U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
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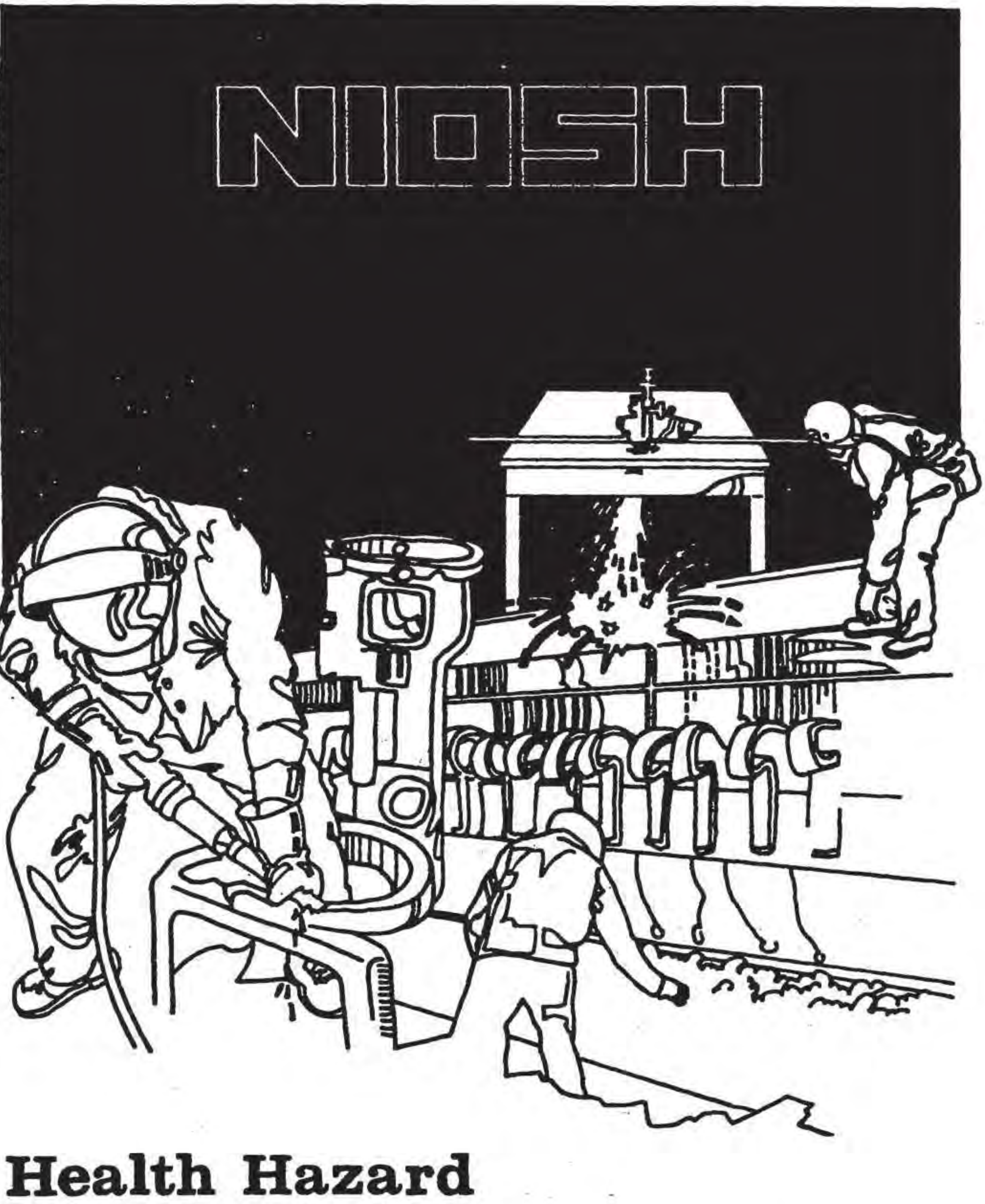

Health Hazard Evaluation Report

HETA 81-295-1155
OLIN (FORMERLY ALLIED) CHEMICAL CO.
MOUNDSVILLE, WEST VIRGINIA

PREFACE

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

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

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AUGUST 1982
OLIN (FORMERLY ALLIED) CHEMICAL CO.
MOUNDSVILLE, WEST VIRGINIA

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I. SUMMARY

On May 4, 1981, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union (ICWU) to conduct a Health Hazard Evaluation (HHE) at the Allied Chemical Company in Moundsville, West Virginia. A previous NIOSH HHE (79-113-728) at another chemical plant implicated a potential hazard to the male reproductive system in workers exposed to dinitrotoluene (DNT) and toluene diamine (TDA). The union requested an HHE at the Moundsville plant because of similar operations and chemical exposures to those of the earlier study.

The plant area of concern produces DNT which is subsequently reduced by the addition of hydrogen to produce TDA, a precursor of toluene diisocyanate. A total of about eighteen operators and helpers run the DNT and TDA units.

NIOSH conducted an initial survey June 4-5, 1981 consisting of a detailed walk-through survey and the administration of reproductive history questionnaires to workers. Based on information gathered during the initial survey there appeared to be an indication that possible reproductive problems were occurring among workers at this facility. Follow-up medical and industrial hygiene surveys were conducted in September, 1981.

The industrial hygiene survey involved personal and area sampling for DNT and TDA in the respective areas. Area samples were taken in both units. A new sampling method was used to monitor personal exposures; however due to laboratory error in preparation of the sampling media, this data was determined to be invalid. A total of 7 area samples for DNT and 11 for TDA were obtained using impinger sampling methods. Area samples for DNT ranged from 26 to 890 micrograms per meter cubed (ug/m^3); mean 207 ug/m^3 (OSHA standard 1500 ug/m^3). Area concentrations of TDA ranged from below detectable limits to 687 ug/m^3, mean 221 ug/m^3 (No applicable OSHA standard). Since operators generally did not spend a majority of the work shift in any one of the areas sampled, with the exception of control rooms, no estimate of actual personal exposure levels to DNT and TDA is undertaken although area values indicate exposure potential.

A total of 52 male workers volunteered to participate in the medical survey. Blood, urine and semen specimens were obtained along with physical examinations. Medical (including reproductive) and occupational histories were also elicited. The wives of workers involved in the study were given a different, more detailed reproductive questionnaire to verify the information given by the workers themselves. There were no significant differences between the exposed and control groups regarding liver function test, renal function tests, or sperm counts and sperm morphologies. The exposed workers did report a higher rate of reproductive problems (i.e. miscarriages) in the past.

Based on the results of the study, there was no biological indication of current reproductive problems in the TDA area of the Allied Chemical Co., Moundsville WV plant. However, the questionnaire data suggest that there may have been adverse reproductive effects from TDA exposure in the past. Laboratory error invalidating personal exposure data prevented evaluation of the current exposure levels associated with the negative findings of the medical survey. Recommendations are presented in Section VIII addressing equipment modifications, personal exposure monitoring, personal hygiene, respiratory protection, and continuing education.

KEYWORDS: SIC 2821 (Plastics materials, synthetic resins, and nonvulcanizable elastomers), reproductive effects, dinitrotoluene, toluene diamine.

II. INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) received a request in April 1981, from the International Chemical Workers Union (ICWU) to conduct a Health Hazard Evaluation (HHE) for their membership of Local 839 involved in dinitrotoluene (DNT) and toluene diamine (TDA) production at the Allied Chemical Company (SIC 2821), in Moundsville, West Virginia. A previous NIOSH HHE, 79-113-728, conducted at another plant using similar chemicals suggested reproductive problems in the form of lowered sperm counts and other reproductive abnormalities in male workers exposed to these chemicals. As a result of that investigation, an HHE request was submitted on behalf of the workers in the DNT and TDA areas at Allied Chemical Company asking for an investigation into whether or not similar reproductive disorders might exist at this facility.

An initial survey was conducted by NIOSH June 4-5, 1981 including a detailed walk-through survey of the DNT and TDA production units and supporting areas and the administration of reproductive history questionnaires to workers. Each worker involved in the DNT and TDA areas of the plant and maintenance men who spend a part of their time in these areas were asked to participate in the questionnaire survey. The information obtained included age, occupational history and a variety of questions regarding past reproductive outcome, use of contraceptives, and the occurrence of hysterectomies or vasectomies. An attempt was made to interview as many of the workers as possible during the two day survey. Those who were unavailable were contacted later by telephone.

