- 4. 10 sural nerves compared, with 3 differences in latency and amplitude.

Although there were some differences in testing individual nerves, there were few differences in detecting an overall pattern of abnormality. Thus, there appears to be reasonable agreement between Shell and NIOSH studies on the presence of possible neuropathy, which supports NIOSH's use of Shell's results for the 18 employees who were not retested by NIOSH in view of negative findings by Shell.

NIOSH results agreed with all except one of the 10 sets of neurological test results done by a local physician; this disagreement was only in assigning a definite vs. a borderline classification to one case.

Agreement between NIOSH and Shell serum triglyceride levels was also fairly good. Out of seven cases in which triglyceride levels were done by both Shell and NIOSH, only one disagreed as to the presence or absence of an abnormality. Shell does serum triglyceride levels fasting, as NIOSH does, and the normal values used by both Shell and NIOSH are the same.

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Comparison of clinical and electrodiagnostic findings

The NIOSH neurologist and electromyographer formed independent impressions of the probability of peripheral neuropathy in individual cases. Out of 43 cases, there were 13 cases in which the neurologist and electromyographer formed different impressions from their data, (10 cases in which the electromyographer indicated probable neuropathy when the neurologist indicated remote or no probability of neuropathy; 3 cases in which the electromyographer indicated low probability of neuropathy when the neurologist indicated a significant probability of neuropathy).

The NIOSH medical officers reviewed the diagnostic impression of the neurologist and electromyographer and developed a final overall diagnosis. There were 13 cases out of the 43 in which the NIOSH diagnosis differed from the neurologist's diagnosis based on history and physical examination alone (11 cases where NIOSH indicated a higher probability of neuropathy; 2 cases in which NIOSH indicated a lower probability of neuropathy than that indicated by the neurologist).

There were 6 cases in which the final NIOSH diagnosis differed from the electromyographer's impression based on data available to him, (4 cases in which NIOSH indicated a higher probability of neuropathy; 2 cases in which NIOSH indicated a lower probability of neuropathy than that indicated by the electromyographer).

These data show that NIOSH tended to agree more often with the electromyographic data than with the clinical data. There are several probable reasons for this:

- 1. The electromyographer had the advantage of being able to do a limited physical examination to verify his electrical findings, but the neurologist did not have access to electrodiagnostic data in forming his diagnostic impressions.
- 2. Symptoms, mild sensory changes, and minimal motor weakness all require patient interpretation or cooperation, as well as considerable diagnostic examination skill by the neurologist.
- 3. Easily reproducible hard signs of neuropathy may be lacking in early or mild cases, and the neurologist had considerable difficulty in some cases in deciding whether or not a minimal abnormality existed. The NIOSH medical officer felt that carefully-done electrodiagnostic studies were more likely to provide objective evidence of early or mild changes in peripheral nerves.

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Other Neurotoxic Effects

Because of reported persistent cerebellar ataxia after massive toluene exposure, the neurologic examinations were reveiwed for any evidence of cerebellar dysfunction in Lube B employees. No evidence of cerebellar abnormality was found.

B. Diabetes

The following information on carbohydrate tolerance in Lube B employees is available:

Fasting serum glucose levels were done on 47 of 49 persons in the operator/supervisor group. One of the two persons without a fasting glucose is a known insulin dependent diabetic. Twenty-five (25) of these fasting glucose levels are from NIOSH data; 22 glucose levels are from Shell data, also on fasting serum specimens.

Oral glucose tolerance tests were done on 25 persons in the operator/supervisor group (12 from NIOSH data, 11 from Shell data, 2 reported normal by a private physician). The known diabetic did not have a glucose tolerance test. The nineteen operators whose neurological testing by Shell was not repeated by NIOSH also did not have glucose tolerance tests done by NIOSH due to scheduling and contracting difficulties in this part of the NIOSH study. All of these 19 operators had fasting serum glucose levels within the normal range. Four operators who were scheduled to have glucose tolerance tests by NIOSH, did not have this test done due to lab error or patient refusal.

Oral glucose tolerance tests done by NIOSH are available on 12 of 13 maintenance personnel. One set of test results was never received from the laboratory.

Some degree of abnormality in fasting serum glucose level or oral glucose tolerance test was found in 11 operators and 2 maintenance personnel. All abnormalities were in men in the 49-59 year age range, except for one borderline-elevated fasting glucose level in an operator in his thirties.

The observed abnormalities are listed in Table 8. Six abnormalities are in the borderline range; seven abnormalities are in the diabetic range.

The distribution of abnormalities in glucose tolerance vs. abnormalities in peripheral nerves is shown in Table 9.

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Correlation coefficients were calculated for fasting serum glucose in relation to work history and various individual parameters of nerve function for ulnar, median, peroneal, posterior tibial, and sural nerves with correction for age. No significant correlations were found.

Data from health interview surveys ¹⁹ done in 1973 on the prevalence of known diabetes are shown in Table 10. This represents diabetes which was previously diagnosed and known to the individual.

Only 3 of the 62 total Lube B area employees reported a history of diabetes that was known to them before screening glucose tolerance studies were done as part of this study. Only one individual is on insulin. All three individuals with a history of diabetes are in the 45-64 year age range; there are a total of 46 of the 62 studied employees in this age range. The health-interview survey data mentioned above shows an expected frequency of known diabetes of about 2 in 50 white males in this age range. Three in 46 known diabetics in the Lube B area are not significantly different from national averages.

Data on the expected prevalence of subclinical diabetes in the general or industrial population is not as good, but the best available data indicates that some degree of glucose intolerance will propably be present in at least 6% of persons in their 50's. Since complete glucose tolerance tests are not available on all Lube B employees, the results are not strictly comparable to population studies based entirely on glucose tolerance tests. But 13 of 60 (22%) Lube B employees had an abnormality in some parameter of glucose tolerance, which is well above the expected 6% of abnormal glucose tolerance in a group of this age.

C. Triglycerides

Triglyceride levels are available on 41 of the 49 persons in the operator-supervisor group (25 from the NIOSH lab, 15 from the Shell lab, 1 from a private physician). Twelve of the 13 maintenance personnel had triglyceride levels done by the NIOSH labs, making an overall total of 53 of 62 persons in this study with fasting triglyceride level from some source.

The distribution of triglyceride levels by age in this group of 53 Lube B employees is shown in Table II.

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"Normal" values for triglycerides are difficult to define. Only fasting triglyceride levels are meaningful; there is normally a marked and somewhat variable rise in serum triglycerides after eating, depending on what was eaten.

The laboratory normals for the NIOSH and Shell labs are 30-175 mg/dl of serum, after at least a 12-hour fast. By this criterion, 19 of the 53 triglyceride levels available are elevated to some degree. These "normal" values are derived from a hospital/clinic type of population, however, and may not be strictly applicable to the Lube B group. Population studies in the medical literature 24,25,26 indicate higher average levels of fasting serum triglycerides in some population groups. These studies show that the 95th percentile for fasting serum triglycerides in white males in their 50's probably lies somewhere in the mid-300's mg/dl of serum. ("Normal" lab values are customarily calculated to include 95% of the population as normal). Only 9 of the 53 available triglyceride values from the Lube B group exceed 300 mg/dl; eight of these 9 values are in men, aged 50-59 years. Six of these eight men in their 50's with values over 300 mg/dl also have some abnormality of glucose tolerance or fasting glucose, and 3 of the 4 men with triglyceride values over 400 mg/dl have some degree of glucose intolerance. Diabetes is often associated with a pattern of hypertriglyceridemia, making it the most likely cause of elevated triglyceride levels in these cases.

Triglyceride levels did not correlate significantly with age-corrected work history or to parameters of individual nerve conduction velocity or amplitude.

No significant differences were found between triglyceride levels in operators and maintenance personnel.

II. Environmental Results

Shell has been conducting an industrial hygiene survey of the Lube B area since June 1976. This has included personal sampling for MEK and toluene, as well as analyses of bulk samples of all process materials, petroleum feedstocks, and drinking water for such known causes of peripheral neuropathy as methyl butyl ketone, normal hexane, carbon disulfide, and heavy metals. Nothing except MEK and toluene has been found in significant amounts; MEK and toluene were generally found at low concentrations (less than 20 ppm), except for occasional higher levels during maintenance operations.

