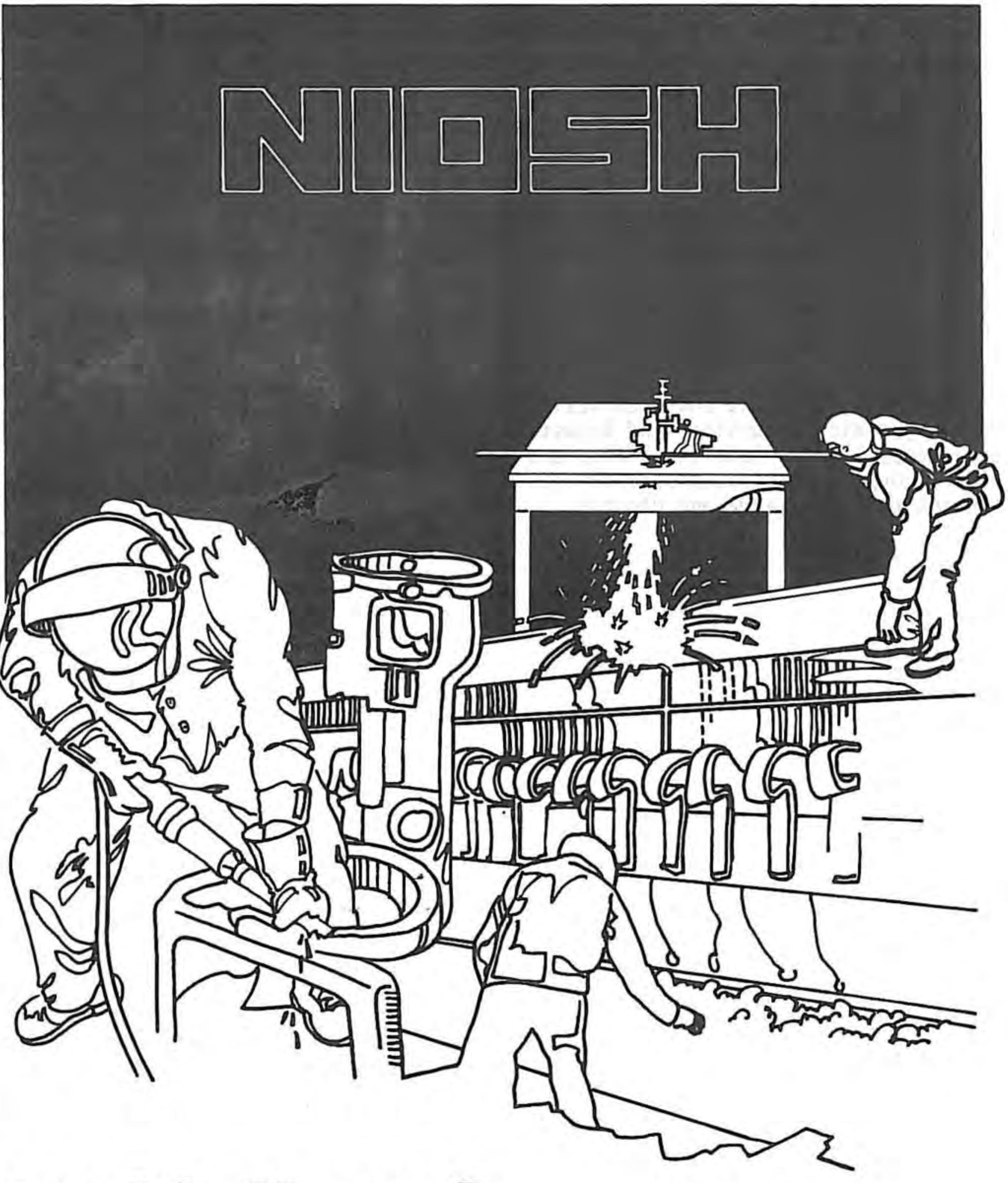
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health



Health Hazard Evaluation Report

HHE 79-126-951
ST. CLAIR RUBBER COMPANY
MARYSVILLE, MICHIGAN

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.