After the information was analyzed, the workers in the TDA area appeared to show a reduced fertility rate when compared with the DNT and non TDA/DNT areas. The reduction, however, was not statisticallly significant. When comparing the TDA workers miscarriage to live birth ratio and the same measurement in the non TDA/DNT areas, the ratio among the TDA workers was significantly higher. Based on this information gathered during the initial survey there appeared to be an indication that previously suspected reproductive problems occurring in DNT and TDA workers involved with the earlier NIOSH HHE might also be occurring among workers of the DNT and TDA areas at this facility.

Subsequently, a follow-up industrial hygiene assessment of the DNT and TDA areas was conducted September 15-17, 1981 and an indepth follow-up medical study of the workers took place September 21-25, 1981. Survey summary letters were sent following each of the two surveys and interim reports followed. Interim I dated July 1981 presented the results of the initial survey and Interim II, dated December 1981, presented some preliminary industrial hygiene information.

III. BACKGROUND

A. General

Allied Chemical Company's Moundsville, West Virginia plant began production of dinitrotoluene (DNT) and toluene diamine (TDA) in October of 1956. This was immediately followed by startup of the toluene diisocyanate (TDI) production unit in November, 1956. The three systems operate in sequence with TDI as the final product. Each unit occupies a separate area, DNT in Building 55, TDA in Building 52, and TDI in Building 53. Limited amounts of storage for each material are located adjacent to the respective process.

The HHE request focused on the DNT and TDA production units, therefore, subsequent discussion will generally be limited to these areas. About 25 workers are regularly involved in the DNT and TDA process. Job titles include: operators, helpers, janitor/laborer, and maintenance. The units operate three shifts per day, 21 shifts per week with rotation.

Production at the time of the walk-through survey was averaging better than 80% of capacity. The units must function in sequence and due to limited storage space are operated at levels reflecting current market conditions. At the time of the follow-up survey the units were operating at 100% of capacity in preparation for a turn-around (shut down) period beginning the following week.

The Moundsville facility was purchased by Olin Chemical Company in early October, 1981.

B. Process Discription

The DNT and TDA production units are located in dedicated areas on opposite sides of the TDI production unit. The DNT unit occupies an enclosed three story structure including control room. The TDA unit occupies a three story structure having enclosed control and filtration rooms with the majority of the process equipment in a more open "rack" area.

DNT is produced by a two stage reaction of toluene, nitric acid, and sulfuric acid. A series of reactors are used in mono- and dinitration processes. Spent sulfuric acid is removed and piped to the sulfuric acid concentration unit for recycling. The reaction is regulated by temperature and reactant ratio. Following nitration the DNT is sent through washing columns using water followed by a soda ash solution which converts "acid" DNT to washed DNT. The washed DNT is then feed stock for the TDA process, and is pumped from the DNT feed tank by a feed pump to the primary reactor vessels in TDA. The 2,4- and 2,6-DNT are the primary isomers in the product DNT and are present in an approximate 80:20 ratio of 2,4- to 2,6-DNT.

DNT, excess hydrogen gas (H_2), and a noble metal catalyst are fed into primary reactors followed by two subsequent finishing reactors resulting in completion of the reduction of DNT to TDA. Water, a reaction byproduct, is removed from the H_2 via heat exchangers and residual hydrogen gas is piped to the boiler house and consumed as supplemental fuel. The TDA and miscellaneous byproducts called "lites" are then sent through a prefilter, which removes the bulk of the catalyst, followed by a polishing column which removes the lites. The lites are piped to the boiler house and consumed as supplemental fuel. TDA and remaining catalyst is pumped through a final filter where residual catalyst is removed. Water removed from the system passes through condensors and is pumped to a carbon treatment plant prior to discharge.

The catalyst collected on the filters must be removed periodically necessitating the opening of the system and removal of filters from the filter room to a filter cleaning area located in a nearby building. The TDA produced is an 80:20 mixture of the 2,4- and 2,6-isomers, having a purity of 97-99%.

TDA is fed into a reactor in the TDI unit as a mixture with orthodichlorobenzene. Phosgene is introduced in the reactor and TDA phosgenation occurs producing TDI as an 80:20 mixture of the 2,4- and 2,6-isomers. TDI is the final product, of which DNT and TDA are precursors. Figure I presents a process flow chart.

IV. EVALUATION DESIGN AND METHODS

A. Industrial Hygiene

1. Protocol

The industrial hygiene evaluation of the DNT and TDA units was conducted September 15-17, 1981. Personal exposure monitoring of all operators and helpers in the two units was conducted on the second shift September 15 and on the day shifts September 16 and 17, 1981. Additionally, selected janitor/laborer categories and maintenance men working in the units or on equipment taken from the units were sampled for DNT or TDA exposures. Area samples for DNT and TDA were also obtained at various locations in the respective units during the two day shifts.

The NIOSH industrial hygienist had requested development of a solid sorbent sampling method for DNT and TDA to be used in personal exposure sampling. Impinger methods had been used in the previous NIOSH study[1] and to provide some comparative data between the new method and impinger methods, side by side area samples were taken. All sampling, both personal and area, averaged close to eight hours in duration.

Inspection of the units and observation of work practices, use of personal protective equipment, locker room facilities, engineering controls, and informal discussions with workers in the areas concerning their duties and concerns about materials used were conducted.

2. Sampling and Analytical Methods

Four different sampling methods were used to evaluate ambient DNT and TDA concentrations in buildings 55 and 52. The methods used were as follows:

DNT: NIOSH Method S215[2] which uses a mixed cellulose ester filter with stainless steel back-up screen followed immediately by a midget impinger. Sample duration approximated a full work shift. Analyses was done by high pressure liquid chromatography with an ultraviolet detector set at a wave length of 242 nanometers. The limit of detection (LOD) was 2 micrograms (ug) per sample.

TDA: NIOSH Method P & CAM 141[3] using 10 ml of Marcali solution in a midget impinger was run at a flow rate of 1.0 Lpm over a full work shift. Analysis for TDA was performed by colorimetry with a detection limit (LOD) of 1 ug/impinger.

DNT and TDA: A solid sorbent method for DNT and TDA developed under contract to NIOSH utilized a 37 mm teflon filter followed by a Tenax GC® sorbent tube with a recommended sampling rate of 1.5 Lpm for 60 minutes. Modification of the method to accommodate equipment limitations; available manpower; to permit obtaining an eight hour time-weighted average; and to limit the number of analyses required resulted in using a flow rate of 1.0 Lpm for a four hour sampling period. Analyses were performed using gas chromatography with a nitrogen-phosphorous detector. The LOD per sample was 0.79 ug of DNT and 0.42 ug of TDA.

DNT and TDA: A modification of the above solid sorbent method conducted at the lab's request used Tenax GC® tubes alone at a flowrate of between 150 and 200 cubic centimeters (cc) per minute for four hour sampling periods. Analyses were conducted again using gas chromatography with a nitrogen-phosphorus detector. Limits of detection for these analyses were 2.35 ug for DNT and 1.15 ug for TDA.

A delay in the completion of the method in written form did not permit review of the method prior to initial field use. Modifications in the method were made to make the method compatible with field equipment limitations and survey team time constraints. At the request of the NIOSH method development project officer, an additional modification of the new method using the Tenax GC tubes alone was also used in obtaining additional area samples. These were taken at the same locations using the other methods.

All sampling media was obtained from the laboratory. It should be noted that the filters used with the Tenax GC® tubes for DNT and TDA in this evaluation were incorrectly assembled. A cellulose backup pad was used behind the teflon filter rather than the specified annulus or stainless steel screen, thus reacting with DNT and TDA vapors before they could be adsorbed on the sorbent tube.