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The MEK and toluene presently used are reported by Shell to be of high average purity (99.9% pure toluene, 99.5% pure MEK). Shell does not have detailed analytical data on the concentration of impurities in MEK and toluene used in past years.

OSHA has conducted two industrial hygiene inspections of the Lube B area on December 22, 1976, and February 2, 1977. Their measurements of MEK, toluene, MBK, n-Hexane, and benzene have been below detectable limits in all but two samples. A personal sample showed 12 ppm toluene for an instrument maintenance worker on February 2. A area sample taken during a filter disassembly showed 63 ppm MEK and 11 ppm toluene on December 22. The results of these samples are compared with Shell data in a summary Table 12. Results of Shell's heavy metals analysis are included here as well as their statment of analytical methods in attachment F.

The question was raised as to the possible presence of CS2 in the sour hydrogen waste gas discharge from the hydrotreater. It was proposed that this known neurotoxin might be present either in the hydrogen feed or as a by-product of reactions of other contaminants with sulfur in the presence of the bauxite catalyst at elevated temperatures and pressures. The sour hydrogen exhaust gases are collected for sulfur reclamation; however, some leakage might occur through seals. In the past, waste water was discharged to the sewer, causing strong odors. It is now processed through a water stripper for sulfur removal. Shell's expert on reaction mechanics advised that CS2 is supressed in the presence of excess hydrogen at 600 Psi and $620^{\circ}F$. He predicted 2 x 10^{-15} mole percent of CS₂ formation. Even with the discharge of 1/2 million cubic feet per day of gas by-products there would be an insignificant CS₂ production. Shell attempted to measure the CS₂ concentration in hydrogen supply and discharge samples, but they reported that the presence of hydrogen sulfide in the percent range masked $\mathcal{E}S_2$ on a gas chromatograph with a specific sulfur detector.

V. CONCLUSIONS

A. Medical

There are several cases of mild peripheral neuropathy in men who work in the Lube B area of the Shell Oil Refinery at Deer Park, Texas. The reported neuropathies are generally mild and do not seem to cause significant functional impairment. However, one individual is seeking compensation for being unable to work due to an alleged neuropathy. No attempt was made to grade the severity of these neuropathies, because essentially all of the neuropathies were felt to be minimal to mild. There are numerous complaints of physical discomfort among this group of workers, however, that may be related to mild neuropathy. Of the 43 workers examined by NIOSH, 27 had symptoms which were felt by the neurologist to be possibly or probably suggestive of peripheral neuropathy.

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Discomfort is a health effect which is, in itself, significant if it can be related to occupational exposure to chemicals.

This NIOSH study has a number of limitations:

- 1. Adequate controls were not available for this study. There are more neuropathies present in men who have been exposed for long periods of time, thus giving the impression of a possible dose-response relationship between working time and neuropathy; but the effects of aging on nerve function cannot readily be separated out in this small group, with it's narrow range of ages.
- 2. There is also the possibility that neuropathies seen today in the older group of Lube B employees are the result of exposure to chemicals years ago, when environmental conditions in the Lube B area may have been different from those measured today. No accurate records are available on chemical exposure and process contaminants in the earlier years of refinery operation.
- 3. Some cases of neuropathy could possibly be related to chemical exposure in other jobs besides Lube B. Although some Lube B employees have spent many years in the Lube B area, others have moved around the refinery in various jobs. Most of the observed neuropathies, however, are in employees who have spent at least several years in Lube B.

There is no good data in the literature to document the prevalence of minimal neuropathies in the middle-aged industrial work force. It is possible that a survey of industrial workers of comparable age in other industries would reveal similar degrees of mild neuropathy, related to the trauma and varied chemical exposures of working in modern industry over a lifetime.

The frequency of peripheral nerve abnormality in this group is, however, suspiciously high. Most of these men have spent much of their working lives in the Lube B area, where there are no significant chemical exposures except to MEK, toluene, and the large hydrocarbons found in the lubricating oils. Shell and OSHA data does not document the presence of any other known cause of peripheral neuropathy. The possibility of neurotoxic contaminants in the materials used in the Lube B area in the past cannot be ruled out, since no records are available on detailed chemical analysis of past process materials.

Additional evidence for the toxic nature of the observed neuropathies could come from properly done nerve biopsy with electron microscopic examination in cases where a neuropathy exists without other probable known cause besides toxic exposure. This procedure has been recommended

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to NIOSH by the expert reviewer who originally reviewed the Shell data for NIOSH. This reviewer indicated that some solvent neuropathies show characteristic changes by electron microscopy.

Additional evidence implicating MEK & toluene as possible neurotoxic agents might possibly be gained from chronic animal exposure studies.

The basic problem in interpreting this study is the lack of good data on the incidence of mild neuropathy in the general population and in the general industrial population. Baseline studies of this sort will probably eventually have to be done in order to deal with the rising number of industrial health hazard requests involving neurologic abnormality.

The prevalence of known diabetes in the Lube B area probably does not exceed the rate expected on the basis of national averages. Whether or not there is an excessive rate of subclinical diabetes, as determined by screening glucose tolerance studies, is less certain; but the data is suspicious for some increase in glucose intolerance. There are too many abnormalities of glucose tolerance to definitely rule out the possibility of work-related effects. Animal exposure studies to MEK and toluene might help determine if these chemicals are capable of causing this kind of metabolic abnormality.

Fasting serum triglyceride levels in Lube B employees are probably not generally excessively high when viewed in the context of recent population studies in the medical literature. Although triglyceride levels in Lube B group may be generally in line with current population norms, there is considerable speculation in the medical literature that these overall "normals" may not be "ideal" values for preventing atherosclerotic disease. Modern living conditions, exercise and dietary habits, and possibly environmental factors have probably caused the average serum triglyceride in the general population to rise to an unhealthy level that contributes to atherosclerosis and heart disease.

B. Environmental

The findings of numerous personal breathing zone samples taken by Shell industrial hygienist are supported by two recent OSHA industrial hygiene inspections. No exposures to known neurotoxins were detected. The Shell analysis of drinking water, process materials, feed stock and final products have not identified any potential exposures to recognized neurotoxins.

The only significant exposures noted were to MEK and toluene during maintenance, leaks or spills. The use of respirators is appropriate for protection from infrequent and brief exposures. It is necessary to

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minimize such exposures by scheduling preventive maintenance to avoid frequent and excessive leakage such as that due to excessive deterioration of rotary filter pedistal bearings.

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Table 1

HHE 77-43

Job Type vs. Degree of Neuropathy

Job	Degree of Weuropathy	Operators & Supervisor	Maintenance	Total
	Present*	8	1	9
	Present**	7	0	7
	Borderline*	3	4	7
	Borderline**	ĭ	1	2
i	Norma l	30	7	37
4	1101 11101	30	,	37
	Total	49	13	62

^{*}No known cause of neuropathy present

^{**}Possible cause of neuropathy present (abnormal glucose tolerance, trauma, deformity, etc)

HHE 77-43

Age vs. Degree of Neuropathy

Age (years):	20-29	30-39	40-49	50-59	60-69	Total
Degree of Neuropathy			All the second sections and the second sections and the second sections and the second sections and the second	T	de orden eta e marea gun y por de marea e que e que e que	
Operators	t et til forste en til en skyr skyr skyr en skyr skyr en skyr et skyr en skyr et skyr e	and the second of the second o				
Present*				8		8
Present**				6	1	7
Borderline*	Tipe of the state			2	·	30
Berderline**				1		1
Norma 1	9	6	3	12		30
Sub Total	10	6	3	29	1	49
aintenance						
Present*				1]
Present**				•		0
Borderline*				2	2	4
Borderline**				1	L	1
Normal			1	6		7
Sub Total	0	0	1	10	2	
Tota l	9	7	4	39	3	13 62

^{*}No known cause for neuropathy present
assible cause of neuropathy present (abnormal glucose tolerance, trauma, formity, etc.)

