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Robinson Run Mine
Shinnston, West Virginia

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PREFACE

The National Institute for Occupational Safety and Health (NIOSH) conducts investigations and studies of possible health hazards in the workplace. These investigations are conducted under the authority of Section 501(a)(11) of the Federal Mine Safety and Health Act of 1977 (30 USC 801-962) 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 a coal mine has potentially toxic effects in the concentrations normally found in the coal mine."

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Joseph C. Cocalis, Carol Y. Rao, and Karen A. Kestenberg of the Field Studies Branch (FSB), Division of Respiratory Disease Studies (DRDS), and Jennifer E. Martin of the Exposure Assessment Branch (EAB) of the Health Effects Laboratory Division (HELD). Field assistance was provided by Coal Mine Safety and Health (CMSH) District 3 of the Mine Safety and Health Administration (MSHA). Analytical support was provided by Robert Glasser and Ardith Grote of the Chemical Exposure and Monitoring Branch (CEMB), Division of Applied Research and Technology (DART). Review and preparation for printing were performed by Molly Pickett-Harner. Desktop publishing was performed by Terry Rooney.

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Highlights of the NIOSH Health Hazard Evaluation at the Robinson Run Mine

NIOSH was asked by the United Mineworkers of America (UMWA) to conduct a health hazard evaluation at the Robinson Run Mine located in Shinnston, West Virginia

What NIOSH Did

- Administered a medical/work history questionnaire to 85 miners to determine the prevalence of nasal, respiratory, and dermal (skin) symptoms.
- Evaluated exposure to the hydraulic fluid used to pressurize longwall shields and to bacteria and fungi in the fluid, in the shearer spray water, and in the mine air.

What NIOSH Found

- The hydraulic fluid emulsion is similar in composition to a metalworking fluid. Susceptible individuals could have an allergic response to some of its components.
- A relationship between nasal, respiratory, and dermal symptoms and exposure to Solcenic HL hydraulic fluid emulsion could neither be established nor ruled out.
- Emulsion spillage or leakage can potentially release formaldehyde at NIOSH Recommended Exposure Limit (REL) concentrations during routine operations and at MSHA Permissible Exposure Limit (PEL) concentrations during large spills.
- The shearer water supply and mine air contained species of bacteria and/or fungi

that are associated (in the literature) with some of the reported symptoms in susceptible individuals.

What Managers Can Do

- Investigate alternative hydraulic fluids that can be used at greater dilutions.
- Implement a preventive maintenance program to identify and prevent system failures, minimize leakage during routine operations, and recover hydraulic fluid during longwall moves.
- Sample for formaldehyde during large spills.
- Provide medical monitoring for all employees who have routine contact with the hydraulic fluid emulsion.
- Provide additional treatment for the feed water to the shearer sprays.

What Employees Can Do

- Follow appropriate health and safety guidelines in the NIOSH Metalworking Fluids Criteria Document.
- Be aware of symptoms suggestive of asthma and dermatitis and the need for self-referral for medical evaluation.



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Health Hazard Evaluation Report 2000-0098

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Shinnston, West Virginia
July 2001**

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SUMMARY

On December 6, 1999, NIOSH received a confidential health hazard evaluation request regarding possible health effects in workers exposed to Solcenic HL hydraulic fluid at the Robinson Run Mine in Shinnston, West Virginia. Solcenic HL emulsion is used in the closed loop hydraulic system that pressurizes the piston-driven roof supports in the longwall section of the underground coal mine. Solcenic HL is a proprietary formulation of mineral oil, alcohol, poly glycol, inorganic salt, organic acid salt, and a triazine biocide. It is similar in formulation to emulsifiable metal working fluids which have been associated with respiratory disorders, work related asthma, and allergic and irritant skin disorders (NIOSH, 1998a).