Bulk samples of material obtained from the walls inside the TDA filter room were analyzed by gas chromatography/mass spectroscopy (GC/MS) to identify the black, tenacious material present on equipment and structural surfaces throughout Building 52. Portions of each bulk were put into methylene chloride. Both bulks were almost completely dissolved with this solvent. The bulk-methylene chloride solutions were initially screened by gas chromotography (equipped with a flame ionization detector) and later analyzed by GC/MS. A 25 meter methyl silicone fused silica capillary column was used for the GC/MS analyses.

B. Medical

1. Protocol

The follow-up medical study was performed in September 1981. The evaluations consisted of a detailed questionnaire eliciting work history (past and present); tobacco, alcohol and drug consumption as well as a medical history, illnesses and treatments which are known to effect the testicles including functional reproductive status. A physical examination consisting of blood pressure evaluation, determinations of pulse, respiration, assessments of cardiovascular and pulmonary status, and abdominal examination were obtained. A special emphasis was placed on the male reproductive system and secondary sex characteristics including body build, hair distribution, evidence of muscle atrophy, inspection of the external genitalia, palpation of scrotal contents and testicles as well as determination of testicular size. A rectal examination for prostatic size was also performed. Blood specimens were taken for analysis of blood urea nitrogen (BUN), creatinine, bilirubin, alkaline phosphatase, aspartate aminotransferase (AST, SGOT) and alanine amino transferase (ALT, SGPT). An additional aliquot of serum was frozen for later assays of testosterone, lutenizing hormone (LH), and follicle stimulating hormone (FSH). A semen specimen was obtained after a 48 hour sexual abstinence period, analyzed for ejaculate volume, sperm count, sperm motility and morphologic pattern. Urine was collected for routine dip stix® analysis.

In addition to these evaluations on the workers, a detailed reproductive questionnaire was administered to the workers' wives who chose to participate in this part of the study. This questionnaire was designed to validate the reproductive portion of the questionnaire administered to the males.

2. Classification of Study Groups

Employees were divided into three exposure categories. First was the exposed group who had current regular exposure in the TDA/DNT areas. The second group were those people with past exposures in the TDA/DNT areas, and maintenance workers who had intermittent exposures three months out of the year. The third group, a control population, consisted of workers who had never had exposure in the TDA/DNT areas and who's overall chemical exposures were minimal. The individuals were assigned to these categories based on comprehensive job histories provided by the company and a work history elicited from the workers themselves.

3. Guidelines for Exclusion From the Comparison Study

Prior to the analysis of the final results, a list of historical information, physical examination findings and other data potentially leading to exclusion from the study were compiled. This was to insure as much as possible that those workers included in the final analysis and comparison had no medical reasons for abnormal semen analysis other than those that might be related to occupational or environmental causes. A control population from the same plant was utilized to negate any socioeconomic or local environmental factors.

There are many factors which can cause an abnormality in semen quality other than environmental or occupational exposures. Radiation exposure, consumption of certain drugs, illnesses and other factors must be eliminated as potential causes for abnormalities by history and/or physical examination. Of the workers evaluated in this study, individuals were excluded because of a vasectomy, history of prostate surgery, hormonal therapy, fever greater than 102°F within three months of the study, shriveled or missing testicles on physical examination or infertility that predated employment. Workers were not excluded based on history of hernia, previous mumps (unless orchitis was involved), previous prostatitis, venereal disease or physical examination finding of hernia, hydrocele, or varicocele.

4. Analytical Methods

Blood specimens were centrifuged, separated and refrigerated. At the end of each day the specimens were packed with ice and sent to Smith Kline Clinical Laboratories in St. Louis, Missouri for the performance of the renal and liver function tests. Urinalysis was performed onsite using the Ames n-multistix® method. Semen specimens were obtained by masturbation into a 125cc clean polyethylene container with a sealing lid after a minimum of 48 hours sexual abstinence. The specimens were brought to the examination site within 60 minutes of production, observed for full liquafication, volume measured, and motility determined. Following this the specimens were frozen in a conventional freezer until time of transport. They were transported frozen on dry ice, and transferred to a freezer immediately upon return to the University of Cincinnati.

At the time of semen analysis the individual semen specimens (identified only by a study number) were allowed to thaw completely and were mixed well by drawing the specimen up and discharging into the storage container from a pasture pipet. Two dilutions were made using a 5% bicarbonate - 1% formaline solution in a white blood cell diluting pipet.[4] Each dilution was counted twice and the results of the four counts were averaged. In instances where a 20% discrepancy existed among the counts, repeat dilutions were made after remixing and additional counts obtained. If in using this method, a large discrepancy still existed, duplicate tubes of 0.25mg beta amylase in 0.01mL 2.3M $(NH_4)_2SO_4$ and 0.01mL semen were mixed and allowed to sit for 30-60 minutes at room temperature. This mixture was then further diluted 1:5, 1:10 or 1:25 with distilled H_2O and counted twice per dilution. Values for all counts were averaged. All the diluted semen specimens were counted using a Levy Hemocytometer chamber and after charging the chamber, a 5-10 minute interval was used to permit reduction in cell movement for a more accurate count. The final average count was logged on the master data sheet for final comparison.

At the same time the frozen specimens were thawed for counting, several slides were made by applying a drop of the well mixed, thawed specimen to a clean glass slide and a smear of the cells made and immediately fixed in a 50% ETOH, 50% ethyl ether fixative bath. After at least 1-2 hours of fixation in this solution specimens were rinsed in distilled H_2O and then manually taken through a multistep process using the Paponuolaou staining technique. On completion of the staining procedure the slide was then evaluated under oil immersion objective and 200 cells counted. Each cell was placed into one of eight morphological categories, i.e., oval, large, small, tapering, amorphous, duplicate heads, duplicate tails, or spermatids. The counts were averaged and a precentage figure of each cell type was recorded for final comparison by statistical analysis.

5. Statistical Methods

The three types of information collected in this study were analyzed by three different statistical methods. First, the sperm counts, ejaculate volumes and morphologic patterns were analyzed by performing an analysis of variance on this information. These data were analyzed using the original scale as well as square root transformation of the sperm counts and an arc sin square root transformation of the sperm counts [5], and an arc sine square root transformation on the proportional data. Mean values were computed with standard deviation median values, ranges and cumulative percent distribution recorded for each group. The cumulative frequency distribution data (sperm counts) were analyzed comparing the exposed, intermediate and control groups by the Kilmogrov Smirrov two sample test [6]. Secondly, the BUN and serum creatinine results as well as the total bilirubin, alkaline phosphatase, SGOT(AST) and SGPT(ALT) were compared using the group distribution previously described. The student T test was applied to these values. Third and finally, the spontaneous abortions, and reproductive histories, before, during, and after TDA/DNT employment at Allied were compared within each group. These results were compared using the chi square test and the Fishers exact test. Throughout all the statistical analysis, a p value of 0.05 was considered to be the level of statistical significance.

V. EVALUATION CRITERIA

A. Industrial Hygiene

1. Dinitrotoluene

An occupational exposure standard of 1.5 milligrams per cubic meter (mg/m^3) is the current value applied by the Occupational Safety and Health Administration (OSHA) over an eight hour work shift.[7] This is also the exposure limit recommended by the American Conference of Governmental Industrial Hygienists.[8] Both sources also indicate that potential contribution to the overall exposure also exists by the cutaneous route either through airborne or direct contact with DNT. The cutaneous route of exposure includes mucous membranes and the eyes.[8] Sufficient DNT may be absorbed through the skin to cause toxic effects. The exposure limit for DNT was determined by analogy with other aromatic nitro and amino compounds.[9] This value is applied to all the DNT isomers and no mention of carcinogenic potential is made.

2. Toluene Diamine

No occupational standard of TDA appears in the OSHA General Industry Standards, nor has any recommended exposure level to this compound been suggested by NIOSH or the ACGIH since the initial NIOSH HHE addressing the health effects of this compound. Additionally, no recommended exposure limits other than the one cited by V.S. Filatova et.al. of 2 mg/m^3 in a Russian article have been found.[10] No basis was given for this referenced value and no isomers were specified.

