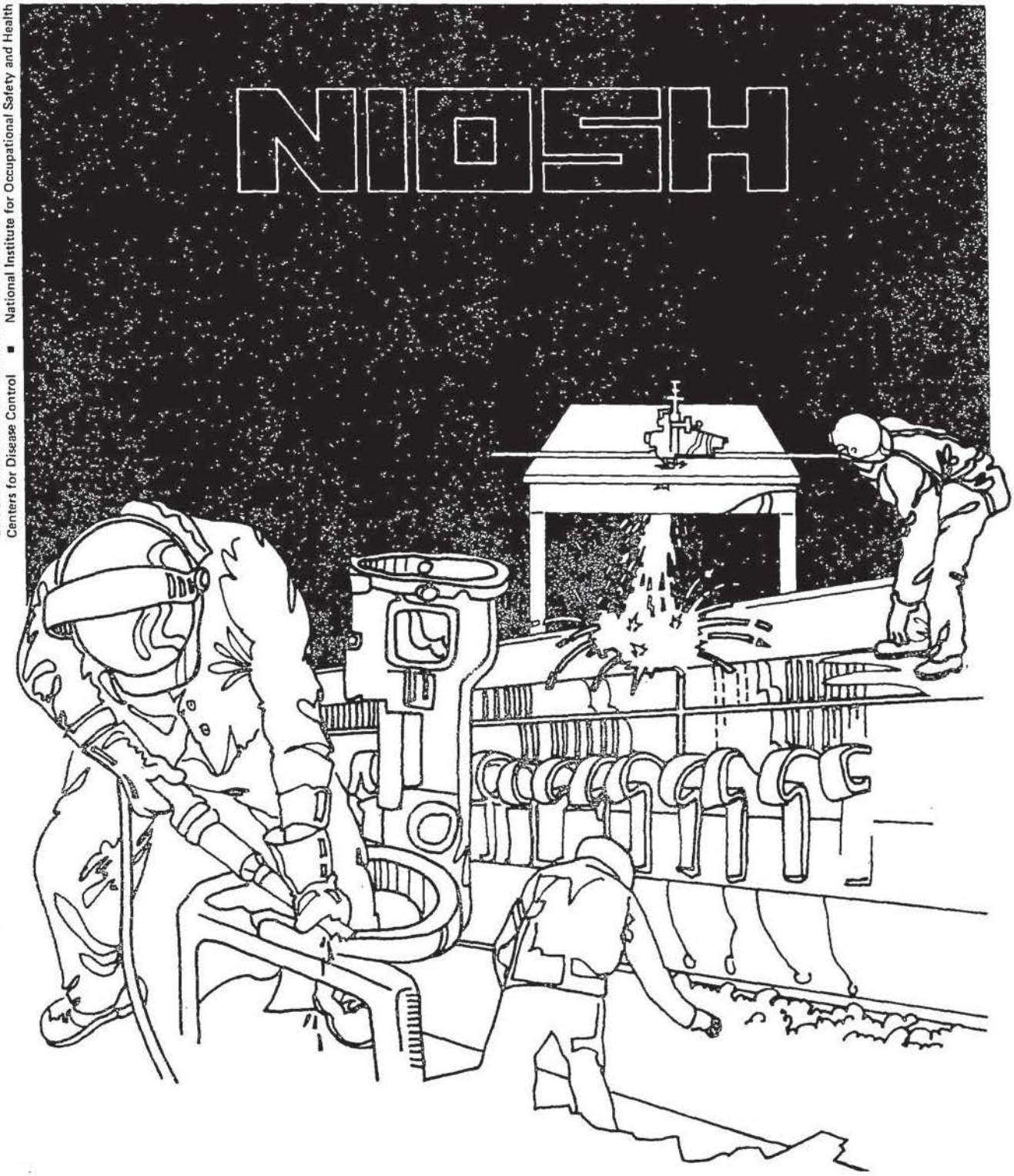
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health



Health Hazard Evaluation Report

HHE 79-140-1038
ARMAK, INC.
McCOOK, ILLINOIS

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.