We conducted telephone and on-site interviews with miners who were concerned that exposures to Solcenic HL emulsion might be putting them at risk for sinusitis, rhinitis, adult onset occupational asthma, and dermatitis, especially during periods of atypical exposure such as when working around large spills. We administered a medical-work history questionnaire on October 18, 19, and 20, 2000. Its purpose was to assess the prevalence of various respiratory and skin disorders and symptoms in relation to possible sources and pathways of exposure, especially to Solcenic HL emulsion. The questionnaire requested demographic data, a brief work history, possible workplace exposures, and included questions designed to identify individuals with sinusitis (nasal), breathing, and dermal (skin) disorders. Because Solcenic HL emulsion is only used at the longwall, miners were grouped as either "longwall miners" (potentially exposed individuals) or "nonlongwall miners" (minimally exposed or nonexposed individuals). The minimally exposed group includes some miners who occasionally assisted with relocation and maintenance of the longwall equipment. There were 85 respondents out of 250 current employees representing 100 percent (33/33) of the longwall workforce and about 25 percent (52/250) of the "nonlongwall workforce."

The prevalence of self-reported sinus or nasal symptoms that required medical attention was 24 percent (8/33) among longwall miners versus 48 percent (24/52) among miners whose primary work areas were other areas of the mine. Because the rate of symptoms was higher in the nonexposed group, there does not appear to be a positive relationship between the routine use of Solcenic HL emulsion and nasal/sinus symptoms. However, self-reporting bias is a possible explanation for the higher rate of symptoms in the nonexposed group; those without symptoms may not have been motivated to respond to the questionnaire. Exposure misclassification is another possible explanation; some of the "minimally exposed workers" may have experienced acute exposures to Solcenic HL emulsion during their temporary assignments to work on the longwall.

The prevalence of self-reported adult onset asthma was 6 percent (2/33) among longwall miners and 6 percent (3/52) among nonlongwall miners [For comparison, McWhorter et al. (1989) estimated the prevalence of active asthma among U.S. adults to be 2.6 percent.] Of the five self-reported cases, two worked on the longwall, two worked throughout the mine including the longwall, and one worked on a continuous mining section. Four of the five, including the continuous mining section worker, reported that "Solcenic" or "hydraulic fluid" exacerbated their

asthma symptoms. Self-reporting bias and misclassification are concerns, and we can neither establish nor rule out a relationship between exposure to Solcenic HL emulsion and self-reported adult onset asthma.

The prevalence of self-reported dermal symptoms that required medical treatment was 21 percent (7/33) for longwall miners and 25 percent (13/52) for other miners. Once again, self-reporting bias and misclassification are concerns, and we can neither establish nor rule out a relationship between exposure to Solcenic HL emulsion and self-reported mine-related dermatitis.

Concurrent with obtaining and evaluating the medical-work history information, we collected and analyzed samples of the bulk Solcenic HL, the Solcenic HL emulsion, emulsion leakage from the mine floor, and area samples of the mine air to characterize the work environment. We identified two agents that warranted further investigation. The first agent was formaldehyde (a breakdown product of the triazine biocide in Solcenic HL), which is associated with upper respiratory and dermal irritation and sensitization and is considered by NIOSH to be a potential occupational carcinogen. The second agent was microbials (i.e., bacteria and fungi) from the shearer sprays and the mine air, which are also associated with upper respiratory symptoms, adult onset asthma, and dermal symptoms.

The maximum concentration of formaldehyde in air during our sampling program was 0.027 parts per million (ppm). This is two orders of magnitude below the MSHA Permissible Exposure Limit (PEL) of 2 ppm, one order of magnitude below the American Conference of Governmental Industrial Hygienists (ACGIH) 2000 Threshold Limit Value (TLV) of 0.3 ppm, and similar in magnitude to the NIOSH Recommended Exposure Limit (REL) of 0.016 ppm. Although the PEL is the legally enforceable limit, employers are encouraged to follow the most protective criterion among the PEL, TLV and REL. The NIOSH REL for formaldehyde is a qualitative value based primarily on the analytical limit of detection. There were no large spills of Solcenic HL emulsion during our sampling program, but we believe that formaldehyde concentrations in air during atypical events have the potential to exceed the MSHA PEL.