B. Toxicology

1. Dinitrotoluene

Dinitrotoluene absorption has been associated with anoxia due to the formation of methemoglobin. Jaundice and anemia have also been reported with chronic exposure.[11] An important characteristic of this compound is its ability to rapidly penetrate the intact skin.[12]

Recent animal studies have shown DNT to be a potent liver carcinogen in rats.[13,14] Hepatocellular dysplasia seen in some male mice may be a similar effect, however, this was not as dramatic or well ordered as in rats.[14] The target organ in mice appeared to be the kidney where a variety of unusual lesions were observed with the male mice developing cystic tumors in some cases.[14] Work addressing the potency and carcinogenicity of DNT in rats associated with the different isomers and pure versus technical grade DNT has also been done. One study has shown the 2,6-DNT isomer to have greater initiating activity in initiation - promotion systems being used to address the question of hepatocarcinogenicity.[15]

Males of all species had decreased spermatogenesis and in the most severe instances cessation of spermatogenesis ocurred along with testicular atrophy.[14,16] No evidence indicative of a dominant lethal effect resulting from DNT exposure has been produced.

2. Toluene diamine

The aromatic amines, including toluene diamine are synthesized by the nitration of the aromatic hydrocarbon with subsequent reduction to the amine. Fat soluble substances (materials soluble in common organic solvents such as alcohols, ether, or chloroform) including DNT and TDA are not only readily absorbed through the intact skin but are very quickly absorbed through the lungs into the blood, immediately becoming systemic in action.[12] Aromatic amine exposures may also result in the production of methemoglobin.

In addition to animal studies showing TDA to produce methemoglobin and liver damage, hepatocellular carcinomas have been produced in rats fed TDA in their diet. Toluenediamine has also been shown to be carcinogenic in mice.[17]

A study done by Soares and Locke with the 2,4- and 2,5-TDA isomers in mice for induction of a dominant lethal effect was negative. No morphologically abnormal sperm were noted in specimens collected from the first group of mice involved in the dominant lethal assay.[16]

Table I presents a summary of the physical properties of DNT and TDA.

VI. RESULTS

A. Industrial Hygiene

A total of 22 personal exposure samples for DNT and TDA along with 51 area samples were collected in Buildings 52 and 55. A new combination solid sorbent and filter method was used for all personal samples and in area samples immediately adjacent to the impinger methods used as a reference. Due to the laboratory's error (See Methods Section IV A2) all samples obtained with the new method tube/filter combination (40 of 71 samples) were determined to be invalid. Therefore, the remaining environmental data will address the area samples obtained with impinger and sorbent tube only sampling trains.

Area samples for DNT obtained in Building 55 had a maximum value of 890 ug/M^3 for the impinger method and 563 ug/M^3 for the Tenax GC® sorbent tube sample. Both samples were obtained on the DNT nitration bridge on the second floor of Building 55. The range of DNT concentrations for the area samples in Building 55 was 83 to 890 ug/M^3 (impinger method) and 157 to 563 ug/M^3 by the solid sorbent method.

TDA area samples in Building 52 had a maximum value of 687 ug/M^3 with the impinger samples and 494 ug/M^3 with the sorbent tubes. Values for TDA ranged from 34 to 687 ug/M^3 by the impinger method and from 47 to 494 ug/M^3 with the sorbent method for Building 52. DNT levels were documented in the TDA filter room. Tables II and III present the sampling results for DNT and TDA by area and day.

Two bulk samples of material coating the filter room walls of the TDA unit (Building 52) were collected and submitted to the lab for analysis by GC/MS. Only one large component was detected by GC in these samples. Comparison to a reference spectrum resulted in an identification of TDA in both bulks. The discoloration associated with this material is considered to be due to oxidation products since aromatic amines are very easily oxidized by air.[19] The significance of this is that the ubiquitous discoloration of surfaces, equipment, work clothes, and personal protective equipment associated with the TDA unit is indicative of contact with TDA vapor or its oxidation products.

B. Medical

Fifty male workers volunteered to participate in the study. Forty-one of these workers participated in the semen portion of the study. Nine chose not to submit semen specimens. Only one worker was excluded for medical reasons.

Workers who participated in the semen portion of the study were divided into exposed, intermediate and control groups (See Section IV B2 Classification of Study Groups). The exposed category consisted of 13 workers, the intermediate 19 workers and the control 8 workers.

Workers who participated in the non semen portion of the study (history, physical examination, blood and urine evaluation) numbered 50. Fifteen workers were in the exposed group, 23 in the intermediate and 12 in the control.

Table IV shows the demographic distribution of the groups in this study. Each group (exposed, intermediate and control) is further divided into group A or group B. All group A's participated in all aspects of the study except the semen portion. All group B's participated in the entire study including the semen portion.

Comparisons among the groups were made in three basic areas. First renal (BUN, Creatinine) and hepatic (bilirubin, alkaline phosphatase, aspartate aminotransferate, alanine aminotransferase) profiles were compared between and among the groups. Second, comparison of semen quality, including volume, sperm count and morphologic distribution were made between and among groups.

Third, data collected from the initial screening survey investigating spontaneous abortions, congenital birth defects and fertility rates were reexamined.

Table V shows the results of the renal and hepatic profiles from the exposed, intermediate and control groups. There were no statistically significant differences ($p<0.05$) between and among groups in any of the tests performed as a part of the renal and hapatic profiles.

Table VI shows the results of the ejaculate volume, sperm counts and morphologic patterns in the exposed, intermediate and control groups. The exposed group had an average sperm count of 126,000,000; the intermediate group - 143,000,000; and the control group - 146,000,000. There were no statistically significant differences between and among groups in any of the tests performed as a part of the semen analysis.

Figures II-IV show the cumulative percent distribution for sperm counts of the exposed, intermediate and control populations. These distributions when analyzed by the Kolmogorov-Smirnov two sample test showed no significant differences between the groups tested.

Table VII shows the reproductive outcome of pregnancies elicited on an earlier study (4) in wives of DNT and TDA employees at Allied Chemical Company compared with pregnancy outcome of workers when employed in non TDA DNT areas. These data show a statistically significant ($p<0.05$) increase in the spontaneous abortions in wives of men working in the TDA areas when compared with other areas of the plant.

VII. DISCUSSION

A. Industrial Hygiene

Area samples confirmed the presence of DNT and TDA in the production areas of Units 55 and 52 that were generally shown by previous company data (see Interim I) to have the highest levels. Specifically the area of highest DNT exposure is the bridge walkway located along the nitrators in Building 55.

In Building 52, TDA levels were the highest in the filter room with atmospheric levels increasing with higher floors. The identification of TDA in residues scraped from structural surfaces in the filter room as well as the ubiquitous discoloration of the unit with TDA indicates that the exposure by percutaneous absorption of TDA is likely in addition to the inhalation of vapors.

Note that except for the control rooms and during repairs, workers in Building 55 and 52 spend only a small fraction of their workshift in the areas sampled. Activities that would bring the workers into these areas are routine rounds, and collection of process samples for laboratory analysis.

Process sampling stations generally consisted of a tap from which samples were collected in bottles and excess product was accumulated in drums and buckets or permitted to run into floor drains.

Workers collecting samples are required to wear organic vapor-acid gas cartridge respirators and heavy polyvinyl chloride gloves. Additional personal protective equipment including goggles, face shields, raincoats, and impervious aprons, coveralls, and shoe covers are provided as needed to prevent contact during release of larger quantities of material.

Potential for exposure to TDA in areas outside of Building 52 should also be noted. Equipment that could not be repaired or cleaned on site would be moved to an adjacent building or the maintenance shop. Items to be removed are reportedly cleaned with a steam hose in the unit, however, internal cavities such as those in pumps potentially may contain residual material.

The incineration of byproducts from Building 52 (TDA) occurs in another area of the plant. Discoloration of the one unit used for this process suggests that TDA and its oxidation products may be present on surfaces in that area.

Identification of TDA unit workers' lockers was simplified in the locker rooms by the yellow-brown TDA stains around the doors and vents. The workers' shoes, hard hats and other work equipment are stored in a locker immediately adjacent to their clean lockers. These locker room and shower facilities serve workers from other plant areas as well.