HE 79-126-951
September 1981
St. Clair Rubber Company
Marysville, Michigan

NIOSH INVESTIGATORS:
William Daniels, IH
Shawn McQuilkin, IH

I. SUMMARY

In July 1979, the National Institute for Occupational Safety and Health (NIOSH) received a request from the United Rubber Workers, Local 47, for a health hazard evaluation at the St. Clair Rubber Company, Marysville, Michigan. The requestor was concerned about possible health hazards resulting from exposure to N-nitrosamines and other substances contained in rubber press emissions.

NIOSH investigators conducted an initial survey in November 1979, and a follow-up environmental survey in June 1980. Area and personal samples were collected to determine exposure to N-nitrosamines, oxides of nitrogen, carbon disulfide, styrene, isopropyl alcohol, and other volatile organic compounds identifiable by gas chromatography/mass spectrometry. During the surveys, confidential medical interviews were conducted with 16 employees.

Analysis of environmental data indicated the presence of N-nitrosamines in samples collected in the pressroom. In area samples, levels of N-nitrosodimethylamine (NDMA) ranged from 0.12 to 0.17 micrograms per cubic meter of air (ug/M^3) with a mean of 0.14 ug/M^3. Levels of N-nitrosomorpholine (NMOR) ranged from 1.1 to 2.4 ug/M^3, with a mean of 1.6 ug/M^3. N-nitrosodiethylamine (NDEA) was detected in one area sample at a level of 0.14 ug/M^3. In personal samples, NDMA was detected in concentrations ranging from 0.05 to 0.15 ug/M^3, with a mean value of 0.10 ug/M^3 and NMOR was detected in concentrations ranging from 0.19 to 0.98 ug/M^3, with a mean value of 0.62 ug/M^3. To date there are no standards for occupational exposure to airborne nitrosamines, however, current research indicates many of these substances are potent animal carcinogens.

Significant concentrations of other organic compounds were not detected in the process emissions. No health effects associated with N-nitrosamine exposure were noted during the employee interviews.

The average levels of N-nitrosamines detected in this survey are considerably lower than those found in other surveys in the rubber industry. However, based on the carcinogenic capabilities that these substances have shown in animals, it would be prudent to further reduce exposure where possible. General recommendations are contained in Section VIII of this report.

KEY WORDS: N-nitrosamines, N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosomorpholine, rubber curing.

II. INTRODUCTION

On July 7, 1979 an authorized representative of the United Rubber Workers of America, Local 47, requested a NIOSH health hazard evaluation of the rubber pressrooms at the St. Clair Rubber Company, Marysville, Michigan. The requestor was concerned with possible health hazards resulting from exposure to N-nitrosamines and other substances during the curing and molding of rubber products.

An initial survey was conducted by NIOSH investigators on November 19-20, 1979. This consisted of an opening conference with union and management representatives, a walk-through inspection of the pressrooms, confidential interviews with employees, and collection of environmental samples. An interim report was disseminated in January 1980. Preliminary findings included the detection of N-nitrosamines in area samples collected near the rubber presses. Recommendations for substitution of rubber system components with the potential for nitrosamine formation, and future plans for a more comprehensive environmental survey were included in the report. Subsequently, a follow-up environmental survey was conducted on June 12, 1980.

III. BACKGROUND

A. Previous NIOSH Health Hazard Evaluations

At the request of the local union, NIOSH conducted a health hazard evaluation (HHE 77-67-499) in the compounding room of this facility in 1977. As a result of this evaluation, NIOSH recommended modification of local exhaust ventilation to improve dust control at the compounding scales.[1] In 1979, a representative of the St. Clair Rubber Company submitted a request for a NIOSH health hazard evaluation (HHE 79-75-784) to determine if these modifications of the ventilation system were effective, and to evaluate employee exposure to additional chemical substances in the compounding and mixing areas. Recommendations for improving work practices and engineering controls designed to reduce exposures were incorporated in the final determination report.[2]

B. General Description of Plant Operations, Products, and Workforce

The St. Clair Rubber Company manufactures various molded rubber products including gaskets, radiator pads, and bumper strips. Total plant operations employed approximately 160 workers for 8 hours a day, on a 2 shift schedule. Approximately 30 operators were assigned to the the 44 presses located in the pressrooms.