Table 3

HHE 77-43

Years of Service at Shell vs. Degree of Neuropathy

Degree of Yea	rs at 0-9	10-19	20-29	30-39	40+	Total
Neuropathy S	neri					
Operators						
Present*			7	3		10
Present**			3	2		5
Borderline*	78		1	1		3
Borderline**				1		1
`'ormal	16		11	3		30
Sub Total	17	0	22	10	0	49
Maintenance	<u>e</u>					
Pr e sent*				1		1
Present**						0
Borderline*			2	3		5
Borderline**						0
Normal			4	3		7
Sub Total	0	0	6	7	0	13
Total	18	0	27	17	0	62

^{*}No known cause for neuropathy present

**Possible cause of neuropathy present (abnormal glucose tolerance, trauma,
deformity, etc.)

Table 4

HHE 77-43 Years of Service in Lube B vs. Degree of Neuropathy

Degree of Years in Neuropathy Lube B	n 0-9	10-19	20-29	30-39	40+	Total
Operators						
Present*	2		6			8
Present**		1	6			7
Borderline*	1	1	1			3
Borderline**			1			Ī
Normal	18	5	7	0	0	30
Sub Total	21	7	21	0	0	49
Maintenance						
Present*	1					1
Present**						0
Borderline*	1	2	1			4
Borderline**		1				1
Normal	3		2	2		7
Sub Total	5 sa 15	3	3	2	0	13
Total	26	10	24	2	0	62

^{*}No known cause of neuropathy present

**Possible cause of neuropathy present (abnormal glucose tolerance, trauma, deformity, etc.)

Table 5

HHE 77-43

Age Distribution of Lube B Employees*

20-24	25-29	30-34	35-39	40+44	45-49	50-54	55-59	60-64	Total
1330									
4	6	4	2	0	3	14	15	1	49
0	0	0	0	0	1	3	7	2	13
4	6	4	2	0	4	17	22	3	62
	4	4 6 0 0	4 6 4 0 0 0	4 6 4 2 0 0 0 0	4 6 4 2 0 0 0 0 0 0	4 6 4 2 0 3 0 0 0 0 0 1	4 6 4 2 0 3 14 0 0 0 0 0 1 3	4 6 4 2 0 3 14 15 0 0 0 0 0 1 3 7	4 6 4 2 0 3 14 15 1 0 0 0 0 0 0 1 3 7 2

^{*}Includes all employees studied by NIOSH, Shell and private Physicians.

Table 6

HHE 77-43

Years of Service at Shell vs. Age

Age (years)	20-24	25-29	30-39	35-39	40-44	45-49	50-54	55-59	60-64	Total
hell Service (years	s <u>)</u>	***************************************								
0-4	4	4	4	1		1				14
5-9		2		1						3
10-14										0
15-19										0
20-24						1	3	3		7
25-29						2	11	8		21
30-34		98			×		3	8	3	14
35-39								3		3
TOTAL	4	6	4	2	0	4	17	22	3	62

Table 7

Shell Oil Refinery
Deer Park, Texas
1977

HHE 77-43

Years of Service in Lube B vs. Age

Age (years)	20-24	25-29	30-34	35-39	40-44	45-49	50-54	55-59	60-64	Total	
Service in Lube B (years)		7									
0-4	4	5	4	1		1	2	3		20	
5-9		7		1		1	2	1		6	
10-14						2	2	2	7	7	
16-19							3		1	4	
20-24							5	4		9	
25-29							3	12	1	16	
TOTAL	4	6	4	2	0	4	17	22	3	62	

Table 8

HHE 77-43

Abnormalities Observed in Glucose Tolerance in Lube B employees*

	G	lucose levels in	mg/dl of Serum	
Case Number	Fasting	l-hour post prandial	2-hour post prandial	Fasting 1 hour 2 hour (F+1+2)
<u>Dperators</u>				
1	121			
2	134	338	270	742
3	92	219	214	525
4	117			
5	91	238	214	543
6	ŀ	Known Insulin-Depo	endent Diabetic	
7	115			
8	143	272	295	710
9	87	264	148	499
10	112	213	134	459
11	219	346	378	943
<u>Maintenance</u>				
12	125	226	173	524
13	130	335	170	635

^{*}Combined NIOSH and Shell Data.

Table 9

HHE 77-43

Lube lacksquare employees - abnormalities of glucose tolerance by degree neuropathy*

Degree of Neuropathy		rmality in Glucose T	
	Absent	Present	Total
Operators			
Present	9	6	15
Borderline	2	2	4
Negative	27	3	30
Sub Total	38	, 11	, 49
Maintenance			
Present	1	0	1
Borderline	4	1	5
Negative	6	1	7
Sub Total	11	2	13
Total	49	13	62

^{*}Combined NIOSH and Shell Data.

Table 10

HHE 77-43

Prevalence of Diabetes reported in health interviews and number of conditions per 1,000 persons, by age and selected characteristics: United States, 1973.*

			Number per 1,000 persons						
Characteristics		All Ages	Under 17 yrs	17-44 years	45-64 years	65 yrs. & over			
Sov	Total	20.4	1.3	8.9	42.6	78.5			
Sex Male Female		16.3 24.1	1.1	6.9 10.8	40.6	60.3 91.3			
Color White All Other		19.9 23.9	1.4	8.3 12.8	39.6 70.0	75.9 104.5			

^{*}Report of the National Commission on Diabetes to the Congress of the United States. Vol. III., Part 1 Scope and Impact of Diabetes DHEW No.(NIH) 76-1021 p. 71.

Table 11
Shell Oil Refinery
Deer Park, Texas
1977

HHE 77-43

Fasting Serum Triglyceride levels by decade of age in Lube B Department*

Fasting Serum Age in Years									
Triglyceride mg/serum	20-29	30-39	40-49	50-59	60+	Total			
<100	2	2	0	7	0	11			
100-199	3	3	2	14	3	25			
200-299	0	0	1	7	0	8			
300-399	1	0	0	4	0	5			
400+	0	0	0	4	0	4			
Tota1	6	5	3	36	3	53			

^{*}Combined NIOSH and Shell Data for operators, supervisors, and maintenance.

Table 12

HHE 77-43

Environmental Measurments in Lube Oil Unit "B"

Activity &		Shell Survey	Data*	OSHA Survey**				
Substance	(n) samples	Range ●f TWA's	Average	Dec. 22,1 (n) 1		Feb. 2, 1 (n)	9// evel	
ilter Operator	22 (one each & 65 min	spl period o	f 3 95 , 310,	2	***	2		
MEK Toluene MBK n-Hexane Benzene		1.0-62 (328 1.4-18 (158 since Nov.)+ 6.3+	(N	0)<1.0 <10.0 0)<1.0 0)<3		(ND) <10.0 (ND)	
Refrigeration Operator MEK Toluene MBK n-Hexane Benzene		1.1-23 (133 1.0-5 (54 4 since Nov.)+++ 2.2	(N	D) <10.0 D) D)<.5	1	(ND) <10.00 (ND)	
Recovery Operator	7			1		1		
MEK Toluene MBK n-Hexane Benzene	3 sampled	1.0-11.0 1.4-6.0	5.8 3.8 23, 1976++	(n)	(D) <10.0 (D) (D)		(ND) <10.0 (ND) (ND)	
Entry Job	4 (one samp)	le period onl	y 330 min.)	Ī		1		
MEK Toluene MBK n-Hexane Benzene	all 4 sa	1.3-5.1 1.0-3.1 ampled since	2.5 1.6 Nov. 23, 19	(1	(D) <10.0 (D) (D)		(DN) 0.01> (DN)	
F <u>ield Maintenance</u>	10++++ (see samp	le period not	ce)		sample by ter being lown)	1	(ND)	
MEK Toluene MBK n-Hexane Benzene	all 10 sai	4.5-41 2.4-51 mpled since	22.1 15.1 Nov. 23, 197	(!	53.0 11.0 ND)		12.0 (ND)	
Shift Foreman MEK loluene MBK	2	1.9-4.0 1.2-3.		5.	4D) <10.0 4D)	Ĭ	(ND) <10.0 (ND)	

Table 12 (con't)