The designation of required respirator areas in Building 55 and 52 was not always clear. In Building 55 the nitration bridge is an area requiring respiratory protection while an aisle across from the bridge and not structurally separated does not require respirators. Obliteration of signs in the TDA by the black TDA oxidation products was observed.

Correct use of respiratory protection by workers is not always observed. Some workers would lift their respirator away from their face to talk while in mandatory respiratory protection areas. The demonstration of DNT and TDA as animal carcinogens suggests that these substances may be potential occupational carcinogens. The use of half-mask air purifying respirators on a routine basis against exposures to potential occupational carcinogens does not provide the best protection. The upgrading of respiratory protection to an air supplied type may be necessary when exposures cannot be controlled satisfactorily by other means.

Areas where workers spend a large portion of their time, such as the TDA control room, are not maintained under positive air pressure relative to the surrounding process equipment areas. Maintaining the control room under positive pressure would provide air flow out of rather than into the control room.

B. Medical

The reproductive study conducted at Allied Chemical Company, Moundsville, West Virginia was performed as a result of an earlier study at another plant that showed apparent reduction of sperm counts in workers with exposure to TDA and DNT. The small number of workers involved in the study mentioned above necessitated additional investigations of these agents and their potential adverse effects on the male reproductive system.

For the present study, no significant differences in sperm counts and morphologies were found between the TDA exposed workers and workers employed in the rest of the plant including a non exposed control group. A reproductive questionnaire tracing reproductive histories of workers in the TDA area as well as those in other non TDA areas, did reveal a slightly reduced fertility rate in the TDA workers and showed a statistically significant ($p<0.05$) increase in the number of spontaneous abortions in wives of workers employed in the TDA area when compared with non TDA exposed workers in the plant. The results of the questionnaires administered to the wives of the workers substantiated the workers reproductive histories. The reproductive survey included pregnancy outcome during the entire history of operation of the Moundsville plant. However, several methodological problems make the interpretation of this difference difficult. The reproductive outcomes were not confirmed by medical records. Thus, there may have been selective reporting of miscarriages, etc., by the exposed group. Other factors affecting reproductive outcome (previous pregnancy history, alcohol use, cigarette smoking, etc.) were not controlled for. Differences between the groups in these factors could account for the reported reproductive problems.

VIII. CONCLUSIONS

Environmentally areas of potential DNT and TDA exposure were documented in Buildings 52 and 55. Personal exposure samples were not obtained because of laboratory error but observations of the work areas, process, and supporting plant areas suggested that potential percutaneous and inhalation exposures do exist. Recently increased efforts had been instituted to maintain and enforce a more comprehensive personal protective equipment program. Additionally, preparations were being initiated to upgrade the production equipment for more complete containment of the process and for the replacement of equipment and piping which required frequent maintenance. Procedures which required routine entry into the system (eg. more than once a week such as filter cleaning) were indicated as having a priority in system modification efforts. A consideration which must be addressed in efforts to control exposures and in environmental surveillance is that the demonstrated carcinogenic potential of both DNT and TDA necessitates controlling and maintaining exposure levels at the minimum level possible.

While there is evidence of decreased fertility rates and an increase in the number of spontaneous abortions in the TDA exposed workers compared with non TDA exposed workers from the same plant, there are no current biologic measurements collected in this study to serve as a substantiator of the historic data.

There are two plausible reasons for this difference. First, is that the reproductive data is inaccurate and no reproductive problems ever occurred and, therefore, no biologic changes would be expected. The second is that reproductive problems did exist at the plant in the past but recent changes in reducing worker exposure to TDA have caused whatever biologic changes that may have existed in the past to revert to normal.

IX. RECOMMENDATIONS

1. Renovation and replacement activities in the DNT and TDA units should include: efforts to control fugitive emissions from seals and fittings; process sampling assemblies which do not allow the discharge or collection of material in the production area; use of sealless pumps and valves; and enclosed drains. A recommended reference is the NIOSH Technical Report: Control of Emissions from Seals and Fittings in Chemical Process Industries, DHHS (NIOSH) publication no. 81-118.[20]

2. Equipment which will be removed from the unit to other areas for servicing should be free of residual product or if this is not possible, precautions to prevent worker exposure and environmental contamination must also be undertaken at the remote worksite.

3. The control rooms, being an area where workers spend a significant portion of the work shift, should be maintained under positive pressure relative to the production area to prevent the infiltration of chemical vapors from the process. Air intake for the control rooms should be located away from potential sources of contamination.

4. Monitoring of workers exposure levels in the DNT and TDA areas should be continued on a periodic basis. Personal and area

monitoring should be conducted subsequent to engineering modifications to evaluate their effectiveness. Additionally, workers encountering DNT and/or TDA byproducts, residues, or contaminated equipment in other areas of the plant in areas outside of Buildings 52 and 55 should be monitored for DNT and TDA exposures.

5. Production unit areas designated as requiring specific personal protective equipment should be clearly defined and signs or markers indicating these areas should be cleaned or replaced as needed.

6. Potential cross-contamination associated with a single locker room and adjacent "dirty" and "clean" lockers should be eliminated by providing change areas separated by showers for workers in the DNT and TDA areas. This area should be set up in a manner which prevents bypassing of the system by workers and prevents contamination of a workers street clothes by soiled work clothes.

7. Air supplied respirators are considered necessary when dealing with spills or system discharges, high exposure areas, decontamination procedures, or activities requiring workers to break into the system.

8. Continuing education programs for the workers should include informing them of the nature of the hazards associated with their work area, the control of these potential hazards, proper work practices, and the correct use of appropriate personal protective equipment.

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XII. DISTRIBUTION AND AVAILABILITY OF REPORT

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

1. Authorized Representative of Employees, Local 839, International Chemical Workers Union
2. Olin Chemical Company, Moundsville, W. VA.
3. International Chemical Workers Union
4. Allied Chemical Company
5. NIOSH, Region III
6. OSHA, Region III

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

TABLE I

Physical Properties of Dinitrotoluene and Toluene Diamine*

	DINITROTOLUENE	TOLUENE DIAMINE
Chemical Formula:	$C_7H_6N_2O_4$	$C_7H_{10}N_2$
Molecular weight:	182.15 grams/mole	122.19 grams/mole
Isomers:	2,3-Dinitrotoluene 2,4-Dinitrotoluene 2,5-Dinitrotoluene 2,6-Dinitrotoluene 3,4-Dinitrotoluene 3,5-Dinitrotoluene	Toluene-2,4-diamine Toluene-2,5-diamine Toluene-3,4-diamine
Melting point:	71°C	99°C
Boiling point:	300°C	292°C
Density:	1.3208	---
Vapor pressure:	1mmHg (20°C)	1mmHg (106.5°C)
Solubility:	water-insoluble alcohol-soluble ether-soluble acetone-very soluble benzene-soluble	water(hot)-very soluble alcohol-very soluble ether-very soluble acetone-unspecified benzene(hot)-very soluble
OSHA Standard:	1.5 mg/m^3 (skin)	None
Status:	2,4 isomer-NCI carcinogensis bioassay positive:rat	2,4 isomer-NCI carcinogenesis bioassay positive:mouse, rat 2,5 isomer-carcinogenic determination indefinite

* Properties given are for the respective 2,4-isomers.