We evaluated the possibility that triazine from spillage of Solcenic HL emulsion might adsorb onto or absorb into rockdust and be converted to formaldehyde after inhalation and deposition of the dust in the respiratory tract. The amount of triazine that might be adsorbed onto or absorbed into rockdust that becomes aerosolized and inhaled was found to be negligible.

In our microbial evaluation, we sampled the Solcenic HL emulsion from the hydraulic lines and found no bacteria and four colony forming units per milliliter (CFU/ml) of basidiomycetes and 2 CFU/ml of an unidentified fungus. These low levels of fungi in the emulsion could have originated from contact with equipment surfaces during sampling. We also sampled the shearer spray water for microbial content and found several species of bacteria that may be pathogenic or that are indicators of pathogenic potential. The shearer spray is fed by surface water that passes through a coarse sand filter before being sprayed to suppress dust from the shearer. Based on good public health practice, we recommend additional filtration or treatment for the shearer sprays.

We sampled the air on June 13-14, 2000, for fungi and bacteria. Fungi concentrations in the mine ranged to 9.6×10^3 CFU per cubic meter of air (CFU/m³) and bacteria concentrations ranged from below the level of detection to 1.4×10^5 CFU/m³. The predominant fungal genera outside the mine was *Cladosporium* and the predominant fungal genus inside the mine were *Cladosporium*, *Penicillia*, and basidiospores. The bacteria found in the mine air included *Actinomycetes*, *Rhodococcus*, *Actinobacter*, and *Pseudomonas*. Although these are ubiquitous environmental microbials, exposures to fungi and bacteria have been associated with sinus/nasal and asthmatic symptoms in susceptible individuals.

In conclusion, the hypothesis that miner exposures to Solcenic HL emulsion caused or exacerbated the reported health effects in some workers can neither be established nor ruled out. Exposure to formaldehyde is possible during atypical events such as large spills. Pathogenic microbial species were also found in both the shearer spray and the mine air, but their relationship to the reported symptoms is unknown. The following recommendations are

based on information derived from studies of metal working fluid exposed workers. Based on best work practices, it would be prudent to:

- Follow appropriate health and safety guidelines in the NIOSH Metalworking Fluids Criteria Document.
- Evaluate substitutes to Solcenic HL or components of Solcenic HL that may be used at dilutions that minimize the risk of nasal/sinus, respiratory, and dermal symptoms.
- Implement a preventive maintenance program for the longwall hydraulic system, with the goal of minimizing leakage and spillage of the Solcenic HL emulsion. Monitor the volumetric rate of consumption of Solcenic HL to identify system failures and to trigger preventive actions. Include routine recovery of the hydraulic fluid during longwall moves, rather than allowing it to spill out into the work area.
- Ensure that the manufacturer's instructions are followed to maintain the concentrations of the triazine biocide above levels necessary to prevent microbial growth in the emulsion, yet below the level that could cause miners to experience dermal effects and/or respiratory irritation.
- Implement a program to avoid skin contact with Solcenic HL emulsion.
- Provide an occupational medical monitoring program for all miners who routinely have skin contact with Solcenic HL concentrate or emulsion or who experience symptoms suggestive of sensitization. Consider implementing a program similar to that outlined in the NIOSH Metalworking Fluids Criteria Document.
- Provide all miners with appropriate education and training, particularly with respect to self-referral for medical evaluation if they develop symptoms suggestive of asthma, hypersensitivity pneumonitis, other respiratory conditions, or dermatitis.
- Sample for formaldehyde during atypical events such as large spills.
- Provide additional filtration or microbial treatment for the feed water supply to the shearer sprays.

NIOSH did not find a health hazard to exist during routine operations. However, nasal/sinus, upper respiratory, and dermal symptoms have been associated in the literature with exposure to components of the emulsion used in the mine and to the bacteria/fungi that were found in the shearer sprays and in the mine air. Air sampling indicates that the MSHA PEL for formaldehyde is unlikely to be exceeded during routine operations, although concentrations at or above the NIOSH REL are possible. Therefore, formaldehyde exposure should be measured during atypical events, such as large spills. To minimize symptoms among susceptible workers and to maintain formaldehyde concentrations below the NIOSH REL, recommendations are made to minimize exposures.