The three major synthetic rubber systems which accounted for the bulk of the company's production were ethylene propylene diene modified rubber (EPDM), styrene butadiene rubber (SBR), and butyl rubber (BR), a copolymer of isobutylene. Approximately 500 distinct rubber formulations were utilized in the manufacture of the various products.

C. Process Description

Raw materials (including polymeric rubbers, activators, catalysts, fillers, and linkers) were compounded, mixed, milled or calendered, and extruded in an area of the plant adjacent to the pressrooms. The assembled raw materials were delivered to the pressroom for vulcanization or curing. The press operator then loaded the mold with the uncured rubber and any additional parts which comprised the final product. Once the press was activated, the raw materials were subjected to heat and pressure and acquired their desired shape. Once curing was complete, the press was opened and the operator stripped the mold of the finished product. The mold was then sprayed with a cleaning wash and the operator repeated the process. Each employeee was responsible for the operation of one or more presses.

IV. EVALUATION DESIGN AND METHODS

A. Initial Survey

The initial environmental survey of November 19-20, 1979, was designed to determine if N-nitrosamines were emitted from the presses during the curing process. Four area samples were suspended near separate presses; one press was curing BR products, another EPDM, and the last two were processing products which contained all three rubber systems (EPDM, SBR and BR). Samples were collected using battery powered pumps operating between 0.75 - 1.0 liters per minute (L/min) attached via tygon tubing to ThermoSorb/N^{TM} cartridges used as the collection media. Other information pertinent to sample collection is given in Table 1-A. A summary of the analytical method is contained in Appendix I.

Personal and area samples were collected to assess exposure to carbon disulfide, styrene, isopropyl alcohol and other organic substances emitted during the curing process. Samples were collected using battery operated pumps attached via tygon tubing to charcoal tubes. Information pertinent to sample collection is included in Table 2. The samples were analyzed by gas chromatography/mass spectrometry for identifiable organic compounds.

Confidential interviews were conducted with 16 press operators. Information was obtained related to employment background, medical histories, and the presence of any work related health problems.

B. Follow-up Survey

Personal samples were collected on June 12-13, 1980, to assess the magnitude of employee exposure to N-nitrosamines at presses manufacturing a variety of rubber products. Samples were collected near the workers breathing zone using battery powered pumps operating at a flow rate of 1.75 L/min. The sampling media and analytical method are described in Appendix 1. Other information pertinent to sample collection is given in Table 1-B.

Personal samples were collected for oxides of nitrogen (nitric oxide and nitrogen dioxide) to assess the role of these substances in the formation of N-nitrosamines. This sampling was conducted during the period which the employees were being monitored for N-nitrosamine exposure. Samples were collected near the employees breathing zone using battery powered sampling pumps operating at a flow rate of 40 cubic centimeters of air per minute (cc/min) for 25 to 28 minutes. The pumps were attached via tygon tubing to sorbent tubes containing a triethanolamine-impregnated molecular sieve. The samples were analyzed for oxides of nitrogen by NIOSH method P&CAM 231.[3]

V. EVALUATION CRITERIA

Nitrosamines as a class are considered to be among the most potent and widespread of animal carcinogens.[4,5,6] Over 75% of tested N-nitrosamines have been shown to be carcinogenic in animals.[7] To date there are no standards for employee exposure to airborne N-nitrosamines. The Occupational Safety and Health Administration has a regulation regarding work practices and handling of liquid and solid N-nitrosodimethylamine in concentrations greater than 1%.[8] In addition, the Food and Drug Administration has limited the amount of N-nitrosamines allowed in beer to 5 parts per billion and the United States Department of Agriculture has limited nitrosamine concentration in cooked bacon to 10 parts per billion. The International Agency for Research on Cancer recommends that NDMA, NDEA, and NMOR be regarded for practical purposes as if they were carcinogenic to humans.[7] NIOSH policy on human exposure to known or suspected carcinogens is to reduce potential exposure to the lowest possible level.[9] Following is a brief summary of the toxicological information for the N-nitrosamines found at this plant.