Source: CRC Handbook of chemistry and physics.[18]

TABLE II

Dinitrotoluene and Toluene Diamine Area Sample Results by Day
Allied (Olin) Chemical Company
Moundsville, WV
HETA 81-295

September 16-17, 1981

SAMPLE DESCRIPTION*			RESULTS IN ug/m^3**			
DATE	LOCATION	SAMPLING TIME (min)	DINITROTOLUENE		TOLUENE DIAMINE	
			SORBENT METHOD	IMPINGER METHOD	SORBENT METHOD	IMPINGER METHOD
9/16	Bldg 55 DNT Control Rm.	515	--	110	--	--
9/16	Bldg 55 DNT Bridge, across from N-3 nitrator (double set)	494	157	160	N.D.	4
			229	--	N.D.	--
9/16	Bldg 55 DNT Bridge, across from N-7 nitrator	487	563	890	N.D.	--
9/16	Bldg 52 TDA Control Rm.	525	--	--	--	46
9/16	Bldg 52 TDA Filter Rm,Level 1 (double set)	488	N.D.	--	47	55
			N.D.	--	80	74
9/16	Bldg 52 TDA Filter Rm,Level 2	519	83	60	494	620
9/16	Bldg 52 TDA Filter Rm,Level 3	495	--	--	--	687
9/16	Bldg 52 TDA Rack, Level 1, between pumps for ADT 1 & 2	457	--	--	--	34
9/17	Bldg 55 DNT Bridge, across from N-3 nitrator	468	170	120	47	N.D.
9/17	Bldg 55 DNT Bridge, across from N-7 nitrator	472	234	83	N.D.	--
9/17	Bldg 52 TDA Filter Rm,Level 1	508	33	--	67	205
9/17	Bldg 52 TDA Filter Rm,Level 2	507	33	26	209	406
9/17	Bldg 52 TDA Filter Rm,Level 3	492	N.D.	--	330	1074***
9/17	Bldg 52 TDA Rack, Level 1,OT1	465	--	--	--	81
	Analytical Limits of Detection (ug per sample):		< 2.35	2	< 1.15	1
	OSHA Standard		1500		---	

* Sample durations indicated are an average for the total number of samples obtained at that location and day. All samples obtained during day shift. APT = agitated tank, OT = wash water tank.
** -- = no sample collected. N.D. = none detected.
*** Pump failure, value suspect. Flow rate at termination very low (approximately 0.5 Lpm).

TABLE III

Dinitrotoluene and Toluene Diamine Area Sample Results by Area
Allied (Olin) Chemical Company
Moundsville, WV
HETA 81-295

September 16-17, 1981

SAMPLE DESCRIPTION*			RESULTS IN ug/m3**			
DATE	LOCATION	SAMPLING TIME (min)	DINITROTOLUENE SORBENT METHOD	DINITROTOLUENE IMPINGER METHOD	TOLUENE DIAMINE SORBENT METHOD	TOLUENE DIAMINE IMPINGER METHOD
9/16	Bldg 55 DNT Control Rm.	515	--	110	--	--
9/16	Bldg 55 DNT Bridge, across	494	157	160	N.D.	4
	from N-3 nitrator (double set)		229	--	N.D.	--
9/17	Bldg 55 DNT Bridge, across from N-3 nitrator	468	170	120	47	N.D.
9/16	Bldg 55 DNT Bridge, across from N-7 nitrator	487	563	890	N.D.	--
9/17	Bldg 55 DNT Bridge, across from N-7 nitrator	472	234	83	N.D.	--
9/16	Bldg 52 TDA Control Rm.	525	--	--	--	46
9/16	Bldg 52 TDA Filter Rm,Level 1	488	N.D.	--	47	55
	(double set)		N.D.	--	80	74
9/17	Bldg 52 TDA Filter Rm,Level 1	508	33	--	67	205
9/16	Bldg 52 TDA Filter Rm,Level 2	519	83	60	494	620
9/17	Bldg 52 TDA Filter Rm,Level 2	507	33	26	209	406
9/16	Bldg 52 TDA Filter Rm,Level 3	495	--	--	--	687
9/17	Bldg 52 TDA Filter Rm,Level 3	492	N.D.	--	330	1074***
9/16	Bldg 52 TDA Rack, Level 1, between pumps for ADT 1 & 2	457	--	--	--	34
9/17	Bldg 52 TDA Rack, Level 1,OT1	465	--	--	--	81
	Analytical Limits of Detection (ug per sample):		< 2.35	2	< 1.15	1
	OSHA Standard		1500		---	

* Sample durations indicated are an average for the total number of samples obtained at that location and day. All samples obtained during day shift. APT = agitated tank, OT = wash water tank.
** -- = no sample collected. N.D. = none detected.
*** Pump failure, value suspect. Flow rate at termination very low (approximately 0.5 Lpm).

TABLE IV

Age, Years at Allied for Exposed, Intermediate and Control Groups

EXPOSED

	MEAN(years)	RANGE(years)	YEARS AT PLANT MEAN(years)	YEARS AT PLANT RANGE(years)
N=15 Group A All but semen portion	35.3	26-50	9.1	3-4
N=13 Group B Entire study	36	26-50	9.9	3.5-24

INTERMEDIATE

	MEAN(years)	RANGE(years)	YEARS AT PLANT MEAN(years)	YEARS AT PLANT RANGE(years)
N=23 Group A All but semen portion	39.2	26-63	14.5	3.5-26
N=19 Group B	41.1	24-63	16.1	3.5-26

CONTROL

	MEAN(years)	RANGE(years)	YEARS AT PLANT MEAN(years)	YEARS AT PLANT RANGE(years)
N=12 Group A All but semen portion	45.6	23-59	18.5	4-27.5
N=8 Group B Entire study	42	23-59	15.8	4-27

TABLE V

Mean and Standard Deviation Results from Exposed, Intermediate and Control Groups in Renal and Hepatic Profiles
Allied Chemical Co., Moundsville, WV

EXPOSED N=15

	BUN mg/DL	CREATININE mg/DL	ASPARTATE U/L AMINOTRANSFERASE	ALANINE U/L AMINOTRANSFERASE	TOTAL BILIRUBIN mg/DL	ALKALINE PHOS. U/L
Mean	15.7	1.2	34	21.8	.58	92
Std.Dev.	4.4	.14	28	9.5	.34	25.8

INTERMEDIATE N=23

	BUN mg/DL	CREATININE mg/DL	ASPARTATE U/L AMINOTRANSFERASE	ALANINE U/L AMINOTRANSFERASE	TOTAL BILIRUBIN mg/DL	ALKALINE PHOS. U/L
Mean	14.3	1.1	28.8	19	.54	88.7
Std.Dev.	4.0	.16	16.8	8.7	.32	21.2

CONTROL N=12

	BUN mg/DL	CREATININE mg/DL	ASPARTATE U/L AMINOTRANSFERASE	ALANINE U/L AMINOTRANSFERASE	TOTAL BILIRUBIN mg/DL	ALKALINE PHOS. U/L
Mean	15.3	1.1	26.5	19.0	.46	87.9
Std.Dev.	2.9	.15	10.2	4.7	.12	22.2

TABLE VI

Semen Volume, Sperm Count and Morphologic Distribution
of the Exposed, Intermediate and Control Groups
Allied Chemical Co., Moundsville, WV

EXPOSED N=13

			MORPHOLOGY							
	SPERM COUNTS $x10^6$	SEMEN VOL.cc	OVAL	LARGE	SMALL	TAPER	AMORPH	DUP HEADS	DUP TAILS	SPERMA-TIDS
Mean	126	3.2	48	1.4	18.7	.7	30	.54	.08	.23
Std.Dev.	96	1.4	11	1.6	9.9	.8	11.7	.66	.28	.83
Median	92									

INTERMEDIATE N=19

			MORPHOLOGY							
	SPERM COUNTS $x10^6$	SEMEN VOL.cc	OVAL	LARGE	SMALL	TAPER	AMORPH	DUP HEADS	DUP TAILS	SPERMA-TIDS
Mean	143	3.0	41.6	1.5	22.4	.94	32.7	.63	.05	.16
Std.Dev.	123	1.3	15	1.5	12	1.4	10.6	.89	.23	.50
Median	88									

CONTROL

			MORPHOLOGY							
	SPERM COUNTS $x10^6$	SEMEN VOL.cc	OVAL	LARGE	SMALL	TAPER	AMORPH	DUP HEADS	DUP TAILS	SPERMA-TIDS
Mean	146	3.5	48	1.2	26	.05	23	.25	.05	0
Std.Dev.	155	1.4	8.9	1.2	6.5	.05	8	.46	.05	0

TABLE VII

Reproductive Outcome in Current Allied Chemical Company Workers after Employment at Allied in DNT TDA and Non DNT/TDA Areas

AREA	REPORTED LIVE BIRTHS	REPORTED MISCARRIAGES	MISCARRIAGE / LIVE BIRTHS
TDA	9	6	66.6%
DNT	7	1	14.2%
Non TDA/DNT	38	3	7.9%