HHE 79-140-1038
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Armak, Inc.
McCook, Illinois

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I. SUMMARY

In August 1979 the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union for a health hazard evaluation at the Armak Company plant in McCook, Illinois. The request, which noted exposure to acrylonitrile, inorganic nickel, and nitrosamines, inquired whether employees in the stills, batch hydro, or etho areas of the plant had suffered an excessive number of deaths due to heart disease or cancer. The McCook plant manufactures aliphatic amines and amine derivatives and employs 200 workers.

Environmental evaluation included review of an extensive OSHA survey conducted from June to October 1978, which included the areas and exposures mentioned in the request. On June 3, 1981 NIOSH conducted air sampling for nitrosamines at an Armak Plant in Morris, Illinois (the amine process was relocated from the McCook plant to the Morris plant in early 1981). OSHA obtained at least 12 acrylonitrile, 12 nickel, and in excess of 75 amine/nitrosamine air samples. No detectable levels were found. Sampling and analytical methods used were consistent with NIOSH methods except for nitrosamines, for which a new, more sensitive method (sample by Thermo Sorb tube, analysis by Thermal Energy Analysis (TEA)) has been developed. Using the new method, NIOSH obtained three area and one personal sample at the Morris plant in June 1981 and analyzed them for seven nitrosamines. Samples were negative at detection levels of 40 nanograms per cubic meter (adjusted for sample volume). Two nitrosamine surveys done by Armak at the Morris plant (1 prior to and 1 during the NIOSH survey) were also negative using the TEA method.

To determine if there had been excess mortality at the McCook facility, an attempt was made to determine the vital status of all persons who worked there from 1949 through 1969. In this way 23 deaths were identified, for which 18 death certificates were obtained. Five of these certificates indicated death due to a cancer, while another 5 indicated death due to heart disease. Comparison of the 14 white male deaths to the United States white male population revealed no excess for either cause of death.

NIOSH found no statistical evidence for increased mortality at the McCook plant due to either cancer or heart disease. However, serious limitations in the data, including few deaths and incompleteness of personnel records, preclude any definitive conclusions. No detectable concentrations of nitrosamines were found at the Morris plant on the day of the survey.

KEYWORDS: SIC 2869 (Manufacture of Amines) - Nickel, acrylonitrile, nitrosamines, amines, mortality, cancer, heart disease.

II. INTRODUCTION

In August 1979 the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union for a health hazard evaluation at the Armak Company plant in McCook, Illinois. The request, which noted exposure to acrylonitrile, inorganic nickel, and nitrosamines, inquired whether employees in the stills, batch hydro, or etho areas of the plant had been suffering an excessive number of deaths due to heart disease or cancer.

An initial walk-through was performed on October 1-2, 1979. Later visits were made on November 19, 1979, during which personnel records were microfilmed for use in a mortality study, and October 23-24, 1979, when further walk-throughs and interviews were performed. Because the process (batch hydro) most likely to produce nitrosamines was relocated in early 1981 from the McCook plant to the Armak plant in Morris, Illinois, sampling for nitrosamines was performed at the Morris plant on June 3, 1981.

Management and union officials were kept informed during the course of the lengthy mortality study by interim reports and letters, as follows:

1. Interim Report #1, November 1979 - reported on the initial visit of October 1, 1979, discussed future actions and presented several recommendations that would improve working conditions and further minimize exposures.

2. Letter, March 14, 1980 - discussed the microfilming of personnel records and requested further information on some former employees.