A. N-Nitrosodimethylamine

The acute toxic effects of animal exposure to NDMA have been reported as gastrointestinal irritation, vomiting, diarrhea, increase in body temperature, and failure of the blood coagulation mechanism.[10] The lethal dose of NDMA causing mortality in 50 percent of rats (LD_{50}) was 40 milligrams per kilogram of bodyweight (mg/kg bw) by oral administration, 37 mg/kg bw by inhalation, and 43 mg/kg bw by intraperitoneal administration.[11,12] Damage to the liver (centrilobular necrosis) after experimental exposure was the primary cause of death.[13] Humans accidentally exposed to NDMA also showed evidence of abnormal liver function, elevated temperature, malaise, and death.[14,15] Studies conducted "in vitro" suggest that metabolism of NDMA in the lung and liver of humans is similar to that of other mammals.[7]

NDMA has been shown to be carcinogenic in all animal species tested, producing tumors mainly in the liver, kidney, and respiratory tract.[7] Addition of the compound to the normal diet of rats at a levels between 50 and 100 mg/kg has led to high incidences of hepatocellular carcinomas and cholangiocellular tumors.[15,16] Studies of animals exposed by inhalation to NDMA have also shown an increased incidence of cancer. Rats exposed daily by inhalation to 0.2 mg/M^3 NDMA for 25 months, had tumors of the lung, kidney and liver earlier and at greater rates than controls.[18]

B. N-Nitrosomorpholine

The acute toxic effects of animal exposure to NMOR are similar to those reported for NDMA. The LD_{50} in rats was 320 mg/kg bw by oral and intraperitoneal administration, and 100 mg/kg bw by intravenious injection.[11,19]

NMOR has been shown to be carcinogenic in a variety of animal species. Following oral administration it had beem shown to cause tumors of the liver, kidney, and blood vessels in rats, tumors of the liver and lung in mice, and, tumors of the liver in hamsters. No inhalation studies have been conducted to date on NMOR.[7]

C. N-Nitrosodiethylamine

Acute toxic effects of NDEA are similar to those of NDMA. The LD_{50} for NDEA when administered orally was 280 mg/kg bw in rats.[11] When administered subcutaneously, the LD_{50} was 250 mg/kg bw in European hamsters, and 230 mg/kg bw in Chinese hamsters.[20,21]

NDEA has been found to be carcinogenic in all animal species tested, causing tumors primarily in the liver, respiratory and upper digestive tracts, and kidney in the animals studied.[7]

VI. RESULTS

Laboratory analysis indicated the presence of 3 specific N-nitrosamines in area samples. NDMA and NMOR were detected in all 4 samples. Concentrations of NDMA ranged from 0.12 to 0.17 ug/M^3, with a mean value of 0.14 ug/M^3 [46 parts of contaminant per trillion parts of air (ppt)]. NMOR concentrations ranged from 1.1 to 2.4 ug/M^3, with a mean of 1.6 ug/M^3 (340 ppt). NDEA was detected in 1 sample at a level of 0.14 ug/M^3 (34 ppt). A detailed listing of these results is given in Table 1.

Two specific N-nitrosamines were detected in the personal samples. NDMA was detected in all ten personal samples at concentrations ranging from 0.05 to 0.15 ug/M^3, with a mean value of 0.10 ug/M^3 (33 ppt). NMOR was detected in 6 of 10 samples at concentrations ranging from 0.19 to 0.98 ug/M^3, with a mean value of 0.62 ug/M^3 (130 ppt). A detailed listing of these results is given in Table 2.

Analysis of the charcoal tubes revealed small amounts of toluene, methyl chloroform, and carbon disulfide. However, the concentrations of these substances were well below the corresponding environmental limits. A detailed listing of these results and the environmental limits is given in Table 3.

Sorbent tubes analyzed for oxides of nitrogen were found to be below the level of analytical detection of 2 micrograms (ug) per tube for nitric oxide, and 3 ug per tube for nitrogen dioxide.

Results of the medical interviews revealed 3 of the 16 employees who felt that they had experienced work related health problems. These included weight loss by one employee and lingering colds suffered by two other employees.

