PB83-110544

SURVEY FOR N-NITROSO COMPOUNDS

at

Chevrolet Warren Manufacturing Plant
235 Mound Rd.
Warren, Michigan

DATE OF REPORT

Preliminary - January 30, 1978
Final - June 21, 1978

Thermo Electron Research Center
Waltham, Massachusetts

and

National Institute for Occupational Safety and Health
Cincinnati, Ohio

Place Visited	Chevrolet Warren Manufacturing Pl 23500 Mound Rd. Warren, Michigan
Date of Visit	December 14, 1977
Persons Making Visit	Steve Fan Thermo Electron Corp.
	William Herbst Thermo Electron Corp.
	John Morrison Thermo Electron Corp.
	Robin Vita Thermo Electron Corp.
	John Fajen NIOSH
	George Carson NIOSH
	Ray Biagini NIOSH
Persons Contacted	R. Metals Plant Manager
	J.H. Frazer Personnel Director
	Robert List Plant Safety Representative
	Jerome Eichbauer Union Safety Representative
	Mike Taubitz Corporate Safety Administrator
	Pat Frazee Corporate Industrial Hygienist
	Jack Zimmerman Chief Chemist - Metallurgy
	Jim Biggs Senior Chemist

Report Written By	Steve Fan John Fajen
Purpose of Visit	To determine the extent of exposure to N-nitroso compounds in the machine shop environment where cutting fluid is used.

INTRODUCTION

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 chemical entities. One of the 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_2O_3, or N_2O_4) 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 catalysts that are present, N-nitrosation can occur at either acidic, neutral, or alkaline conditions. Some known N-nitrosation catalysts include formaldehyde, chloral, ozone, and metal ions.

The interest in the N-nitroso compounds in metalworking fluids stemmed from the report that several brands of metalworking fluids randomly selected from the local suppliers in the Boston area contained N-nitrosodiethanolamine (NDELA) with the concentrations ranging from 0.02% to 3%.[1] N-nitroso compounds have been regarded as one of the most potent families of animal carcinogens. Although N-nitroso compounds are suspected to be human carcinogens, they have not been directly associated with human cancer because there are no population groups identified as having been inadvertently exposed. NDELA has been found to be an animal carcinogen. When it was fed at an average daily dose of 600 mg/kg in the diet for 240 days, liver carcinomas were observed in 15 out of 16 rats and adenomas of the kidney were induced in four rats.[2] Neoplasms of the

nasal cavity and tracheal tumors were also observed in 39 out of 56 golden hamsters that were injected subcutaneously with a total dose of 15 g of NDELA per kg body weight in either 7 or 27 subdoses over 78 weeks. [3] Besides metalworking fluids, NDELA has been found in popular consumer cosmetics, [4] medicated hair care products, [5] and unburned processed tobacco. [6]

The majority of synthetic and semisynthetic fluids are formulated with sodium nitrite and triethanolamine as the major ingredients, the concentrations of which could be as high as 18 and 45%, respectively. Commercial triethanolamine may contain as much as 15% of diethanolamine as impurity. Thus the essential precursors for the formation of NDELA are present in the synthetic and semisynthetic metalworking fluids. During the formulation of the fluids, heat is often applied to assist in the dissolution of ingredients. The metalworking fluid products are also frequently stored on the shelf for long periods of time before being used. Ample opportunity exists for the formation of NDELA from its precursors in metalworking fluids.

In the workplace where metalworking fluids containing N-nitroso compounds are used, the workers may be exposed to N-nitroso compounds by dermal contact and inhalation. The skin penetration of NDELA is currently under investigation by researchers associated with the Food and Drug Administration (FDA) and the National Institute of Occupational Safety and Health (NIOSH). NDELA is a relatively nonvolatile compound. It is not known whether NDELA in the metalworking fluid will be vaporized or present as an aerosol in the air.

NIOSH has contracted with Thermo Electron Corporation to conduct

environmental monitoring in a wide variety of industrial facilities to determine workers' exposure to N-nitroso compounds in the workplace. A mobile van with complete laboratory facilities to perform N-nitroso compound analysis has been developed and was used in this study.

PLANT DESCRIPTION

The facility has been operated as the Chevrolet Warren plant since 1960. The plant was housed in one building and occupied 2 million square feet. Currently, the facility has an employment force of 4300 with 4000 in the production area and 300 in the administrative area. The plant was operated on three shifts with 2100, 1700, and 200 workers on each shift. The major products of the facility were automotive components, rear axles, and control arms.

Only two kinds of metalworking fluids were used in the facility and both were soluble oil type fluids, i.e., Norton Wheelmate 810 and GM C-60. The metalworking fluid used in the machining was supplied from 11 central systems with the capacities varying from 4000 to 27,000 gallons. Generally, the fluids in the central system were prepared from the stock metalworking fluids by diluting in water as 3-5% emulsion. Once a week, sodium hypochlorite was added to 3 ounces/gallon as bactericide to prevent the development of odor.

SAMPLING

Only three samples were collected at the plant; two stock metalworking fluids and one fluid from the central system.

Sample No.	Sample Description
I-1	Wheelmate 810 Lot No. 7115 Norton Co. Worcester, Mass.
I-2	General Motor C-60 Stock fluid from the storage tank
I-3	General Motor C-60 Fluid from central system (location Y-13) Sample I-2 diluted about 25 to 1

ANALYTICAL METHODS

A. Sample Preparation

0.5 ml of the sample was stirred with 20 ml ethyl acetate and 10 ml acetone in the presence of about 250 mg sulfamic acid for 10 minutes. The extract was filtered through sodium sulfate and analyzed by HPLC-TEA (High Performance Liquid Chromatography - TEA).

B. Analysis by HPLC-TEA

HPLC-TEA was constructed by sequentially connecting a high pressure pump (Altex Model 110), an injector (Rheodyne Model 7120), a μPorasil column (Waters Associates) and a TEA (Thermo Electron Model 502/LC). TEA is an N-nitroso compound specific detector. Acetone and hexane at a ratio of 1 to 1 were used as the elution solvent at a flow rate of 2 ml/min.

RESULTS

NDEIA was not detected in the three samples at concentrations above 1 μg/ml. No other TEA-responsive peak was detected either. The metalworking fluids used in the plant were the soluble oil type, in which no nitrite was added. Consequently, N-nitroso compounds were not likely to be formed in this type of metalworking fluid.