3. Letter, July 7, 1980 - a status report.

4. Letter, November 1980 - a status report and a request for information on some former employees.

5. Letter, December 1980 - a request for information on some former employees.

6. Letter, September 1981 - reported results of environmental testing at the Morris plant.

III. BACKGROUND

The Armak plant at McCook, Illinois, which was originally owned by Armour Industrial Chemical Company, opened in 1949. In 1971 Akzona Incorporated of Asheville, North Carolina acquired the plant and continued the manufacture of aliphatic amines and amine derivatives using "coco", "talo", or "soya" fractions as the basic raw material. Of the 200 workers who operate three shifts per day, approximately 65 (32%) were assigned to the batch hydro, stills, and etho areas at the time of the request.

Intermediate and finished products are manufactured in closed system reaction vessels. The potential for exposure to one or more of the chemical ingredients or products is greatest during the beginning and end of a production run, when employees introduce chemicals to reactors, change and blow out chemical lines, and clean filter systems. Unless valves or gaskets are leaking, there should not be significant exposure to chemical vapors during the reaction time.

IV. EVALUATION CRITERIA

A. Nickel

Nickel is an irritant of the eyes and upper respiratory tract. It is a skin sensitizer, sometimes producing a chronic eczema.(1) Nickel has induced tumors in laboratory animals. Furthermore, workers who were involved in the refining of nickel before 1924 have developed an excessive number of cancers of the lung and nasal passages.(2) While improvements in the refining process have removed this excess mortality, nickel should be considered a human carcinogen. The threshold limit value (TLV) of the American Council of Governmental Industrial Hygienists (ACGIH) is 0.1 mg/m^3 for nickel. The NIOSH recommended standard is 0.015 mg/m^3.

B. Acrylonitrile

Acrylonitrile is an irritant of the eyes and of the skin, causing blistering after long contact. It can also cause nausea, vomiting, headache, and light-headedness.(3) Acrylonitrile has been shown to cause a variety of cancers in rats. In addition epidemiologic studies done by E. I. duPont de Nemours and Company have suggested an excess risk of lung and colon cancer among exposed workers.(4) The TLV for acrylonitrile is 20 parts per million (ppm); the OSHA standard is 2 ppm, which was established when its carcinogenic potential was discovered. The NIOSH recommended standard is 4 ppm.

C. Nitrosamines

While nitrosamines are not directly used in any process at Armak, it is known that the reaction of nitrite with secondary amines can produce nitrosamines.(5,6) Thus, since amines are generally present in several processes at Armak, it is possible that nitrosamines are produced at the plant as a result of the reaction of amines with nitrites present in air.

The significance of this possibility is that a large number of N-nitroso compounds have been found to be carcinogenic in animals. Some of these are very potent, causing tumors in many different species. While there is no proof that these compounds are human carcinogens, their potency in a variety of species makes this very likely.(7) There are currently no standards for air levels of nitrosamines, although OSHA regulates the handling of liquids or solids containing more than 1% of N-nitrosodimethylamine (NDMA) by weight or volume. However, NIOSH recommends that occupational exposure to carcinogens be as low as possible.

V. METHODS

A. Environmental

1. McCook, Illinois plant

Since an extensive environmental survey was conducted by the Calumet City OSHA office from June to October 1978 in the areas mentioned in the request, additional sampling was not performed by NIOSH, with the exception of nitrosamines. Through the coordination of the NIOSH region V office, the OSHA file on this plant was reviewed at the Calumet City OSHA office. Sampling and analytical methods (except for nitrosamines) were consistent with NIOSH methods.

2. Morris, Illinois plant

The air sampling for nitrosamines conducted by OSHA at the McCook plant from June through October 1978 was felt to be obsolete since a newer, more sensitive method had since been developed.(8) After a period of field testing, arrangements were made to use the new method to determine if there were exposure to airborne nitrosamines from nitrosation of fugitive amine vapors. In early 1981, however, the process most likely to generate amines (batch hydro) was relocated to the Armak plant in Morris, Illinois.