VII. DISCUSSION AND CONCLUSIONS

A. Chemistry of N-nitroso Compounds

N-nitroso compounds are chemicals with the general formula R_1R_2NNO, where R_1 and R_2 can be virtually any organic group. These compounds can be formed by the reaction of various entities. The amine fragment (R_1R_2N-) can come from a primary, secondary, or tertiary amine. The nitrosyl group (-NO) can be derived from nitric oxides (NO, NO_2, N_2, N_2O_3, or N_2O) or nitrite. N-nitrosation of the amine fragment can also occur via transnitrosation by other, more labile, N-nitroso compounds. Depending on the reactants and the catalyst that are present, N-nitrosation can occur in either acidic, neutral, or alkaline conditions. Some known N-nitrosation catalysts include formaldehyde, ozone, and metal ions.[22]

B. Sources of N-nitrosamines

Although the source of the N-nitrosamines in this survey is not known for certain, recent studies have identified major potential sources of N-nitroso compounds in other rubber manufacturing plants. The following is a brief discussion of the major sources and their possible role in this survey.

1. Direct Use of N-nitrosamines in Process Formulations

Nitrosamines used as additives in various rubber compositions have been shown to be a primary source in introducing N-nitrosamines into the environment. N-nitrosodiphenylamine (NDPhA) has been detected in air, water, and soil samples in facilities where it was used as a vulcanization retarder.[23] A review of the materials utilized in formulations at St. Clair Rubber did not reveal the use of N-nitrosamines in any of the rubber products. Therefore, this factor would not contribute to the presence of the N-nitrosamines detected in the environment.

2. Artifactual formation of N-nitrosamines during collection and analytical procedures.

The possibility of artifactual formation of N-nitrosamines during collection or analysis of environmental samples must be considered based on the reactive nature of this class of chemicals. Under certain conditions, oxides of nitrogen have been known to nitrosate amines to form the corresponding N-nitrosamines. Additionally, NDPhA has been shown to transfer the nitrogen moiety of its structure to other secondary amines to form other N-nitrosamines.[24]

Thermosorb/N™ cartridges have been shown to be capable of both retaining a wide variety of N-nitrosamines and to be artifact resistant.[25] Additionally, recent studies have not shown evidence that NMOR is produced as an artifact during subsequent sample analysis.[26,23] During the survey at St. Clair Rubber, oxides of nitrogen were not detected in samples collected during the nitrosamine sample collection, nor was NDPhA detected in the workroom environment. This evidence would seemingly indicate that artifactual nitrosamine formation is not a major factor in this survey.

3. The presence of N-nitrosamines as impurities in process additives

N-nitrosamines have been identified as impurities in various components used in rubber manufacturing. In one recent study, NDMA was found to be a contaminant in dimethylamine, while NMOR was found to be a contaminant in both morpholine and bismorpholinecarbamylsufenamide[23], indicating a possibility of contamination in additives containing the corresponding amine structures. During the survey at St. Clair Rubber, the individual components of the various rubber systems were not tested for the presence of N-nitrosamines as impurities, thus the contribution of this factor to the presence of N-nitrosamines was not determined.

4 Formation of N-nitrosamines during compounding and curing.

Chemical reactions which take place during compounding and curing are thought to be a major source of nitrosamine formation. Dialkylamino stabilizers and accelerators, almost universally used in rubber compounding, can be nitrosated to form the corresponding N-nitrosodialkylamine, although neither the nitrosating agent nor the exact mechanism of nitrosamine formation has been identified.[27,28] The survey at St. Clair Rubber revealed the use of zinc dimethyldithiocarbamate and copper dimethyldithiocarbamate, respectively in the EPDM and SBR rubber systems. It is probable that the dimethylnitrogen moiety of these catalysts is nitrosated to produce NDMA. Furthermore, diethyldithiocarbamate is a catalyst for the butyl rubber system and would, if the diethylnitrogen moiety were nitrosated, produce NDEA. This could explain the finding of a quantifiable level of NDEA in the area sample at the press processing butyl rubber.

VIII. RECOMMENDATIONS

While N-nitroso compounds were detected in all air samples collected in the plant, the average level was considerably lower than those found in other rubber manufacturing plants (levels of NMOR as high as 250 ug/M^3 have been detected in area samples in a plant producing passenger car tires).[29,30] Since no standards exist for occupational exposure to airborne N-nitrosamines, it has not been determined whether the levels detected in this survey could possibly cause adverse health effects. However, based on the carcinogenic potential of these substances, effort should be made to further reduce employee exposures where possible.