AREA	PERSON YEARS EXPOSURE TO PREGNANCY	LIVE BIRTHS / 100 PERSON YEARS	MISCARRIAGE / 100 PERSON YEARS
TDA	102	8.8	5.888
DNT	66	10.6	1.51
Non TDA/DNT	345	11.0	.87

TOLUENE DIISOCYANATE MANUFACTURE (TDI)

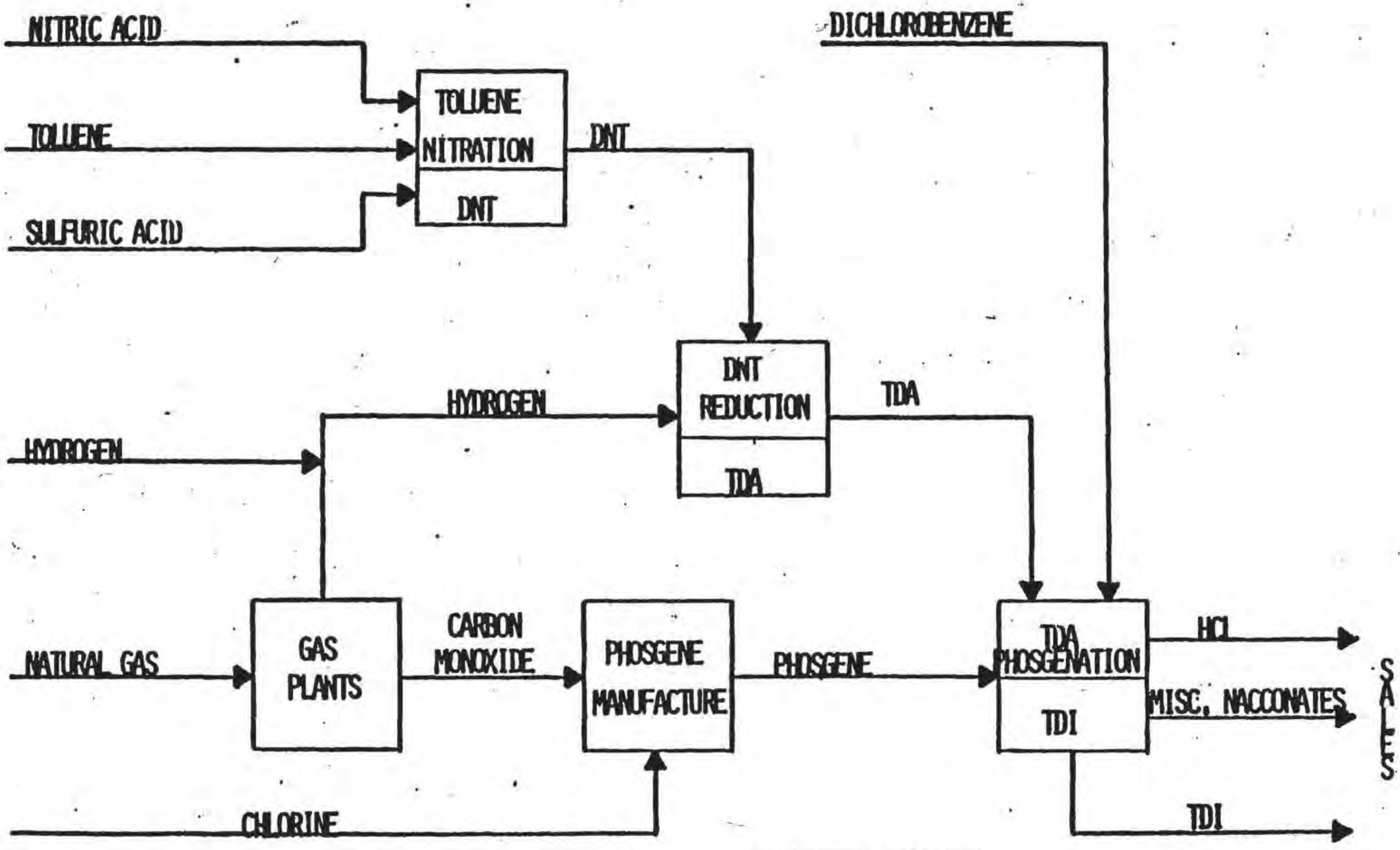


FIGURE 1
Material Flow

FIGURE 2

EXPOSED GROUP
HETA 81-295
ALLIED CHEMICAL CO
MOUNDSVILLE W. VA.

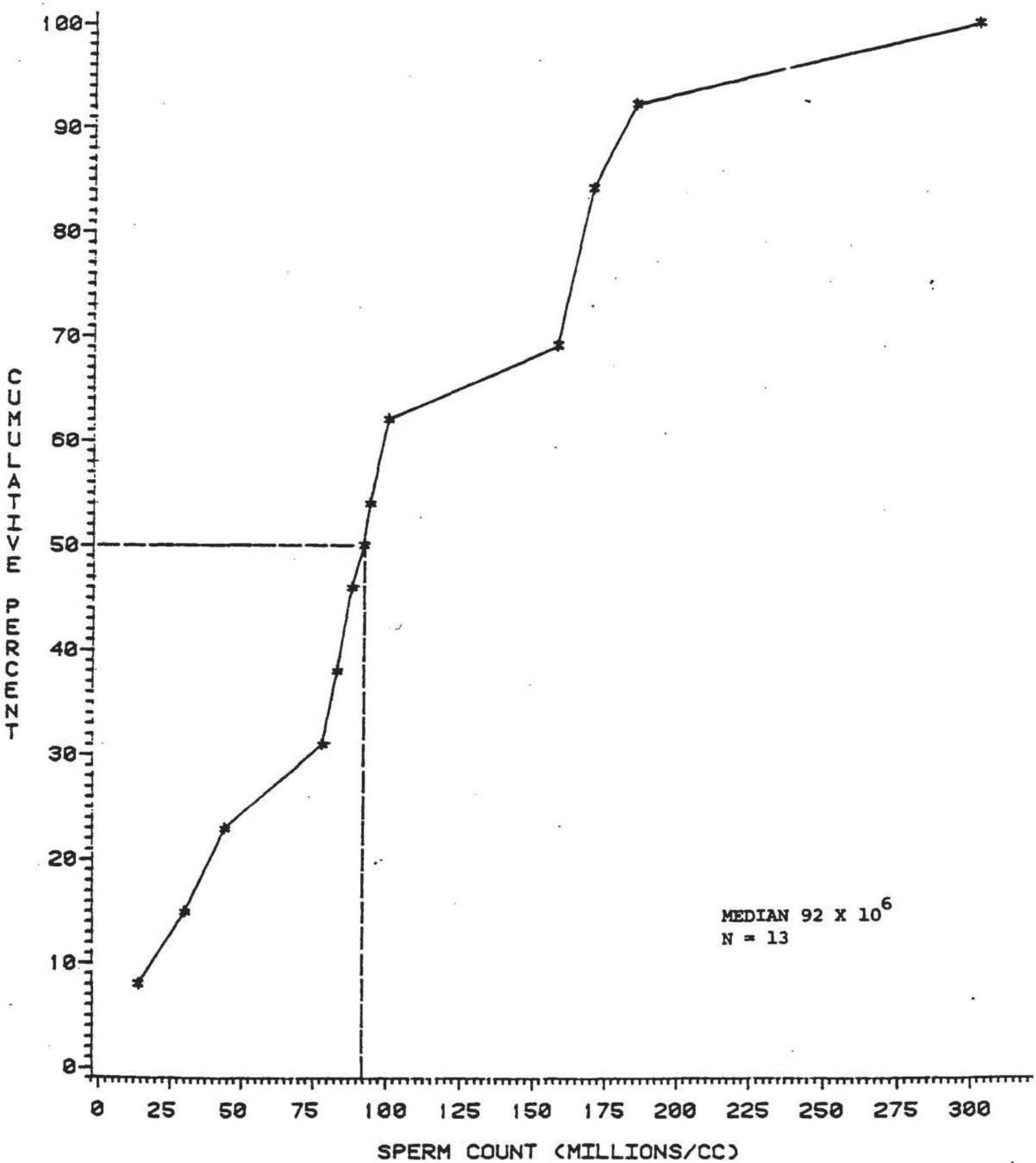


FIGURE 3

INTERMEDIATE GROUP
HETA 81-295
ALLIED CHEMICAL CO
MOUNDSVILLE W. VA.