On June 3, 1981, four samples (three area and one personal breathing zone) were collected at the Morris plant on Thermo Sorb/N tubes at a sampling rate of 1 liter per minute. Analysis was performed by the OSHA Analytical Laboratory in Salt Lake City, Utah. Each sampling tube was desorbed with a dichloromethane/methanol solution and analyzed by gas chromatography (GC) and high-pressure-liquid-chromatography (HPLC) with thermal-energy-analyzer (TEA) detection.

B. Medical

The request asked if Armak employees had experienced excess mortality from cancer or heart disease. To determine this, the personnel records at the McCook plant, which included hourly employees employed since the plant opened in 1949, were microfilmed. Individuals who worked for less than one year were excluded, as were individuals who began employment after December 31, 1969. Thus, we did not include those persons with exposures so brief or so recent as to make it unlikely that employment at Armak was a factor in the eventual development of cancer or heart disease.

In this way, we identified a total of 228 past and present employees. A list of these individuals was submitted to the Social Security Administration for comparison against their files of known living and dead individuals. For those persons whose vital status was not known to the Social Security Administration, vital status was sought by verifying addresses through the the U. S. Postal Service. For those employees found to have died, death certificates were then sought from the state where the death occurred. A total of 23 deaths were identified. We were successful in obtaining death certificates for 18 of these deaths. Of these 18, 14 were white males and 4 were black males. The death certificates were coded by a qualified nosologist using the revision of the International Classification of Diseases (ICD) in effect at the time of death.

The proportion of deaths due to cancer and heart disease for a "normal" comparison population, the U. S. white male population, was determined. After appropriate adjustments were made for age and calendar time period, we calculated the number of deaths from cancer and heart disease that would have been expected for the group of 14 Armak deaths had they occurred at the same rate as for the U. S. white male population. Finally, we compared this number of expected deaths to the number that had actually occurred. No attempt was made to evaluate the 4 black male deaths statistically, since this number is so small.

VI. RESULTS

A. Environmental

1. McCook plant

In the areas mentioned in the request (batch hydro, stills, and etho), OSHA collected at least 12 acrylonitrile, 12 nickel, and more than 25 amine/nitrosamine air samples. No detectable levels were found. However, the sampling method used for nitrosamines (silica gel tube) is no longer recommended by NIOSH, since a more sensitive method is now available. Therefore, the OSHA results are considered inconclusive.

The OSHA file and NIOSH interviews revealed that there may have been, in previous years, significant exposure to nickel dust in the batch hydro area. OSHA swipe testing of various sufaces in the area showed significant contamination (swipe samples ranged from 0-45 mg of nickel). However, no airborne environmental exposure data was available from before 1975 when a dust form of the nickel catalyst was most often used. The nickel catalyst used since 1975 is in the form of a "nickel mud" (under water) and does not generate an airborne dust.

The following areas and operations were of concern to those employees interviewed as occasional sources of irritating vapors. On some occasions the employees reported having to leave these areas for fresh air. (This information was included in the Interim Report #1, forwarded in November 1979.)

Hydro area	filter press clearing operation charge tanks third floor, especially when lines are blown out pumper tasks disconnecting and cleanout of pumping lines
Etho area	filling of scale tanks drum filling operations
Stills area	pump room ground floor disconnecting and cleaning of pump lines

2. Morris plant

The production processes are essentially the same at the Morris plant as at the McCook plant. However, the Morris plant is newer and more automated; therefore, exposures may not be truly representative of the McCook operation. On the day of sampling, secondary and tertiary amines were being produced in all four reaction vessels. Except for an initial stage where chemicals can be added to the reactors and a final stage where the product is filtered, the amine operation is outdoors. One outside operator and one boardman (at the control panel inside) take care of a set of reaction vessels each shift.

Results of the nitrosamine sampling are presented in Table 1. Three area and one personal breathing zone samples were obtained. Two of the area samples were positioned where there was the highest potential for exposure. One was at the sample drawoff point, second level, between reactors 1 and 2, and the other was in the filter room. The third area sampler was attached to the perimeter fence upwind of the reactors so that if positive results were obtained in the other samples the contribution, if any, from ambient levels could be determined. The one personal sampler was attached near the breathing zone of the outside operator.