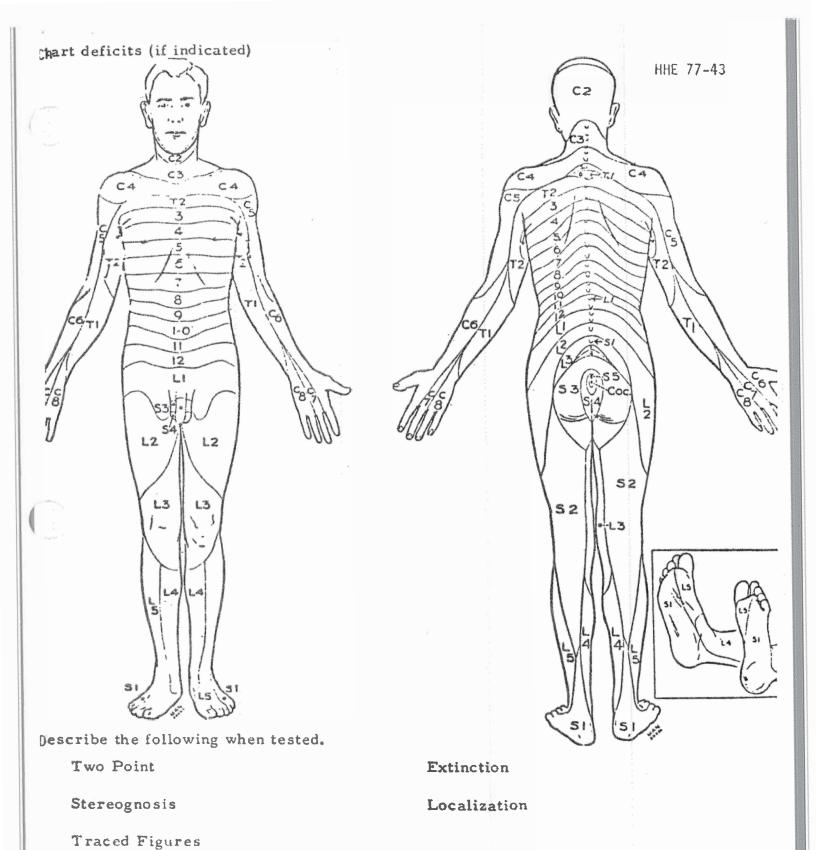
Activity & Substance	She'll Survey Data*			OSHA Survey** Dec. 22, 1976 Feb. 2, 1977			
	(n) samples	Range of TWA's	Average	Dec. 22, 1976 (n) level	(n)	level	
Board Man	1			1	1		
MEK Toluene MBK	1.9			(ND) <10.0 (ND)		(ND) <10.0 (ND)	
n-Hexane Benzene	sample taken since Nov. 23, 1976+			t			

- * Shell personal breathing zone samples were collected on charcoal tubes over a full term typically 400 minutes or greater. The TWA's are for 8 hours unless otherwise noted. This data was collected between June 12, 1976 and February 2, 1977 and reported to NIOSH in a letter dated March 10, 1977.
- ** OSHA personal samples were collected for full term. All personal sample volumes were greater than 20 liters and the one area sample was 19.61 liters.
- *** The none detected (ND) is based on a laboratory and sampling sensativity as follows:

- + One sample was unusually high due to repair work on a leaking line on filter #2. It was not included in the computed average.
- ++ Samples taken since November 23, 1976 have been analyzed for hexane and benzene. None was detected in personal samples. The detection limits are .1 ppm for n-hexane and .05 ppm for benzene.
- +++ One sample was unusually high due to a solvent spill in the refrigeration section. It was not included in the calculated average.
- **** The sampling period for maintenance personnel varied depending on their activity. These samples ranged from 55 minutes to 7 hours. Most were greater than 2 hours.

I Cranial Nerves: (note Right	tests used)		Left	·	
		I			
		II			
		III			
		IV			
		v			
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Heel-shin:					
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IVDeep Tendon Reflexes:	Biceps	R			
	Triceps	R	L		
	Brachioradi	ialís R	I		, pany
	Patellar	R	L		
	Achilles	R			
	Plantar	R		de de	

Muscle Strength and Atrophy: (Grade strength on	
Muscle Strength and Atrophy: (Grade strength on	
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Right	Left
Wrist flexors	
Wrist extensors	
Elbow flexors	
Elbow extensors	
Deltoid	
Hip flexors	
Knee flexors	
Knee extensors	
Ankle plantar-fle	xors
Ankle dorsi-flexo	rs
Foot invertors	
Foot evertors	
Other muscles as needed to document peripheral neu	ropathy(such as intrinsic muscles of hands of feet)
VII Sensory (please note the scale used in grading (If abnormal, please map abnormality or Right Touch	
Pin prick	
Joint mosition	
Vibration	
Other sensory as needed to document degree of loss	



Name HHE 77-

Nark						HHE 7	7-				
Nerve	Side		Modality		Latency	(milliseconds)		Conducting Distance(cm)	Nerve conduction velocity	Amplitu	de
	L	R	Motor	Sensory	Proximal	Distal)ifference		D/∆=cm/sec.	Sensory(uv)	Motor(mv)
Median											
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Other	-										
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ė.											

NEUROLOGICAL EXAMINATION PROCEDURE:

Unless otherwise indicated, procedures of examination were the usually acceptable procedures.

1. Cranial Nerves

All cranial nerves were examined. Coffee and pipe tobacco are used to test smell sensation. Taste is tested for three primary tastes—salt, sweet, and bitter.

2. Sensory Nerves

Examination of sensation is done next, after cranial nerve testing, while the subject is still alert and not fatigued with other procedures of a neurological examination. Cotton wool is used to test for light touch, a safety pin for pain, and a 128 cycle tuning fork for vibration. Two-point discrimination is tested on every patient with two blunt points applied on the tip of the finger, and on the dorsum of the feet. Hot and cold sensation is not tested.

3. Motor Nerves

Muscle power is recorded by numbers ranging from the normal of five to complete paralysis by O (zero). The following muscles are tested on every patient.

(a) All muscles of shoulder girdle and scapula:

Deltoid
Supraspinatus
Infraspinatus
Rhomboid
Serratus anterior
Pectoralis major
Latissimus dorsi

(b) All muscles of elbow joint:

Biceps Brachio radialis Triceps (c) All muscles of forearm and wrist:

Extensor carpi radialis Extensor carpi ulnaris Extensor digitorum Flexor carpi radialis Flexor carpi ulnaris

(d) All intrinsic muscles of hands and fingers:

Abductor pollicis longus Extensor pollicis brevis Extensor pollicis longus Opponens pollicis Abductor pollicis brevis Flexor pollicis longus Adductor pollicis Lumbricals and interossi Flexor digitorum sublimis Flexor digitorum profundus Adductor digiti minimi

(e) Similarly, the muscles of the hip girdle, of thigh and knee, of lower leg and ankle, of foot and great toe are tested.

4. Deep Tendon Reflexes

Deep tendon reflexes are recorded by 0 (zero) as absent, <u>+</u> as decreased, + as normal, ++ to +++ as varying degree of exaggeration, depending on the examiner's judgment.

5. Autonomic Function

Autonomic function is judged by postural change of blood pressure with patient in sitting and standing position, by trophic changes on all extremities, and by pupillary reflexes.

MEDICAL/NEUROLOGIC EVALUATION FOR HHE 77-43

I. General Medical

Fasting triglyceride level in serum Glucose tolerance test (oral)

II. Neurological

A. General neurological exam with special emphasis on eliciting signs and symptoms of peripheral neuropathy. Medical history related to possible causes of neuropathy (i.e. - alcohol, medications, trauma, diabetes mellitus, etc.) is also needed. Comments and diagnostic impressions required.

Attached is a copy of the neurological recording form used in the initial evaluation of these workers to indicate approximately what we would like done in this second confirmatory examination.

B. EMG and Nerve Conduction Studies

1. Lower Extremities (bilateral)

- a. Peroneal and posterior tibial latencies and conduction velocities.
- b. Sural nerve latency and amplitudes (antidromic stimulation at 21 cm and 14 cm).
- c. EMG's on: extensor digitorum brevis
 abductor hallucis
 tibialis anterior
 gastrocnemius
 quadriceps

2. Upper Extremities (one limb, dominant arm)

- a. Median and ulnar nerves, motor and sensory conduction velocities and distal latencies.
- b. If nerve conduction studies are abnormal, check EMG's on first dorsal interosseous and abductor pollicis brevis.

Parameters needed on EMG's are:

- Insertional activity (normal, increased, decreased)
- 2. Positive waves (0 to 4+)
- 3. Fasciculations (0 to 4+)
- 4. Fibrillations (0 to 4+)
- 5. Abnormal motor unit potentials (normal, abnormal; Indicate amplitude, duration, polyphasic character if abnormal).