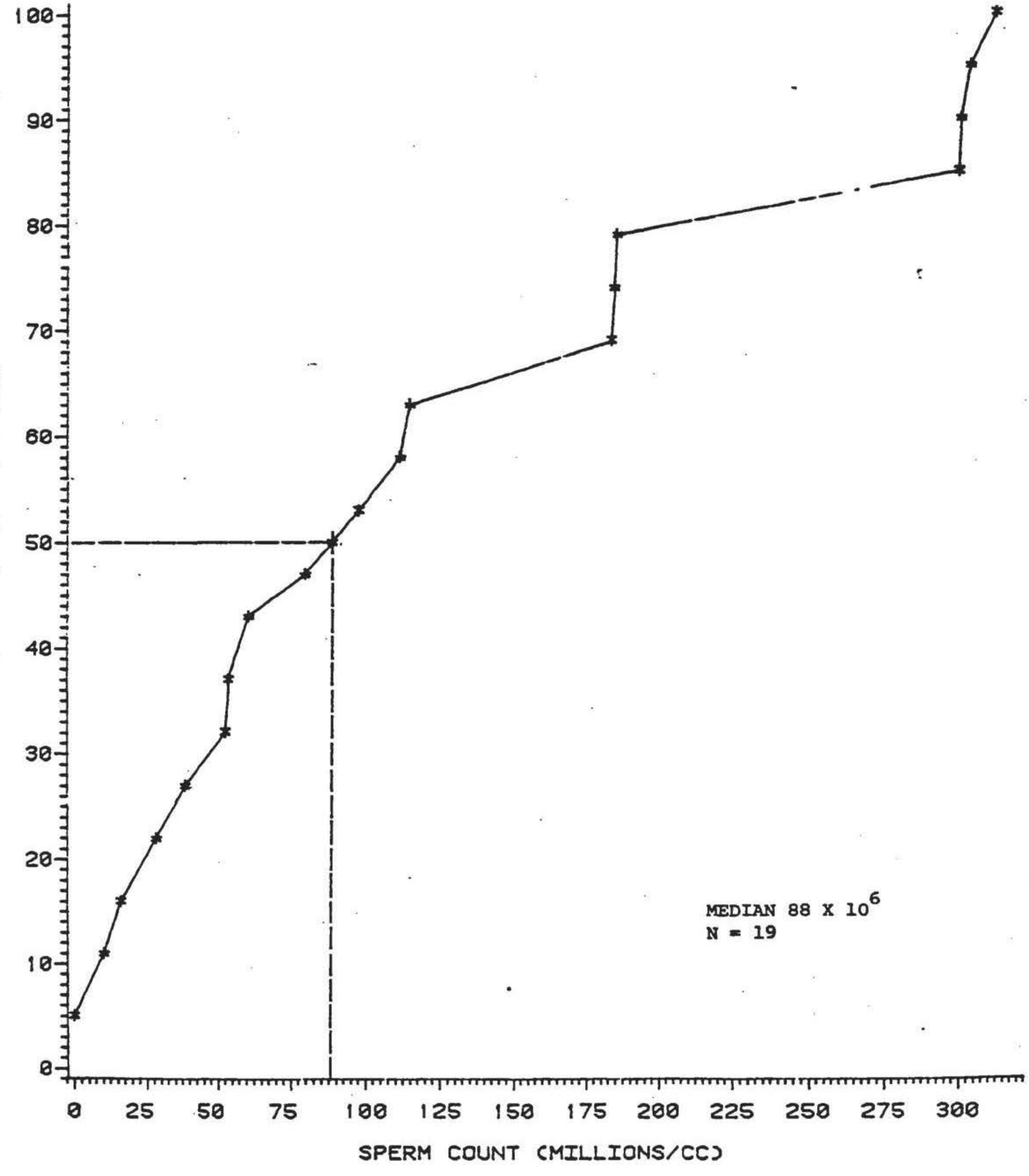
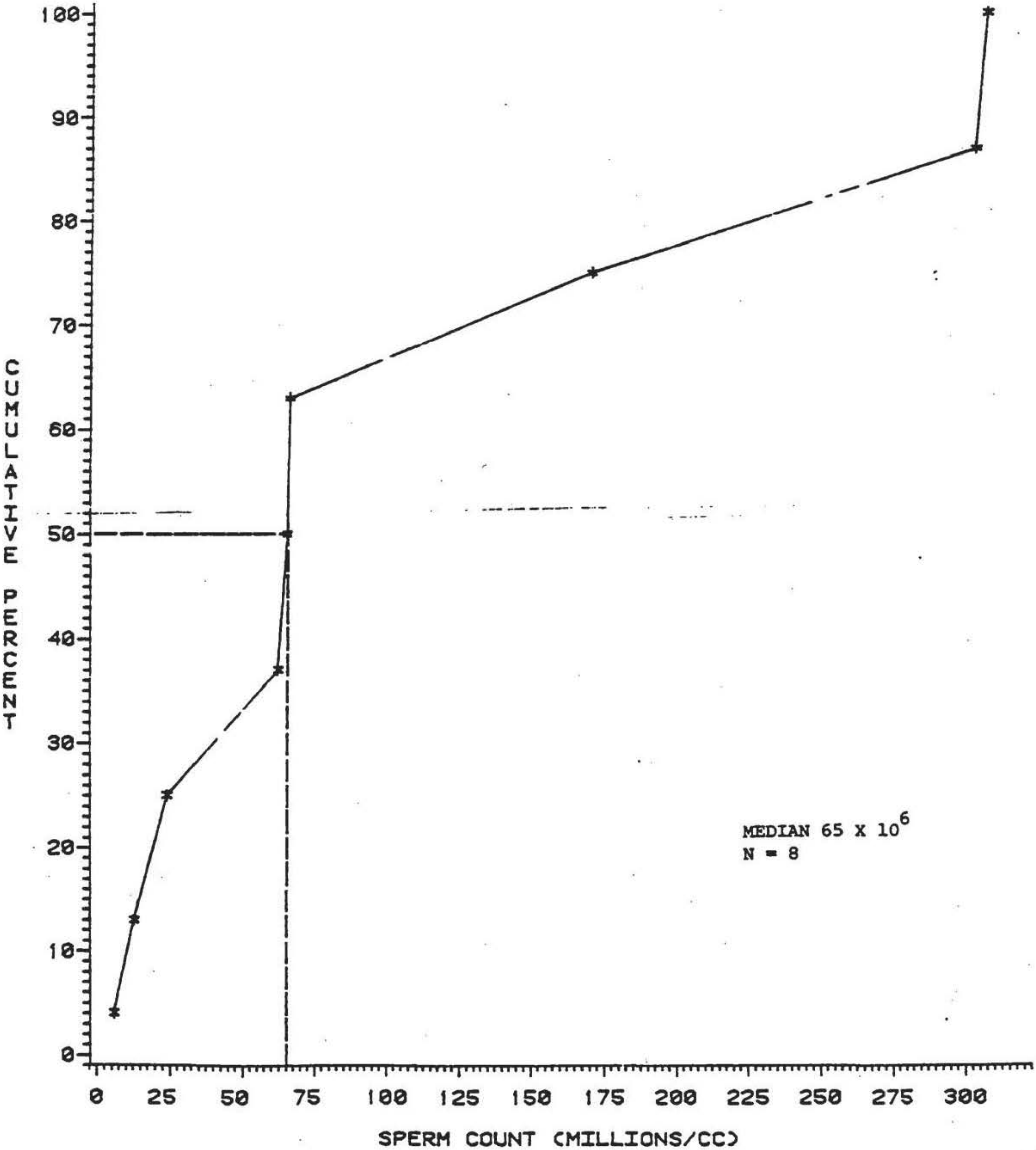


FIGURE 4

CONTROL GROUP
HETA 81-295
ALLIED CHEMICAL CO
MOUNDSVILLE W. VA.



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