Two generalized approaches can be taken to control workplace exposure to these substances. Control of the precursors which lead to the formation of N-nitrosamines (e.g., preventing introduction of N-nitrosamines in process formulations and insuring that additives containing the amino or dialkylamino moieties are not contaminated with the corresponding nitrosamine) is one method of decreasing the possibility of N-nitrosamines exposure. Secondly, controlling process emissions (e.g., increasing general room ventilation or the addition of local exhaust ventilation) would further reduce levels of N-nitrosamines in the pressroom environment.

NIOSH, the Rubber Manufactuers Association, and other researcher groups are currently conducting further studies of the possible health effects associated with N-nitrosamine exposure. The company and union should closely monitor the findings of these studies and their relation to the exposure levels found at this plant.

IX. REFERENCES

1. Health Hazard Evaluation Report HE 77-67-499, National Institute for Occupational Safety and Health, DHEW, 1977.

2. Health Hazard Evaluation Report HE 79-075-784, National Institute for Occupational Safety and Health, DHEW, 1981.

3. NIOSH Manual of Analytical Methods, Volume 1, Second Edition, National Institute for Occupational Safety and Health, DHEW, October 1978.

4. Magee, P.N., N-nitroso Compounds and Related Carcinogens. Chemical Carcinogens. Washington D.C.: American Chemical Society, 1976. (Monograph 173).

5. Walker, P., Gordon, J., Thomas, L., Ovellette, R., Environmental Assessment of Atmospheric Nitrosamines, MITRE, (U.S. EPA No. 68-02-1495) 1976.

6. Mirvish, S.S., "Formation of N-nitroso Compounds: Chemistry, Kinetics and in Vivo Occurrence". Toxicol. Appl. Pharm., 31, 325-351. 1975.

7. Bogovski, R., Preussman, E.A. Walker and Davis, W., Evaluation of the Carcinogenic Risk of Chemicals to Man, IARC MONOGRAPHS, Vol. 1, International Agency for Research on Cancer, World Health Organization Lyon, France (1972).

8. Code of Federal Regulations, Title 29, Chapter XVII, Occupational Safety and Health Administration, Depatrment of Labor, July 1, 1980.

9. Working with Carcinogens, National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare, # 77-206, 1977.

10. Jacobson, K.H., Wheelwright, J.H., Clem, J.H., Shannon, Studies on the Toxicology of N-nitrosodimethylamine Vapor, AMA Archives of Industrial Health, 12, 617-622; 1955.

11. Druckrey, H., Preussmann, R., Ivankovic, S. & Schmahl, D. (1967) Organotrope carcinogene Wirkungen bei 65 verschiedenen N-Nitroso-Verbindungen an BD-ratten. Z. Krebsforsch., 69, 103-201

12. Heath, D.F. (1962) The decomposition and toxicity of dialkylnitrosamines in rats. Biochem. J., 85, 72-91

13. Magee, P.N. & Barnes, J.M., Carcinogenic nitroso compounds. Adv, Cancer Res., 10, 163-246, 1967.

14. Shank, R.C., "Toxicology of N-nitroso Compounds, Toxicology Appl. Pharm., 31, 361-368, 1975.

15. Barnes, J.M., Magee, P.N., Some Toxic Properties of Dimethylnitrosamine, British Journal of Industrial Medicine 11, 167 (1954).

16. Schmahl, D., Preussmann, R., Naturwissenschaften, 46, 175, 1959.

17. Argus, M.F. & Hoch-Ligeti, C. (1961) Comparative study of the carcinogenic activity of nitrosamines. J. nat. Cancer Inst., 27, 695-709

18. Moiseev, G.E., Benemanskii, V.V., Carcinogenic Activity of Low Concentration of N-nitrosodimethylamine in Inhalation. Chemical Abstracts, 83, 1, 73618, 1975.

19. Lee, K.Y. & Lijinsky, W. (1966) Alkylation of rat liver RNA by cyclic N-nitrosamines invivo. J. nat. Cancer Inst., 37 401-407

20. Mohr, U., Althoff, J. & Page, N. (1972b) Tumors of the respiratory system induced in the common European hamster by N-diethylnitrosamine. J. nat. Cancer Inst., 49, 595-597

21. Reznik, G., Mohr, U. & Kmoch, N. (1976) Carcinogenic effects of different nitroso-compounds in Chinese hamsters. I. Dimethylnitrosamine and N-diethylnitrosamine. Brit. J. Cancer, 33, 411-418

22. Fajen, J.M., Ringenburg, V., Survey for N-nitroso Compounds at B.F. Goodrich, Industry Wide Studfies Branch, National Institute for Occupational Safety and Health, April 15, 1980, Unpublished.