Medical/Neurologic Evaluation for HHE 77-43
Page 2

6. Firing pattern:

0 = full interference

1 = non-specific reduction

2 = decreased recruitment

3 * single unit

4 = no units under voluntary control

5 = pattern consistent with lack of voluntary effort

7. Comments and Diagnostic Impression

Special Parameters required on nerve conduction studies are:

- 1. Measurement of conducting distance should preferably be made with a flexible tape.
- 2. Surface temperature measurements proximally and distally over nerve (at recording and stimulating sites).

III. INTERPRETATION AND COMMENT OF MEDICAL/NEUROLOGICAL FINDINGS

IV. INFORMED CONSENT

A NIOSH approved informed consent must be obtained from each study participant prior to any medical/neurological testing, and returned to NIOSH as part of the subject's medical file.

Attached is a copy of the NIOSH approved consent form to be used.

V. PROCEDURE FOR NOTIFICATION OF EXAMINEES OF MEDICAL FINDINGS

Should any significant abnormality which requires immediate attention be detected, the examining physician will notify the examinee of such finding immediately and suggest follow-up health care by his personal physician, and a written report of such findings will be submitted to NIOSH immediately.

Previous experience in toxic neuropathy screening programs suggests some alteration in the protocol:

Changes are as follows:

- One lower and one upper extremity will be studied. The side studied selected on the basis of screening exam for weakness or other neuropathy signs. If abnormalities are discovered the opposite limb and paravertebral muscles related will be sampled.
- 2) Sural latency will be measured at the standard accepted 14cm distance (3 measures are superfluous).
- 3) Muscles sampled will include at least:

Extensor Digitorum Brevis 1st Dorsal Interosseus (of foot) Extensor Hallucis Longus Medial Head Gastrocnemius Vastus Medialis

1st Dorsal Interosseus of hand Abductor Pollicis Brevis

Others may be added as indicated.

4) A tibial "H" reflex latency by the method described by Braddom may be added to cases in which radiculopathy is suspect, and to sample maximal segment velocity in otherwise denormal cases.

NERVE CONDUCTION STUDIES: Electrode Placement, Normal Findings, Procedure Guidelines

EFFERENT (MOTOR) CONDUCTION

PERONEAL NERVE

îtimulate-

- Above Fibular Head-peroneal n. courses across and then medial to fibular head into popliteal space.
- 2) Below fibular head-Nerve courses anteriorly and deep
- 3) Ankle-Anterior lateral aspect (20% of individuals may have accessory nerve to extensor Dig. Brevis-It courses under lateral malleolus).

Active Electrode*

Extensor Digitorum Brevis (anterior lateral aspect of proximal mid tarsal area)

Normal Findings
Distal Latent Period - Less than
6.0 msec.
Conduction Velocity
Below Fibular Head 50 ± 6

M/S Across Fibular Head 50 ± 6

POSTERIOR TIBIAL NERVE

Itimulate-

- 1) Popliteal Space
- 2) Posterior to medial malleolus

Active Electrode*

(lateral Plantar B)
Abductor Dig. Q.P. (directly under tip of lateral malleolus at junction of sole and normal skin)

(Medial Plantar Branch)
Abductor Hallicus (directly under navicular tubercle)

Normal Findings
Distal Latent Period
To Abductor Dig. Q. 5.9 ±
0.8 msec.
To Abductor Hallicus 5.3 ±

0.8 msec.

Conduction Velocity 51 ± 6 M/S

FEMORAL NERVE

Stimulate-

- Proximal to inguinal ligament and lateral to femoral artery (needle electrode facilitates)
- 2) Distal to inguinal ligament (needle electrode facilitates)
- 3) Distal to Hunter's triangle (anterior medial thigh)

Active Electrode*

Vastus Medialis

Reference Electrode over Patella.

Normal Findings

Expected Latent Periods (Adult)
Above inguinal ligament to
vastus medialis 7.1 msec.
Below inguinal ligament to
vastus medialis 6.0 msec.
Conduction velocity 69± 9 M/S

SCIATIC NERVE

Stimulate-

Sciatic Notch-Needle stimulating electrode is essential

Active Electrode*

(Lateral Division= Common Peroneal) (Medial Division= Posterior Tibal)

Pick up at same locations as tibial and Peroneal N.

Normal Findings
Conduction Velocity 55 ± 7 M/S

FACIAL NERVE

Stimulate-

1) Angle of jaw (straddle mastoid process)

Active Electrode*

1) Frontalis (mid-brow)

2) Nasalis (Lateral Nostril)

Normal Findings

Latent Period less than 4.0 msec.

RADIAL NERVE

Stimulate-

- 1) Erb's point (supraclavicular fossa)
- Posterior lateral upper arm (post fold of deltoid)
- 3) Lateral antecubital space

Active Electrode*

1) Extensor Indicis Proprius

Normal Findings

Conduction Velocity

Erbs Point to above Elbow 72 + 6 M/S

Above Elbow to Ext. Ind. P. 62 ± 6 M/S

ULNAR NERVE

Stimulate-

- 1) Erb's point (supraclavicular fossa)
- 2) Proximal to ulnar groove
- 3) Distal to ulnar groove
- At wrist (8 cm. proximal to active electrode) Just over flexor carpi ulnaris tendon

Active Electrode*

i) abductor digiti quinti (over prominence of muscle)

2) adductor pollicis (over lateral palmar crease)

Normal Findings

Distal Latent Period

To abductor Dig. Q 3.2 ± 0.5 msec.

To adductor poll. 3.4 ± 0.6 msec

Conduction Velocity

Forearm Segment 62 ± 5 M/S
Across Elbow 63 ± 6 M/S
Upper Arm Segment through
Axilla 70 + 7 M/S

NERVE CONDUCTION STUDIES:

Electrode Placement, Normal Findings, Procedure Guidelines

EFFERENT (MOTOR) CONDUCTION

PERONEAL NERVE

Itimulate-

- 1) Above Fibular Head-peroneal n. courses across and then medial to fibular head into popliteal space.
- 2) Below fibular head-Nerve courses anteriorly and deep
- 3) Ankle-Anterior lateral aspect (20% of individuals may have accessory nerve to extensor Dig. Brevis-It courses under lateral maileolus).

Active Electrode*

Extensor Digitorum Brevis (anterior lateral aspect of proximal mid tarsal area)

Normal Findings

Distal Latent Period - Less than 6.0 msec.

Conduction Velocity

Below Fibular Head 50 ± 6

Across Fibular Head 50 + 6

POSTERIOR TIBIAL NERVE

Itimulate-

- 1) Popliteal Space
- 2) Posterior to medial malleolus

Active Electrode*

(lateral Plantar B)

Abductor Dig. Q.P. (directly under tip of lateral malleolus at junction of sole and normal skin)

(Medial Plantar Branch)

Abductor Hallicus (directly under navicular tubercle)

Normal Findings

Distal Latent Period

To Abductor Dig. O. 5.9 ±

0.8 msec.

To Abductor Hallicus 5.3 ±

0.8 msec.

Conduction Velocity 51 + 6 M/S

FEMORAL NERVE

Stimulate-

- 1) Proximal to inguinal ligament and lateral to femoral artery (needle electrode facilitates)
- 2) Distal to inguinal ligament (needle electrode facilitates)
- 3) Distal to Hunter's triangle (anterior medial thigh)

Active Electrode*

Vastus Medialis

Reference Electrode over Patella.

Normal Findings

Expected Latent Periods (Adult)

Above inguinal ligament to vastus medialis 7.1 msec.

Below inguinal ligament to vastus medialis 6.0 msec.

Conduction velocity 69± 9 M/S

SCIATIC NERVE

Stimulate-

Sciatic Notch-Needle stimulating electrode is essential

Active Electrode*

(Lateral Division= Common Peroneal) (Medial Division= Posterior Tibal)

Pick up at same locations as tibial and Peroneal N.

Normal Findings

Conduction Velocity 55 ± 7 M/S

FACIAL NERVE

Stimulate-

i) Angle of jaw (straddle mastoid process)

Active Electrode*

- 1) Frontalis (mid-brow)
- 2) Nasalis (Lateral Nostril)

Normal Findings

Latent Period less than 4.0 msec.

