SURVEY FOR N-NITROSO COMPOUNDS

at

Chrysler Forge and Axle Plant
6700 Lynch Rd.
Detroit, Michigan

DATE OF REPORT

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Thermo Electron Research Center
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and

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16. Abstract (Limit: 200 words): A survey was conducted on December 14, 1977 at the Chrysler Forge and Axle Plant (SIC-3312) in Detroit, Michigan to determine the extent of exposure to N-nitroso compounds in the machine shop environment where cutting fluid was used. The facility employed about 3500 workers over three shifts. Air samples were collected near machines using Cimcool-Five-Star-B (CFSB), Chrysler-Cycleweld-NP6058 (CC), and Grotan (56573047) to detect N-nitroso compounds released during machine operation. Stock solutions and diluted fluid samples taken from the machines were also analyzed to measure N-Nitroso compounds, specifically N-nitrosodiethanolamine (1116547) (NDE1A). Undiluted stock solutions of CFSB contained about 600 micrograms per milliliter NDE1A; CC and Grotan contained less than 1 microgram per milliliter. Diluted (10 to 1) CFSB collected from machines contained 5 micrograms per milliliter or less NDE1A, lower than expected. No other N-nitroso compounds were detected. Atmospheric concentrations of 30 to 50 nanograms per cubic meter NDE1A were detected near one of three machines using CFSB; none was detected in any other air sample. The authors suggest that the lower concentrations of NDE1A in the used fluids are probably due to decomposition of NDE1A to non-N-nitroso compounds. They conclude that the general facility atmosphere was not contaminated by NDE1A and that daily exposure in the contaminated area was about 120 nanograms over 8 hours.

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Place Visited	Chrysler Forge and Axle Plant 6700 Lynch Rd. Detroit, 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
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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] Many N-nitroso compounds have been demonstrated to be animal carcinogens.[2] Although they are suspected to be human carcinogens, N-nitroso compounds 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 kidneys 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 is a gear and axle assembly plant. It was built originally in 1914. At present time, the total area of the plant was more than one million square feet. Total number of employees was 3500 operated on three shifts with approximately 1200 employees on each shift.

Only two kinds of metalworking fluids were used in the plant. A soluble oil type fluid, NP6058, was used the most in the plant. Synthetic fluids were required for a few machine operations. Cimcool Five Star B was used in these operations. Since synthetic fluids are known to contain N-nitroso compounds, [1] most of the effort in this study was concentrated on the machines which used the synthetic fluid.

DESCRIPTION OF SAMPLING METHOD

A. Stock Bulk Fluid

Three stock bulk fluids were sampled. Two were metalworking fluids and the other was a bactericide. The bactericide (Grotan) was added to the fluid when an odor developed in the metalworking fluid in the machine. The bulk samples (100 ml) were obtained in plastic bottles. The pertinent information for each samples are as follows:

Sample No.	Sample Description
H-5	Cimcool Five Star B Control No. 71130Z Cincinnati Milacron Cincinnati, Ohio Synthetic metalworking fluid
H-13	Chrysler Cycleweld NP6058 Shipped from Chrysler Chemical Plant in tank. Soluble oil type metalworking fluid
H-14	Grotan Bactericide Product No. 67425 Hellenite Chem. Co.

B. Diluted Metalworking Fluid

The description of the diluted fluid samples collected from the machines is presented in Table I. Totally, six samples were collected. Five samples were from the machines using Cimcool Five Star B, while one sample was from the machine using NP6058.

C. Description of Air Sampling Method

All air samples collected were area samples. Air was pumped through two midget impingers in series at ambient temperature. Each impinger contained 15 ml of 0.1 N KOH. The pertinent data for the air samples are described in Table II. All the air samples were obtained around the machines which used Cimcool Five Star B. The air sample control was collected in the Safety Office which was outside the machine operation area.

ANALYTICAL METHODS

A. Sample Preparation

1. Bulk Fluids

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 10 g sodium sulfate and analyzed by HPLC-TEA (High-performance Liquid Chromatography - Thermal Energy Analyzer).

2. Air Samples

The sample (in 15 ml, 0.1 N KOH) was extracted successively with 75, 75, and 50 ml of ethyl acetate. The extracts were combined and concentrated to approximately 500 µl by rotary evaporator. The concentrated sample was analyzed by HPLC-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

The results of the analyses of stock bulk fluids are presented in Table III. The synthetic metalworking fluid, Cimcool Five Star B, contained N-nitrosodiethanolamine (NDELA) at a level of 600 µg/ml. The soluble oil type metalworking fluid (NP6058) and the bactericide (Grotan)

did not contain NDELA at a concentration above 1 µg/ml.