Each sample was analyzed for the following nitrosamines:

N-nitrosodimethylamine (NDMA)
N-nitrosodiethylamine (NDEA)
N-nitrosodipropylamine (NDPA)
N-nitrosodibutylamine (NDBA)
N-nitrosopiperidine (NPIP)
N-nitrosopyrrolidine (NPYR)
N-nitrosomorpholine (NMOR)

The lower limit of detection was 0.01 micrograms (ug) per sample. Considering a sampling volume of approximately 0.25 cubic meter (m^3) the sampling and analytical method was capable of detecting any of the seven nitrosamines at ≥ 0.04 ug/m^3.

No detectable levels of nitrosamines were found except for a trace of NDEA, which was attributed to a positive blank. Analysis of a blank Thermo Sorb/N tube detected 0.01 ug of NDEA. This amount was found on each of the samples, including two that NIOSH had provided to Armak and which Armak used at the same time as NIOSH.

These negative findings were supported by a previous survey by Armak on May 19, 1981 (using the TEA method), in which 6 samples were obtained. No detectable levels of nitrosamines were found.

B. Medical

Table 2 lists the age at death, race, sex, underlying cause of death, and latency (number of years between first employment and death) for the 18 deaths for which we have death certificates. The union had developed a list of employees whom they recalled as having died. There were on this list 19 employees who would, according to information provided by the union, have met the criteria for inclusion in our study but whom we did not find in the personnel records. A further search by the company located only 3 of these 19.

Among the 18 deaths for whom death certificates were found, 14 were white males. Among a comparable group of white males in the general population, about 3 deaths from malignant neoplasms would have been expected - 4 were observed. However, this difference is not statistically significant, that is, it may well have occurred by chance. About 5 deaths from arteriosclerotic heart disease would have been expected - 5 were observed.

VII. DISCUSSION

The above analysis of deaths should be viewed circumspectly, since it is not possible to perform a reliable statistical analysis on such a small number of deaths from relatively common causes. Only if a very large excess of deaths for a particular cause of death had occurred, would we have been able to find it. It is also apparent that the records that we microfilmed were incomplete. This makes the data, which is based on those records, also incomplete. While we have no reason to believe that workers were deleted from the files in any systematic way, the absence of these records makes the data difficult to interpret.

Hence, we were unable to determine whether an excessive number of deaths due to cancer or heart disease has occurred at the McCook plant. Unfortunately, even in the most favorable situations it is often difficult to establish a relationship between a particular exposure and a particular cancer. This is especially true when, as in the present situation, the number of workers involved is relatively small. This should certainly not be interpreted as a demonstration that no risk of cancer is present. Such risk is always present where carcinogens are in use.

Environmental data collected during this phase of our health hazard evaluation indicate that there is not a significant health risk from exposure to nitrosamines at the Morris facility under normal operating conditions. As stated above, we cannot be sure that this exposure data is truly representative of the McCook operation. Furthermore, the exposures of greatest relevance to this study would be those that occurred during 1949-1969. It should be noted that we do not know how high exposures were during that period.

VIII. RECOMMENDATIONS

Since there is potential for leaks as equipment wears, it is recommended that nitrosamine sampling be repeated at least every six months.

Union and management should continue to keep track of deaths that occur among present and past employees. The occurrence of several cases of a particular type of cancer would require further investigation.

IX. REFERENCES

1.) Proctor NH and Hughes J. Chemical Hazards in the Workplace. Philadelphia: Lippincott, 1978.

2.) Doll R, Morgan LG, and Speizer FE. Cancers of the Lung and Nasal Sinuses in Nickel Workers. British Journal of Cancer. 24(4): 623-632, 1970.

3.) NIOSH. Occupational Diseases: A guide to Their Recognition. June 1977.