RADIAL NERVE

Stimulate-

- 1) Erb's point (supraclavicular fossa)
- 2) Posterior lateral upper arm (post fold of deltoid)
- 3) Lateral antecubital space

Active Electrode*

1) Extensor Indicis Proprius

Normal Findings

Conduction Velocity

Erbs Point to above Elbow 72

+ 6 M/S

Above Elbow to Ext. Ind. P.

62 + 6 M/S

ULNAR NERVE

Stimulate-

- 1) Erb's point (supraclavicular fossa)
- 2) Proximal to ulnar groove
- 3) Distal to ulnar groove
- 4) At wrist (8 cm, proximal to active electrode) Just over flexor carpi ulnaris tendon

Active Electrode®

- 1) abductor digiti quinti (ove: prominence of muscle)
- 2) adductor pollicis (over latera palmar crease)

Normal Findings

Distal Latent Period

To abductor Dig. Q 3.2 ± 0.5

To adductor poll. 3.4 ± 0.6 msec

Conduction Velocity

Forearm Segment 62 ± 5 M/S Across Elbow 63 + 6 M/S

Upper Arm Segment through

Axilla 70 + 7 M/S

MEDIAN NERVE

Itimulate-

- 1) Erb's point
- 2) Medial aspect antecubital space (just lateral to brachial artery)
- Wrist between (8 cm. proximal to active electrode) palmaris longus tendon & flexor carpi radialis tendon.

Reference Electrode is placed over the endon or another electrically silent area.

Active Electrode*

Thenar muscles (prominence of abductor pollicis brevis)

Normal Findings

Distal Latent Period 3.7 ± 0.3 msec.

Conduction Velocity 57 ± 5 M/S

AFFERENT (SENSORY) CONDUCTION

MEDIAN

Stimulating Electrodes

I Orthodromic

Ring electrodes 4 cm. apart around index and middle fingers with cathrode at base of

digit.

II Antidromic

Reverse of above ie. Stimulating become pick up electrodes (active-proximal) and pick up electrodes become stimulating (distal is cathode) radialis tendons)
Normal Findings

Distal Latent Period
Orthodromic and Antidromic 3.2 ± 0.2 msec.

Conduction Velocity 57 ± 4

Active & Reference Electrodes

4 cm, apart mounted in plastic

bar with active placed distally

14 cm. from cathode (between

palmaris longus & flexor carpi

M/S

ULNAR

Stimulating Electrodes

I Orthodromic Ring electrodes around ring and little finger 4 cm. apart.

Cathode at base of digit.

Il Antidromic Reven

Reverse of above. Caution! Motor artifact is annoying!

Active & Reference Electrodes 4 cm. apart with active placed distally 14 cm. from cathode (over flexor carpi ulnaris tendon)

Normal Findings

Distal Latent Period
Orthodromic; and Antidromic 3.2 ± 0.25 msec.
Conduction Velocity 57 ± 5

M/S

Orthodromic

Stimulating Electrodes

2 strips 4 cm. apart over dorsum of web space; cathode placed proximally. Or ring

electrodes around the thumb.

Recording Electrodes

4 cm. apart mounted in plastic bar over the dorsolateral aspect of the radius (junction of middle and distal thirds)

Normal Findings

Distal Latent Period - 3.3 ±

0.4 msec.

Conduction Velocity 55 ± 5

M/S*

SURAL NERVE
Antidromic

Stimulating Electrodes

Mid-ventral calf (cathode

placed distally)

Recording Electrodes

4 cm. apart mounted in plastic bar just under lateral malleolus.

Normal Findings

greater than 40 M/S*

^{*}Subtract .1 ms from latency and divide into distance.

NOTES

PROCEDURE FOR "H" REFLEX

- 1) Stimulate nerve with cathode proximally with low intensity (25-30v)
- 2) Frequency of stimuli 1 per 2 or more seconds, to avoid blocking response.
- 3) Recording electrodes placed over appropriate muscle belly and tendon.

GENERAL GUIDELINES FOR STUDIES

- 1) Do motor (efferent) studies first to locate nerve trunk for afferent studies?
- 2) Be alert for anomalous innervation, e.g. cross over from median to ulnar, etc!
- 3) To isolate response, use needle electrode to pick up!
- 4) Must use surface electrodes to demonstrate myasthenic response!
- 5) Always stimulate in distal position for myasthenic response (i.e. close to muscle) to avoid excessive movement artifact. Immobilize part to be stimulated.
- 6) Note amplitude, duration and shape of evoked potential at both stimulation sites and compare.
- Beware of stimulus spread with increased duration and voltage and thus misinterpretation of results.
- 8) When determining conduction across a possible entrapment site; Note amplitude and duration of evoked potential as well as calculating the conduction velocity. The ulnar nerve conduction across the elbow should be measured with the elbow flexed to at least 1100 so that segment of nerve measured will more nearly approximate the distance on the surface.
- 9) With children and infants, electrodes may be miniaturized, however, careful determinations with adult stimulating and recording electrodes are satisfactory.
- 10) For ambiguous afferent nerve action potentials, turn down intensity and repeat stimulus 20-25 times. Noise will average out and signal will be defined on a photograph with exposure on bulb.

Attachment E

HHE 77-43

Table 1 Glucose Tolerance with Age*

A. Adapted from FAJENS (5)

AGE	FAST	1 HOUR	2 HOURS	SUM OGTT/2 HOURS
-50	110	185	140	435
50-60	110	195	150	455
60-70	110	205	160	475
70-80	110	215	170	495

B. Adapted from ANDRES (2)

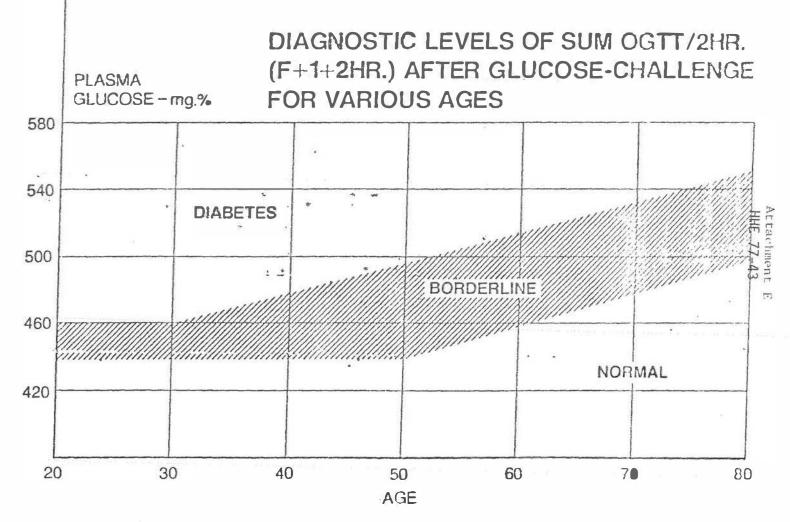
AGE	FAST	1 HOUR	2 HOURS	SUM OGTT/2 HOURS
-30	110	185	165 (185) *	460
30-40	112	191	175 (195)	478
40-50	114	197	186 (205)	496
50-60	116	203	195 (215)	514
60-70	120	215	215 (245)	550

^{*} In parentheses are given the approximate values for patients above normal but not clearly diagnostic of diabetes by the Andres criteria. In Figure 1, and in the text, this range of values has been designated "probable diabetes." The data was calculated from the Andres monogram for whole blood glucose by addition of 15% on plasma glucose and "rounding off."

^{*} Report of the National Commission on Diabetes to the Congress of the United States; U.S. Department of Health, Education, and Welfare; Public Health Service, National Institute of Health, DHEW Publication No. (NIH) 77-1021, p. 57-59.

The values drawn are based on information derived from Fajans and Andres, as shown on Table 1.

Figure 2



The Sum-OGTT/2 hours is useful in arbitration of equivocal tests. A patient with a single abnormal 1-hour or 2-hours value would be diagnosed on the basis of the total sum of the 2-hour OGTT.

