SURVEY FOR N-NITROSO COMPOUNDS

at

White and Bagley Company
Worcester Center Blvd.
Worcester, Mass.

DATE OF REPORT
Preliminary - November, 1977
Final - December, 1977

Thermo Electron Research Center
Waltham, Massachusetts

and

National Institute for Occupational Safety and Health
Cincinnati, Ohio

PLACE VISITED:	White and Bagley Company Worcester Center Blvd. Worcester, Mass. 01608
DATE OF VISIT:	September 20, 1977
PERSONS MAKING VISIT:	Steve Fan Thermo Electron Research Center David Fine Thermo Electron Research Center William Herbst Thermo Electron Research Center Martin Wolf Thermo Electron Research Center Ronald Young NIOSH
PERSONS CONTACTED:	Edward Ahern Technical Director William Robidous Assistant Superintendant
REPORT WRITTEN BY:	Martin Wolf Ronald Young
PURPOSE OF VISIT:	To determine the extent of exposure to N-nitroso compounds in the manufacturing of cutting fluids.
COLLECTIVE BARGAINING UNIT:	None

INTRODUCTION

N-nitrosamines, which are substances having an N - - N = O linkage, include a vast number of compounds. The search for n-nitrosamines in the environment has classically been associated with nitrite preserved foodstuffs and tobacco smoke. However, with the development by Fine et al, of highly semsitive detection techniques utilizing thermal energy analysis, significant levels of n-nitrosamines have been found in air, soil, pesticides, cutting fluids, and in cosmetics. The National Institute for Occupational Safety and Health has contracted with Thermo Electron Corporation to conduct environmental monitoring in a wide variety of industrial facilities with potential for n-nitroso compound formation from precursor compounds. A mobile monitoring van which makes real-time measurements possible has been developed.

The formation of diethanolnitrosamine in cutting fluids was first postulated and reported by Zingmark and Rappe in Sweden.[1] They measured diethanolnitrosamine in a specifically formulated "grinding fluid" containing nitrite and triethanolamine. They concluded that the potential hazard of working with these types of products should no be underestimated.

Historically, nitrosamines have been regarded as one of the most potent families of animal carcinogens. Although nitrosoamines are suspected to be human carcinogens, their carcinogenic potential in man has not been proven.

PLANT DESCRIPTION

White and Bagley has been manufacturing grinding fluids and lubricants

for over 90 years. The company occupies two buildings, connected by an enclosed bridge, located in downtown Worcester, Massachusetts. One building conatins 5000 gallon storage tanks for receipt and storage of raw materials. As required, these materials are pumped to the other building for blending. The sodium nitrite is stored and used as a 40% aqueous solution. It is combined with 80% triethanolamine (aqueous) in an enclosed 5000 gallon tank. The piping systems for nitrite containing and nitrite free products are independent of each other. This nitrite/amine solution is pumped to open blending tanks on the second and third floors of the building where other materials are added to form the final products. The products are then pumped to the first floor for packaging.

SAMPLING

The following bulk samples were taken:

A. Packaged Products

1. E55 Grinding Coolant

   Contains triethanolamine and sodium nitrite. An aliquot was removed from a sealed 32 gallon drum and labelled sample C-1.

2. 1500 Grinding Concentrate

   Contains treithanolmaine and sodium nitrite. An aliquot was removed from a sealed 32 gallon drum and labelled sample C-2.

3. 2906 Grinding Coolant

   Sample C-7

4. 3100 Grinding Concentrate

   Sample C-8

B. Blending Tanks

1. E55 - an aliquot of E55 was removed from an open blending tank.

   Sample C-3

2. 2527 Grinding Coolant, which is similar to E55, was sampled from a closed blending tank.

   Sample C-4

C. Raw Materials

1. 80% triethanolamine - was sampled from a storage tank.

   Sample C-5

2. 40% sodium nitrite was sampled from a storage tank.

   Sample C-6

D. Laboratory Batch - a small batch of 1500 grinding concentrate was prepared in our presence.

   Sample C-9

ANALYTICAL METHODS

The procedure described by Fine et al was used to analyze the samples.[2] An aliquot (0.5 ml) of each sample was stirred with 20 ml ethylacetate and 10 ml acetone in the presence of sulfamic acid. The mixture was filtered through sodium sulfate and the filtrate analyzed by high

performance liquid chromatography - Thermal Energy Analysis (HPLC-TEA). The chromatographic conditions were:

Pump:	Altex Model 110
Injector:	Rheodyne 7120
Detector:	Thermo Electron TEA-502
Column:	Lichrosorb Si60 (4mm X 300mm)
Solvent:	Hexane/Acetone, 50:50
Flow rate:	2.0 ml/min.

RESULTS

The results of analysis are summarized in Table I. N-Nitrosodiethanolamine was detected in every sample except the 40% sodium nitrite. Concentrations ranged from 20 to 500 µg/ml (ppm). An unidentified, nonpolar, TEA-responding material was observed in Samples #1, 2, 5, 6, 7, and 9.

CONCLUSIONS

The presence of N-nitrosodiethanolamine (NDELA) represents a potential health hazard from dermal contact or inhalation. The occurence of NDELA in the 80% triethanolamine is one obvious source of product contamination. However, the laboratory batch of 1500 grinding concentrate contained 7 times as much NDELA as would come from the triethanolamine alone, and the packaged product contained almost 90 times the level of NDELA expected if triethanolamine were the only source of contamination.

RECOMMENDATIONS

1. Cutting fluid formulation should be developed that do not contain the essential precursors for the formation of nitrosamines.
2. Impervious gloves and clothing should be provided to avoid skin contact.
3. All exposed areas of the body and any area that becomes wet with cutting fluids should be washed with soap or mild detergent. Frequent showering is recommended.
4. Customers should be notified of the nitrosamine contamination, so that adequate precautions can be taken.

REFERENCES

1. Zingmark and Rappe (1976) AMBIO 5:80-81.
2. Fan et al. (1977) Science 196:170.

Table I

Concentration of an Unknown and N-nitrosodiethanolnitrosamine in Grinding Fluids

Sample	Concentration (µg/ml)	
Packaged Product	Unknown[1]	NDELA
C-1	20	27
C-2	900	500
C-7	7	90
C-8	N.D.[2]	63
Blending Tanks		
C-3	N.D.[2]	33
C-4	N.D.[2]	90
Raw Materials		
C-5	>200	22
C-6	>200	N.D.[3]
Laboratory Batch		
C-9	>200	66

1. Based on response factor for NDELA
2. N.D. - not detected (<10 ppm)
3. N.D. - not detected (<1 ppm)