The metalworking fluids were diluted from 10 to 35 times before being used on the machines. Generally, the concentrations of NDELA in diluted metalworking fluids collected from the machines were less than 5 µg/ml (Table IV). This was lower than what was expected. For example, the stock Cimcool Five Star B contained 620 µg/ml of NDELA and H-6 was diluted 10 to 1 from the stock fluid. Upon dilution, the concentration of NDELA in H-6 should be 60 µg/ml. Instead, only 5 µg/ml of NDELA was found. The same pattern was observed in the other samples diluted from stock Cimcool Five Star B. These results indicated that additional NDELA was not formed from its precursors during machine operation. Furthermore, no other TEA responsive material was found in these diluted fluids, which also indicated that NDELA was not transformed to other N-nitroso compound. The disappearance of NDELA in the diluted fluids could only be explained by either the vaporization to the air or the decomposition to non-N-nitroso compound.

The results of air samples are presented in Table V. NDELA was detected in two air samples (H-3, H-4) which were collected in the same bay location, BB13. Diluted Cimcool Five Star B were used in these two machines. The concentration of NDELA in the fluid used in the machines was 2 µg/ml. However, the metalworking fluid was splashing in the air during machine operation. The possibility existed that NDELA in the fluid droplet floating in the air might contaminate the air sample trap through the open inlet, although extreme care was taken in the selection of air sample location to prevent the contamination from splashing. Assuming 3 m^3 of air is inhaled in an 8 hour working day, for the worst case, the

daily exposure of the workers to NDELA operating the machine was 120 ng. For comparison, the exposure to nitrosamines by ingesting 10 g of bacon would be 100 ng of N-nitrosodimethylamine and 500 ng of N-nitrosopyrrolidine. [17] The negative results found in two air samples (H-8 and H-11), which were collected on the machines using diluted Cimcool Five Star B, indicated that NDELA was not a general contaminant in the environment of the facility.

SUMMARY

Two stock metalworking fluids (NP6058 and Cimcool Five Star B) and one bactericide (Grotan) were sampled. Cimcool Five Star B, a synthetic fluid, contained 600 µg/ml of NDELA in the bulk. Nitrosamine was not detected above 1 µg/ml in NP6058, a soluble oil type fluid, and Grotan.

Six diluted metalworking fluids were sampled from the machines. Five of them were diluted from Cimcool Five Star B and one from NP6058. The concentration of NDELA in these samples were less than 5 µg/ml in all cases. Considering the concentration of NDELA in the stock fluid (600 µg/ml) and the extent of the dilution (10 to 35 times), the results indicated that NDELA might degrade to other materials during machine operation.

NDELA was not contaminated in the general air environment of the plant. However, 30-50 ng/m^3 of NDELA was detected near the machines located in bay BB13. The daily exposure to NDELA by the operator was about 120 ng. NDELA was not detected on two other machines which also used diluted Cimcool Five Star B as metalworking fluid.

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Table I.

The Description of the Diluted Metalworking Fluids Collected in the Detroit Forge and Axle Plant on December 14, 1977

Sample No.	Machine	Bay Location	Fluid	Dilution
H-2	Landis Grinder 2960	BB13	Cimcool 5 Star B	
H-6	Ex-cello 900	HH7	Cimcool 5 Star B	9.5
H-7	Snyder 2278	HH7	Cimcool 5 Star B	35
H-9	Ex-cello 903	HH7	Cimcool 5 Star B	26
H-10	Snyder 2279	HH7	Cimcool 5 Star B	24
H-11	Barnes No. 1 Unit 26	F2	NP6058	

Table II.

The Data for the Air Samples Collected in the Detroit Forge and Axle Plant on December 14, 1977

Sample No.	Machine	Location	Sampling Time (Min)	Flow rate (ℓ/min)	Total Volume (ℓ)
H-1		Safety Office	180	1.75	315
H-3	Landis Grinder 2959	BB13	188	1.8	338
H-4	Landis Grinder 2959	BB13	188	1.85	348
H-8	Ex-cello 900	HH7	180	1.6	288
H-11	Barne No. 1 Unit 6	F2	179	1.8	322

Table III.

The Concentration of N-nitrosodiethanolamine (NDELA)

in Stock Bulk Fluid Samples

Sample No.	Bulk Fluid	Concentration (µg/ml)
H-5	Cimcool 5 Star B	620
H-13	NP6058	trace
H-14	Grotan	ND[a]

a. Not Detected. Detection limit 1 µg/ml.

Table IV.

The Concentration of N-nitrosodiethanolamine in Diluted Metalworking Fluid Used in the Machines

Sample No.	Fluid	Dilution	Concentration (µg/ml)
H-2	Cimcool 5 Star B		2
H-6	Cimcool 5 Star B	9.5	5
H-7	Cimcool 5 Star B	35	3
H-9	Cimcool 5 Star B	26	ND[a]
H-10	Cimcool 5 Star B	24	ND[a]
H-12	NP6058		1

[a] Not detected. Detection limit, 1 µg/ml.

Table V.

The Concentration of N-nitrosodiethanolamine in the Air Samples

Sample No.	Concentration (ng/m^3)
H-1	ND[a]
H-3	52
H-4	trace[b]
H-8	ND[a]
H-11	ND[a]

[a] Not Detected. Detection Limit, 50 ng/m^3.

[b] Approximately 30 ng/m^3.