Keywords: Underground coal mining (SIC Code 1222), longwall, formaldehyde, triazine, biocide, hydraulic fluid, Solcenic, Solcenic HL, metalworking fluid, emulsion, microbial, spray water, sinusitis, asthma, bacteria, fungi.

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INTRODUCTION

On December 6, 1999, NIOSH received a confidential health hazard evaluation request regarding Solcenic HL exposures and possible health effects. Miners who intermittently came into contact with Solcenic HL expressed concerns that exposure to the emulsion may be related to “employees experiencing ill health.” Specific concerns that were identified through employee interviews and are addressed in this study include treatment by health care providers for recurring sinusitis, rhinitis, adult onset occupational asthma, and dermatitis.

This study was not designed to address other United Mine Workers of America (UMWA) health concerns related to allegations of a high incidence of heart disease and cancer at the mine. The UMWA presented NIOSH with a list of miners with heart disease and cancer that they believe are of occupational origin. NIOSH’s Pittsburgh Research Laboratory (PRL) is planning a larger-scale epidemiological study of heart disease among miners.

In addition, the UMWA has submitted a health hazard evaluation (HHE) request regarding possible elevated rates of hematuria in these miners. This was a result of a referral from a nephrologist. A separate HHE to investigate renal health-effects has been assigned to NIOSH’s Hazard Evaluation and Technical Assistance Branch (HETAB) in Cincinnati.

BACKGROUND

The Robinson Run mine uses the continuous and longwall methods to mine coal from the 7.5-16 foot thick Pittsburgh coal seam. Continuous miners are used to develop entryways for the longwall panel. The longwall panel is a 1000 foot wide passageway whose roof is supported by 98 hydraulic shields. A track mounted, chain driven shearer with a rotating drum takes a 2-foot deep cut from the seam of coal as it moves up and down the 1000-foot face. The

shearer is equipped with water sprays that are used for dust suppression. The cut coal falls onto a panline and is transported to the headgate (fresh air entry point to the longwall panel). At the headgate, the coal passes through a stage loader and onto a beltline where it is transported out of the mine along a fresh air entryway. The longwall panel is ventilated with approximately 60,000 cubic feet per minute of fresh air that passes from headgate to tailgate. The longwall sections are associated with high relative humidity (i.e., >70 percent) during the summer months as a result of intake air being cooled to mine temperature (about 70-74 degrees Fahrenheit dry bulb during the summer) and as a result of water sprays being applied as a dust suppressant at the shearer and along the beltline.

Approximately 250 miners work at the Robinson Run mine. During a production shift, typical jobs on the longwall include:

- stage loader operator (headgate area),
- shieldman (positioned along the face, i.e., headgate to tailgate),
- shieldman helper (positioned along the face)
- two shearer operators (positioned along the face),
- two electrician/mechanic (one usually at face),
- two timbermen (sometimes relieve shearer operator), and
- scoop operator (mainly in the headgate area).

There are two production shifts per day, seven days per week, with maintenance performed on the swing shift. Any of the 250 miners may be positioned on the longwall during teardowns and setups (longwall moves) which occur over a 3-6 day period 2-3 times per year.

Solcenic HL

Solcenic HL is a hydraulic fluid that is mixed into a 4 percent emulsion with water and then pressurized to about 4500 pounds per square inch in a closed loop system that holds up the supports (shields) on an underground coal mine longwall panel. It is manufactured by Century Lubricants Company, 2140 S. 88th Street, Kansas City, Kansas 66111-8701.

Century Lubricants is a subsidiary of Fuchs Petrolub AG.

Century Lubricants requested that NIOSH treat the formula for Solcenic HL, which is similar in formulation to an emulsifiable metal working fluid, as trade secret. Based on the Material Safety Data Sheet (MSDS) for Solcenic HL, which is included as Appendix A, components include:

- triazine compound,
- mineral oil,
- alcohols,
- organic acid salt,
- poly glycol, and
- inorganic salt.

The triazine compound acts as a biocide by decomposing into formaldehyde.