23. Fajen, J.M., Carson, G.A., Rounbehler, D., N-nitrosamines in the Rubber and Tire Industry, Science, Volume 205, September 1979.

24. Challis, B.C., Edwards, A., Hunma, S.A., Environmental Aspects of N-Nitroso Compounds, International Agency for Research on Cancer, Lyon, France, 1978.

25. Rounbehler, D.P., Reisch, J., Coombs, J., Fine, D.H., Nitrosamine Air Sampling Sorbents Compared for Quantitative and Artifactual Formation. Analytical Chemistry, 52: 273, 1980.

26. Fan, S., Fajen, J., Rounbehler, D., Survey for N-Nitroso Compounds at Akron Chemical Plant, B.F. Goodrich Co., July 1978, National Institute for Occupational Safety and Health and Thermo Electron Research Center, Waltham, Mass., Unpublished.

27. Ireland, C.B., Hytrek, F.P., Lososki, B.A., Aqueous Extraction of N-nitrosamines from Elastomers, American Industrial Hygiene Journal, Volume 41, December 1980.

28. Yeager, F.W., Van Gulick, N., Lososki, B.A., Dialkylnitrosamines in Elastomers, American Industrial Hygiene Journal, Volume 41, February 1980, pages 148-150.

29. Health Hazard Evaluation Interim Report HE 79-109, National Institute for Occupational Safety and Health, DHEW, 1979.

30. Health Hazard Evaluation Report HE 80-67-749, National Institute for Occupational Safety and Health, DHEW, 1980.

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared By:	William J. Daniels Industrial Hygienist NIOSH - Region V Chicago, Illinois
Environmental Evaluation:	Shawn McQuilkin Industrial Hygienist NIOSH - Region V Chicago, Illinois
	Richard S. Kramkowski Regional Consultant NIOSH - Region V Chicago, Illinois

Originating Office:
Division of Surveillance Hazard
Evaluations & Field Studies
Hazard Evaluation and
Technical Assistance Branch
Cincinnati, Ohio

Analytical Laboratory Services:
Thermo Electron Inc.
Waltham, Massachusetts

NIOSH Measurement Support Branch
Cincinnati, Ohio

XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Services (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH publications office at the Cincinnati address. Copies of this report have been sent to the following:

A. United Rubber Workers of America,

B. St. Clair Rubber Company, Marysville, Michigan

C. U. S. Department of Labor, OSHA - Region V

D. NIOSH Regional Offices/Divisions

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

TABLE 1-A
RESULTS OF AREA AIR SAMPLES FOR NITROSAMINES
NOVEMBER 19-20, 1979

SAMPLE LOCATION (Press #)	RUBBER TYPE(s)	SAMPLE TIME (Minutes)	SAMPLE VOLUME (Liters)	NDMA (ug/M3)	NDEA (ug/M3)	NMOR (ug/M3)
660	SBR, BR, EPDM	202	151	0.14	ND	2.4
605	SBR, BR, EPDM	202	202	0.12	ND	1.1
658	BR	405	340	0.14	0.14	1.3
609	EPDM	374	374	0.17	ND	1.6
Blank	---	---	---	ND	ND	ND

TABLE 1-B
RESULTS OF PERSONAL AIR SAMPLES FOR NITROSAMINES
JUNE 12-13, 1980

EMPLOYEE LOCATION (PRESS #'s)	RUBBER TYPE(s)	SAMPLE TIME (Minutes)	SAMPLE VOLUME (Liters)	NDMA (ug/M3)	NMOR (ug/M3)
655-56-57	SBR	223	390	0.07	0.85
625-26-27-31	BR, SBR, EPDM	221	387	0.10	0.54
637-40-58	BR, SBR, EPDM	221	387	0.14	ND
636-38-52-54	BR, EPDM	221	387	0.12	0.19
618-20-21-22	BR, SBR	211	369	0.09	0.27
618-20-21-22	BR, SBR	234	410	0.08	ND
625-26-27-31	BR, SBR, EPDM	231	404	0.05	ND
606-10-38-50-59	BR, SBR, EPDM	231	404	0.07	ND
643-53-58	BR, EPDM	234	410	0.15	0.98
628-32-33-34-35	BR, SBR, EPDM	226	396	0.08	0.86