Attachment F HHE 77-43

This attachment includes data and laboratory procedures received from Shell Oil Refinery, Deer Park, Texas in their letter of March 10, 1977. The contents are as follows:

	Page
Quantitative Analysis of MEK	1
Specifications and Typical Analysis of Toluene	2
Composition of Dry Solvent	3
Analysis of Solvent Mixture for Heavy Metals	4
Analysis of Process Streams for Heavy Metals	5
Analysis of Bright Stock for Heavy Metals	6
Charge and Product Properties	78
Analysis of Drinking Water for Heavy Metals	9
Analytical (& Sampling) Methods	10-12

ATTACHMENT F HHE 77-43 LUBE B - MEK UNIT

QUANTITATIVE ANALYSIS OF MEK

SAMPLE DATE 12-22-76

COMPONENT	% BY WEIGHT				
MEK	99.4%				
IPA	0.1%				
SEC-BUTANOL	.23%				
C ₈ 's	. 22%				
MBK	< 10 ppm<				

CODE NUMBER: 83-380

Toluene Column Tops. Charge is sulfolane extract of

2.

stabilized reformate.

Treatment:

None (reformate is hydrotreated).

Yield:

2700 B/CD

Key Control Tests: Purity, Dist.

Production Method:

Properties Gravity, Specific at 60°F Gravity, API @ 60°F Color, Hazen Odor Corr. Cu. Strip at 212°F, D-849 Kinematic Viscosity at 77°F, cs Non-Volatiles mg/100 ml Cloud Point, C Acid Wash Color H_S and SO_ Sulfur, ppm Insoluble Matter pcw Acidity Separated Water K. F. Water, pcw RI at 20°C Distillation, C IBP	Specification 0.869 - 0.873 Max. 10 (1) (2) Max. 1 Max. 30 Max. 2 Nil Max. 30 Max. 0.10 Nil None	Typical .8708 31.0 5 Passes 1B 0.7 1 5 04 Passes 1 None Passes Passes 0.005 1.4965
10% Rec DP Distillation Range, °C Purity, pcv (GLC) Sat., ppm Benzene, ppm	1° including 110.6 ±0.1°C Min. 99.9 Max 500	110.4 110.5 110.6 0.2 99.94 300
Xylenes, ppm Miscellaneous Properties (3) Peroxide No. Meq/liter ASTM D-1563 Carbonyl, ppm ASTM D-1089 Chlorides (Sodium Biphenyl extraction), Bromine Index SMS-57 Color Reaction Test, 24 hrs.	Max 300 (5) Max 300 ppm Max 2	50 20 N11 N11 L. T. 1 LT10 (4)

⁽¹⁾ Not darker than a solution of 0.0030 g K2Cr207 in one liter of water.

⁽³⁾ Based on limited data.

⁽⁴⁾ Property varies with unit operations and age of CR-3 cobalt-molybdenum

⁽⁵⁾ Maximum 200 ppm for Mobay Chemical Co.

COMPOSITION OF DRY SOLVENT

SAMPLE DATE: 12-22-76

		Response	
	Emergence	Factor	
Component	Time, Sec.	(Relative to benzene)	<u> </u>
C, Hydrocarbon	117-207	1.0	0.025
Co Hydrocarbon	217-263	1.0	0.077
C' Hydrocarbon MEK	458	1.752	49.086
Benzene	554	1.0	0.009
IPA }	554	2.10	0.020
Unknown	590	1.0	0.009
MIBK	786	1.53	0.034
SBA	803	2.0	0.109
Unknown	862	1.0	0.005
Toluene	955	1.03	50.618
Methyl n-butyl			
ketone	1025	1.34	Absent
MIBC	1826	2.0	0.008

ATTACHMENT F HHE 77-43 LUBE B - MEK UNIT

ANALYSIS OF SOLVENT MIXTURE FOR HEAVY METALS

FEBRUARY 1, 1977

SAMPLE RESULTS*

Metal	Dry Solvent	Wet Solvent
Arsenic	<.001	<.001
Bismuth	<.001	<.001
Thallium	<.001	<.001
Antimony	<.001	<.001
Cadmium	∢.001	<.001
Copper	.002	.005
Lead	<.001	<.001
Nickel	<.004	<.004
Vanadium	<.001	<.001
Mercury	<.001**	<.001**
Phosphorous	.8	7

^{*}All metals except phosphorous were determined by atomic absorption spectrophotometry. The measurements are in the units of milligrams per liter which is very nearly parts per million (weight). (See attachment 9 for description of analytical method.)

^{**}The laboratory reports that digestion of sample by the permangamate method was not complete and therefore the accuracy of the determination is in doubt. A more accurate method of mercury determination is under development.

HHE 77-43 LUBE B - MEK UNIT

ANALYSIS OF PROCESS STREAMS FOR HEAVY METALS

FEBRUARY 9, 1977

PROCESS MATERIAL

Dewaxed Bright Stock Raffinate
Dewaxed Heavy Raffinate
Dewaxed 100 Raffinate
Dewaxed 250 TQ Raffinate
Dewaxed MQ 250 Raffinate
Crude Wax 160/170
Crude Wax 140/150
Crude Wax 130/137
100 Raffinate
250 TQ Raffinate
250 MQ Raffinate
Heavy Raffinate
Bright Stock Raffinate

ANALYSIS

less than 10 ppm of:
lead
mercury
cadmium
vanadium
nickel
arsenic
bismuth
copper
antimony
thallium

less than 100 ppm of: phosphorous

ATTACHMENT F HHE 77-43 LUBE B - MEK UNIT

ANALYSIS OF BRIGHT STOCK FOR HEAVY METALS

ANALYSIS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY.

FEBRUARY 1; 1977

Antimony		<	.001 ppr	ħ
Thallium	363	٧	.001 ppr	n
Bismuth		٧	.001 ppr	n
Vanadium	9	٧	.001 pp	ц
Arsenic	se gi	<	.2 pp	n
Phosphorous	х.		3.5 pp	m
Lead	20	4	.002 pp	m
Mercury	an o	٧	.01 pp	m*
Nickel			.011 pp	n
Copper	2	T :	.026 pp	m
Cadmium		•	.020 pp	m

therefore the accuracy of the determination is in doubt. A more accurate method of mercury determination is under development.

7.

Attacment F
HHE 77-43
CHARGE AND PRODUCT PROPERTIES

	HVI 100		VI 100 HVI 250		HVI	НЕАVУ		STOCK	
Dewaxing Mode									
Charge Viscosity Index									
(Projected)*	90	92	88	90	91	93		89	91
Product Oil									
Viscosity, SU @100F	90	93	257	270	580	740		2900	3000
SU @210F	38	39	49	50	69	73		150	160
Viscosity Index	90	98	89	93	89	93		8,	91
Clear Pt (Solv.Dil.)	0	-14	-8	18	-15	0		0	+12
Pour Point, OF	5	20	1.0	25	0	15		15	25
Crude Wax									
Melting Pt., OF	. 113	118	128	137	146	154		168	170
Oil Content, %wt	8	25	10	21	24	36		26	44

^{*}This test is a measure of extraction severity at the phenol extraction unit.

ax Splitting (Brt. Stock Raw Wax Only	HHE	77-43	HVI	250	<u>H</u>	vr	BRT. ST	rock
Charge-Product Wax from Deciling								
Melting Point, OF	170		180					
Product Wax - HMP								
Melting Point, OF Oil Content, %wt	180		187					
Soft Wax-Microcrystalline								
Melting Point, OF Congeal point, OF Oil content, %wt	140 135 .7		145 139 1.5					
Deciling Mode								
Charge (Crude Wax)								
Melting Point, OF Product Wax (Raw Wax)	113	118	128	137	146	154	168	17 C
Melting Point, OF Oil Content, %wt.	124	126 1.0	138 0	143	158 .7	162 2.0	170	

ATTACHMENT F HHE 77-43 LUBE B - MEK UNIT

ANALYSIS OF DRINKING WATER FOR HEAVY METALS

FEBRUARY 1, 1977

SAMPLE RESULTS*

	Metal	Water Blank (Double Deionized)	Drinking Fountain Outside of Control Room	Kitchen Sink Inside Control Room	EPA Maximum Continant Levels In Drinking Water (milligrams/lit
	Arsenic	< .001	₹.001	< .001	0.05
	Bismuth	< .001	< .001	< .001	No limit establ
	Thallium	< -001	< .001	₹.001	No limit establ
	Antimony	< .001	< .001	∢.001	No limit establ
	Cadmium	< .001	<.001	< .001	0.010
	Cooper	<.001	.036	.023	No limit establ
1	d	<.001	₹.001	< .001	0.05
	Nickel	< .004	∢ .004	₹ .004	No limit establ
	Vaṇadium	.⊲.001	< .001	< .001	No limit establ
	Mercury	< .001	₹.001	< .001	0.002
	Phosphorous	< .01	.05	.03	No limit estab:

i metals except phosphorous were determined by atomic absorption spectrophotometry. I measurements are in the units of milligrams per liter which is very nearly parts per mill weight. (See attachment 9 for description of analytical method.)

