UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

SUBJECT: Review A Study Of Formaldehyde Exposure From Metalworking Fluid Operations Using Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-Triazine

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## INTRODUCTION

Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine (Grotan), a bacteriostat, fungicide, and microbicide (slime-forming bacteria and fungi) formulated as a soluble concentrate liquid, is used in a variety of indoor non-food uses (e.g., adhesives, coatings, and metalworking cutting fluids) and industrial settings (e.g., oil recovery drilling muds/packer fluids and secondary oil recovery injection water). Application methods include metering pumps and open pouring for preservative treatments. The potential for mixer, loader, applicator exposure to this chemical exists.[1]

## BACKGROUND

Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine is a nitrogen-containing compound, which may decompose in an aqueous solution of metalworking fluids and release formaldehyde.[2] The carcinogenicity of Formaldehyde is the major hazard for potential health effects.

Substances which contain more than 0.1% formaldehyde must have labels and Material Safety Data Sheets (MSDS) indicating that it contains formaldehyde which is a carcinogen. This requirement is consistent with OSHA's Hazard Communication Standard (CFR 1910.1200). A revised standard requires manufacturers to assess whether a product may release formaldehyde, which could result in an eight hour time-weighted-average exposure above 0.1 ppm under "foreseeable conditions of use". If so, the product must be labelled indicating that it contains formaldehyde and that further information can be obtained from the MSDS. If the product may release formaldehyde above 0.5 ppm, the label must comply with appendices found in the OSHA formaldehyde standard, including the potential for respiratory sensitization, and contain the words, "Potential Cancer Hazard".

## PURPOSE OF THE JOINT VENTURE'S FORMALDEHYDE STUDY

Members of the Joint Venture determined that their products were exempt labelling requirements, due to preemption by EPA FIFRA requirements which regulate biocide labels. However, members of the Joint Venture decided to initiate a comprehensive workplace exposure monitoring study to assess the potential for Triazine to release formaldehyde under normal conditions of use at a number of different metalworking operations.

**Development of a Study Protocol**

Members of the Joint Venture discussed the various items which could influence the release of formaldehyde in the workplace. These included:

- The nature of the work and equipment used for machining.
- The concentration of Triazine in the metalworking fluid.
- The pH and temperature of the metalworking fluid.
- The size of the workplace.
- The ventilation which exists at a workplace.
- The level of bacterial contamination of the metalworking fluid.

**Study Protocol**

1. Site Selection

Aluminum can manufacturers were selected for testing because they consistently maintain an efficacious concentration of Triazine in metalworking fluids. A total of 12 locations and 550 samples were collected for analysis. Most Triazine users add concentrated biocide once or twice a week to maintain their metalworking fluid systems. Formaldehyde was monitored during the addition of concentrated Triazine, and immediately after addition when Triazine was at the highest concentration in the metalworking fluid. Typically, this was done in one day with monitoring for three to four hours in the morning before the addition of Triazine, monitoring for a short time (5-15 minutes) during the addition of Triazine , and additional monitoring for three to four hours after Triazine was freshly added to the metalworking fluid.

2. Methods of Exposure Monitoring

Monitoring was performed on employees cutting metal with machines using Triazine-containing metalworking fluid, in areas where employees typically worked, and at sources (e.g. metalworking fluid sumps) where the highest concentrations of formaldehyde were expected. Background formaldehyde levels were also measured at areas not using Triazine-containing metalworking fluid.

Formaldehyde were monitored by traditional NIOSH Method 3500 which employs the use of midget impingers containing 0.1% sodium bisulfite solution. It is reported to have a range of 2-40 ug with a limit of detection of 0.5 ug.

The other methods used for monitoring formaldehyde were DNPH (2,4-dinitro phenylhydrazine) Passisive Dosimeters-GMD 570 series, and DNPH Silica-Gel Tubes for higher sampling rate and low detection limit.

During most surveys, a freshly made solution of formaldehyde (in water) containing one microgram/microliter was taken into the field along with several micro-syringes. Samplers were spiked with known quantities of formaldehyde to approximate the quantities expected from a four hour sample at 0.1 ppm. These spiked samples were place alongside normal samples to verify that formaldehyde was able to be accurately measured.

3. Other Data Collected

In addition to exposure data, samples of the metalworking fluid were obtained prior to and after the addition of Triazine. These were taken back to a laboratory and analyzed within three to seven days for pH and Triazine levels.

**ACTION REQUESTED**

As requested by Kathryn Davis/Ron Kendall of ARB/SRRD, OREB reviewed "A study of Formaldehyde from metalworking fluid operations using hexahydro-1,3,5-tris (2-hydroxyethyl)-s-triazine" submitted by Nancy S. Bryson of Crowell & Moring, the representative for Triazine Joint Venture Formaldehyde Study on May 4, 1994 with MRID #43223201.

**STUDY DESIGN**

According to the study, air samples were taken at each location where no metalworking fluid was being used to determine background levels of formaldehyde. A number of these locations had detectable levels of formaldehyde. A statistical evaluation of the results of this study confirmed that there was a predictive relationship between Triazine levels in metalworking fluid and formaldehyde exposure. Regression analyses of the data indicated that levels of 250 ppm or less of Triazine were necessary to insure that no employee would be exposed to formaldehyde levels above 0.1 ppm. At the recommended dosage of Triazine in metalworking fluid (1000-1500 ppm), personal exposures would be expected to exceed 0.1 ppm of formaldehyde approximately 30-50 percent of the time.

**RESULTS**

The results from this study confirm that most metalworking fluid operations which use Triazine biocides will have some employee exposures above the 0.1 ppm level. However, the results of this study indicate that employees involved in these operations will not be exposed to formaldehyde levels at or above the OSHA Action Level of 0.5 ppm, or to exposures which would exceed the Short-Term Exposure Level of 2 ppm. The only exception could be employees who perform prolonged maintenance activities in poorly ventilated areas.

**CONCLUSIONS**

OREB has reviewed and evaluated the results of this study and concluded that the study meets the requirements of Subdivision U Pesticides Assessment Guidelines for the applicator and post-application exposure scenarios for machine workers using metal cutting fluids.

Based on an exposure of 0.1 ppm on daily basis, the carcinogenicity risk of exposure to formaldehyde is $2.3 \times 10^{-4}$. This calculation is based on the following information: 0.1 ppm = 0.125 $mg/m^3$ of formaldehyde, an inhalation rate for an average worker is 20 $m^3$ per 8 hr per day, with body weight of 70 kg, 250 work-day per year and 35 years of exposure during the lifetime of 70 years, and the Q* for formaldehyde is 0.0187.

cc: Winston Dang/OREB
Chemical File
Circulation
Correspondence

1. Use information based on the LUIS reported dated April 24, 1992 (memo 6/7/92) from Phyllis Johnson BEAD and the product labels (EPA Reg. Nos. 1258-1071, 1448-243, and 1769-241).
2. H.W.Rossmoore, "Disinfection, Sterilization and Preservative" 4th ed. 1991, Edited by Seymour S. Block, 1991, Chapter 17, "Nitrogen Compounds."