ABBREVIATIONS:

NDMA = N-nitrosodimethylamine
NDEA = N-nitrosodiethylamine
NMOR = N-nitrosomorphiline
ug/M^3 = micrograms per cubic meter of air
ND = below limit of detection of 7 ng/ThermoSorb/N^{TM}

BR = Butyl rubber
SBR = Styrene butadiene rubber
EPDM = Ethylene propylene diene modified

TABLE 2
RESULTS OF GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSIS OF SAMPLES FOR ORGANIC CONTAMINANTS
November 20, 1981

PRESS #(s)	SAMPLE TYPE	SAMPLE VOLUME (Liters)	SAMPLE TIME (Min.)	CONTAMINANT/ CONCENTRATION DETECTED	CONTAMINANT/ CONCENTRATION DETECTED
660	Area	31.6	202	ND	
660	Personal	13.6	200	Toluene/Trace*	
604,605	Area	27.6	202	Toluene/Trace*	
658	Personal	24.1	183	ND	
656	Personal	16.3	400	ND	
609	Area	34.4	374	Toluene/Trace*	Methyl Chloroform/ 5 ppm
638	Personal	34.0	398	Toluene/Trace*	Carbon Disulfide/ 0.05 ppm**

All values for contaminants are Time Weighted Average concentrations for the duration of the sampling period.
*Trace amounts of toluene were identified in these samples, possibly as an impurity in the desorbing solvent.
**A 25% desorption efficiency for carbon disulfide at this level; concentration possibly as high as 0.19 ppm.

Abbreviations: ppm = parts of contaminant per million parts of air
ND = no contaminants detected

Environmental criteria:

Substance	Environmental Limit	Source
Methyl Chloroform	350 ppm 8-hour TWA	OSHA
	350 ppm 15-min. ceiling	NIOSH
Carbon Disulfide	20 ppm 8-hour TWA	OSHA
	30 ppm 30-min ceiling	OSHA
	1 ppm 10-hour TWA	NIOSH
	10 ppm 15-min. ceiling	NIOSH

APPENDIX 1

ThermoSorb/N Air Sample Cartridges

Thermosorb/N cartridges have been shown to be capable on both retaining a wide variety of N-nitrosamines and to be artifact resistant[1]. When received for analysis, cartridges were eluted by backflushing with 2 ml acetone. Studies have shown that the first 0.1 ml of acetone quantitatively elutes all of the nitrosamines that were tested[2]. The acetone eluate from these cartridges were (without further sample preparation) then examined by gas chromatography - thermal energy analysis (GC-TEA).

Analysis by GC-TEA

The following were the GC-TEA conditions used:

Gas Chromatography:

Inlet Temperature:	150°C
Column Temperature:	140°C to 200°C at 4° per min.
Column:	10 ft. x 1/8 in. O.D. stainless steel
Packing:	10% Carbowax 20M + 2% KOH on Chromosorb W-AW, 80/100 mesh
Carrier:	Helium @ 30 cc/min.

TEA Analyzer Conditions:

Pyrolizer:	475°C
Oxygen:	5 cc/min
Pressure:	1.0 TORR
Attenuation:	x4

APPENDIX REFERENCES

1. Rounbehler, D.P., Reisch, J., Coombs, J and Fine, D.H., Nitrosamine air sampling sorbents compared for quantitative collection and artifactual formation. Analyt. Chem. 52:273 (1980).

2. Rounbehler, D.P., Reisch, J. and Fine, D.H., Nitrosamine Air Sampling Using a New Artifact Resistant Solid Sorbent System, ASTM STP 271, pp.80-91 (1980)

DEPARTMENT OF HEALTH AND HUMAN SERVICES
PUBLIC HEALTH SERVICE
CENTERS FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

Third Class Mail