ATTACHMENT F HHE 77-43 ANALYTICAL METHODS

FEBRUARY 11, 1977

1. Personal sampling method

Personal sampling is done in accordance with the NIOSH standardized charcoal tube sampling/analytical method S-3 (also P & CAM 127). The charcoal tube holder is attached to the shirt collar in order to sample air from the breathing zone. Both Sipin Model Sp-1 and MDA Accumater 808 personal sampling pumps have been used to collect samples. The charcoal tubes are capped and transferred to the Industrial Hygiene Laboratory at the Westhollow Research Center. The tubes undergo the standard carbon disulfide desorption and GLC analysis.

2. Solvent analysis

Samples of finished MEK, wet solvent, and dry solvent were collected in quart-size glass bottles and capped. The samples were transported to the Westhollow Research Center by courier. Each sample was examined by GC - mass spectrometry for qualitative analysis and by GC - flame ionization detector for quantitative analysis. Instrumentation and settings were as follows:

Instrument: Hewlett-Packard 5700 A - Flame Ionization Detector,

Infotronics Model CRS 101 Integrator

Column: 50" x 0.02" SCOT Carbowax 1540

Perkin-Elmer Serial SC 4876

Conditions:

Injection Port 250°C Detector 250°C

Column Oven 80°C Isothermal

Carrier Gas Helium 8.5 psig inlct pressure

Sample 1 ul split 3/1

DAYE FEBRUARY 23, 1977

SHELL OIL COMPANY

DEER PARK MANUFACTURING COMPLEX

SAFETY AND INDUSTRIAL HYGIENE
MANAGER

FROM MANAGER ANALYTICAL - CHEMICAL/OIL WESTHOLLOW RESEARCH CENTER

SUBJECT METHOD DESCRIPTIONS FOR LUBE EXTRACTION PLANT SAMPLES

The following brief descriptions of analytical methods used by our Industrial Hygiene Laboratory for analysis of samples taken at the Deer Park lube extraction plant have been prepared at the request of Industrial Hygienist, Deer Park Manufacturing Complex.

Airborne Vapors

Airborne vapors collected on charcoal tubes were analyzed for MEK, toluene, benzene, and n-hexane by the standard NIOSH procedures as described in P&CAM No. 127, NIOSH Manual of Analytical Methods (1974), and in Methods S3 (2-Butanone) and S90 (Hexane) from the NIOSH Standards Completion Program, Sets A and G respectively. All four components were desorbed with carbon disulfide and analyzed by gas chromatography in a single run using a 15 ft. x 1/8 inch column with 10% TCEP on Chromosorb W-AW at 65°C. Calibrations were made using external standards.

Metals by X-Ray

The method is known as Energy-Dispersive X-Ray Spectrometry (EDXS). In this technique samples are bombarded with a beam of x-rays which causes elements in the sample to fluoresce. This fluorescence is accompanied by the production of photons whose unique energies specifically identify the unknown elements. The number of photons at each energy are counted, which is a measure of the concentration of each element in the sample.

These photons are detected with a lithium-drifted-silicon, Si(Li), solid-state radiation detector. The impulses from the detector are sorted electronically by a computer-based multichannel analyzer and displayed in histogram form.

Our configuration employs a "secondary-target" technique which allows for maximum excitation of the elemnets of interest. This allows us to determine most elements to less than 10 ppm.

Analysis of the samples indicated no metals present at levels above $10~\rm{ppm}$ (our limit for phosphorus is $100~\rm{ppm}$).

To insure the accuracy of our method, we prepared synthetic standards at low ppm levels and found the instrument to be working satisfactorily.

Metals by AA

 Brightstock oil ~50 gm sample with 5 gm sulfur added was charred and placed in 450°C muffle furnace overnight. The residue was dissolved in HNO3 and diluted to 25 ml. Pb, Cd, V, Ni, Sb, Bi, Cu, and Tl were run on this sample using graphite furnace atomic absorption.

Arsenic was determined after digestion of a 3 g sample with sulfuric acid and hydrogen peroxide. The sample was diluted to 25 ml and As determined by graphite furnace atomic absorption. Nickel and nitric acid were added to the sample in the graphite furnace. This matrix modification technique allows the use of higher charring temperatures without loss of arsenic.

Mercury was run by standard cold vapor techniques after a permanganate digestion of the sample. This method is not suitable for this type sample and the validity of the result is in doubt.

 Water samples and wet/dry solvents were analyzed for Pb, Cd, V, Ni, Sb, Bi, Cu and Tl by direct injection into a graphite furnace. No sample pretreatment was involved.

Arsenic was determined by graphite furnace atomic absorption using nickel/nitric acid treatment in the furnace tube for matrix modification

Mercury was determined by standard cold vapor techniques following permanganate digestion. This method was not suitable for the solvents and they were not analyzed for mercury.

Analysis of Liquid Samples for Organic Composition

The GC and GC/MS analysis of the wet and dry solvents (MEK/Toluene) and the solvent sewer sample have already been described in the memo from Manager - Chemical/Oil, WRC, to Manager, Manufacturing Safety and Health, dated January 18, 1977 with a copy to

Attachment A HHE 77-43 U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE CENTER FOR DISEASE CONTROL NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH CINCINNATI, OHIO 45202

CONSENT FORM

I	, age		voluntar	rily agr	ee to
participate in a health hazard eval					
Park, Texas, conducted by the Natio	: Ins	titute f	or Occupat	cional S	afety
and Health (NIOSH). This evaluatio	r co	nducted	under the	authori	ty of
section 20(a)(6) of the Occupationa	l Kafet	y and He	ealth Act a	and in a	ccord-
ance with Federal regulations (42 C	ode of	Federal	Regulation	ns Part	85).
I understand that I will be asked q	uestion	s about	my current	t and pa	st
health, and that I will be requeste	d to un	dergo a	medical/no	eurologi	cal
examination by NIOSH approved physi	cians.				

I understnad that I will be asked to provide a small amount of blood which will be drawn from my arm by a needle and will later be a did to provide additional small amounts of blood which will also be drawn from my arm by a needle for determination of blood sugar as a triglycerides. Drawings of blood may cause small discomfort but involves little or no risk to health. I may also be asked to supply a urine specimen.

A neurological examination will be performed by a neurologist and includes tests for taste, reflexes, motor coordination of all limbs, muscle strength, and feelings of sensation.

A nerve conduction velocity test will be performed using an electrical impulse on nerves in the arm and in the leg. Skin temperature at the points of stimulation and recording will be determined. The stimulus for nerve conduction testing is similar to the feeling experienced when you bump your "crazy bone."

An electromyographic test (EMG) will be performed on several muscles using needle electrodes. Slight discomfort, similar to a pin prick, may be experienced during these tests.

The benefit to me is that all medical findings will be sent to me and, if I want, to my doctor. I understand that at any time during the study I have the right to ask questions of NIOSH and that I am free to withdraw my consent and to discontinue participation in the study at any time without prejudice to myself.

All information gathered in this evaluation will not be disclosed in a manner which will identify me except with my written permission (see request and authorization for release of information) or except as required by law. The information will be used by NIOSH primarily for purposes of the health hazard evaluation and also for occupational health research.

SIGNATURE	DATE	*
investigator	DATE	

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*Neurological Evaluation Form: NIOSH project NHE 77-43 : Shell Oil, Pasadena. Texas

Significant past medical history (medical conditions requiring regular medication,	
regular medical attention, surgery, etc.):	
History of any neurological condition:	
Symptoms suggestive of peripheral neuropathy: (weakness, numbness, abnormal sensation	on,et
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IIOther significant History:	_
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