4.) NIOSH. Acrylonitrile. Current Intelligence Bulletin (Number 18). July 1, 1977.

5.) Mirish, S. Formation of N-Nitroso Compounds: Chemistry, Kinetics, and in Vivo Occurrence. Toxicology and Applied Pharmacology. 31, 325-351, 1975.

6.) Lijinsky, W and Epstein, SS. Nitrosamines as Environmental Carcinogens. Nature. 225: 21-23, 1970.

7.) Doull, J et al. Casarett and Doull's Toxicology. New York: Macmillan, 1980.

8.) Fine DH, Rufeh F, Lieb D, and Roundbehler DP. Description of the Thermal Energy Analyzer (TEA) for Trace Determination of Volatile and Nonvolatile N-nitroso Compounds. Analytical Chemistry. 47 (7), June 1978.

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

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XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

For the purpose of informing the "affected employees" the employer should post this report for at least 30 days in a prominent place near where employees work.

Copies of this report will be available from NIOSH, Division of Standards Development and Technology Transfer, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226 for 90 days. Thereafter, copies will be available from the National Technical Information Service (NTIS), Springfield, Virginia. Information concerning its availability through NTIS can be obtained from the NIOSH Publications Office at the above Cincinnati address.

External Distribution:

International Chemical Workers Union (ICWU)
ICWU, Local 524
Armak, Inc.
NIOSH - Region V
Department of Labor (OSHA) - Region V

Table 1

Nitrosamine Results
Armak, Inc.
Morris, Illinois
June 3, 1981

Location Job	Sample Type	Sampling Period	Sampling Volume (liters)	Nitrosamines[1] (ug/m^3)
Outside Operator (Old Reactor)	BZ[2]	1420-1820	228	N.D.[3]
Filter Room	A[2]	1423-1826	231	N.D.
Second Level (Between reacors 1 and 2)	A	1432-1830	230	N.D.
Upwind, perimeter fence	A	1440-1833	224	N.D.
Blank	-	-	-	0.01 NDEA

[1]Each sample was analyzed for the following 7 nitrosamines:

N-nitrosodimethylamine (NDMA)
N-nitrosodiethylamine (NDEA)
N-nitrosodipropylamine (NDPA)
N-nitrosodibutylamine (NDBA)
N-nitrosopiperidine (NPIP)
N-nitrosopyrrolidine (NPYR)
N-nitrosomorpholine (NMOR)

[2]BZ - breathing zone; A - area

[3]N.D. - not detected. The limit of detection was 0.01 ug/sample for each nitrosamine (0.04 ug/m^3, adjusted for sample volume). Results were corrected for the trace of NDEA found in the blank.

Table 2

Summary of death certificates
1949-1969
Armak, Inc.

	Race	Sex	Age at death (years)	Latency[1] (years)	Underlying causes of death
1.	Black	Male	54	12	Fatty metamorphosis of the liver
2.	White	Male	52	10	Arteriosclerotic cardiovascular disease
3.	White	Male	52	6	Chronic Alcoholism
4.	White	Male	64	15	Lymphoma
5.	White	Male	51	27	Hypertensive arteriosclerotic heart disease
6.	White	Male	42	10	Coronary insufficiency
7.	White	Male	61	24	Arteriosclerotic heart disease
8.	White	Male	65	23	Hodgkin's Disease
9.	Black	Male	43	12	Homicide
10.	White	Male	31	9	Traumatic injury
11.	Black	Male	64	18	Carcinoma of prostate
12.	White	Male	55	6	Carbon monoxide intoxication
13.	White	Male	32	11	Carbon monoxide intoxication
14.	White	Male	57	28	Arteriosclerotic cardiovascular disease
15.	White	Male	40	11	Electrocution
16.	White	Male	52	19	Carcinoma of stomach
17.	Black	Male	76	25	Bronchogenic carcinoma
18.	White	Male	52	18	Bronchogenic carcinoma

[1]Number of years from date of first employment to death.