In 1997, Solcenic HL was introduced into the hydraulic lines at the Robinson Run mine replacing Solcenic 2 and 3, B Series. The reason for the change was that new equipment specifications called for a hydraulic fluid with greater lubricity.

Solcenic HL concentrate was delivered, at 3-5 week intervals, in 5,000-gallon truckloads to an 8,000-gallon tank that is located in a surface building. The dilution ratio is 24 parts water to one part Solcenic HL concentrate. The 4-percent emulsion is piped from the surface by gravity feed some 3.5 miles into the mine to replenish losses in a closed loop system. Based on a estimated annual delivery of 65,000 gallons of concentrate (one truckload every four weeks) and a dilution rate of twenty four parts water to one part concentrate, approximately 1,500,000 gallons of the diluted emulsion were piped into the hydraulic system in the preceding year. Most of emulsion used in the hydraulic system ends up as leakage into the mine environment. Sources of leakage include hydraulic line couplings, shield control boxes, pistons used to move shields, hydraulic line breaks, hydraulic line maintenance, and shield teardown and setup activities.

Rockdust (calcium carbonate) is applied throughout the mine to roof, walls, and floor to inhibit the

propagation of coal dust explosions. It is also used to soak-up large puddles of spilled Solcenic HL emulsion when major spillage occurs. After being applied to the mine floor to soak-up spilled emulsion, the rockdust typically is left in place. Concerns were raised that triazine biocide used to control microbial growth in the emulsion would adsorb onto or absorb into the rockdust, become aerosolized with rockdust, and convert to formaldehyde, a known irritant and carcinogen, after depositing in the upper respiratory system.

Microbials

Given the moisture-laden environment and the high potential for respiratory exposures, microbial contaminants in the mine were of interest. Underground miners have been shown to have higher prevalence of fungi detected in throat swabs than non-miners (Šrám *et al.*, 1993). There are indications that microbial exposures in an underground mine may be a contributing factor in the development and exacerbation of adverse respiratory symptoms. A study has shown that the source of the water for dust control systems was associated with respiratory symptoms (Wang *et al.*, 1999). Potential microbial contamination of the water was a plausible explanation. One case report has linked occupational asthma in an underground coal miner with exposures to fungi (Gamboa *et al.*, 1996). Currently, there are no exposure standards for airborne levels of noninfectious microbials in the work environment (Rao *et al.*, 1996).

All microorganisms produce antigens – molecules, often proteins or polysaccharides, that stimulate the immune system. A single exposure to an antigen may result in sensitization. If the sensitized person is exposed again to the same antigen, a hypersensitive or allergic response may occur to an antigenic dose that would elicit little or no reaction from nonsensitized persons. Allergic reactions to inhaled antigens may be limited to the upper respiratory tract (e.g., allergic rhinitis), or they may affect the distal airways (e.g., allergic asthma), or the distal portions of the lung (e.g., hypersensitivity pneumonitis). Because these are some of the same health concerns

reported by miners, microbial exposure was investigated as a confounding exposure.

There are three potential sources of microbial exposures addressed in this report: bacteria and fungi in shearer sprays, bacteria and fungi in the mine air, and bacteria and fungi in the hydraulic fluid emulsion itself.

The dust suppression system in the mine uses surface water from two ponds formed by the impoundment of streams. The water passes through a 150-micrometer filter before being sprayed onto the longwall face during shearing operations. The water at the surface is treated intermittently with copper sulfate to prevent or reduce the effect of algae blooms. A consultant to Consolidation Coal Company sampled the spray water at the face of the mine between July 8 and October 10, 2000 (Alarie, 2000). He found:

- <1 Colony Forming Unit per milliliter (CFU/ml) of *Legionella* spp,
- negative results for *Legionella pneumophila*,
- 13.5 Endotoxin Units per milliliter (EU/ml),
- 1 (positive) Total Coliform,
- 650 CFU/ml Viable Bacteria ,
- 10 CFU/ml *Actinomyces*, and
- <10 CFU/ml Viable Fungi.

He recommended that appropriate remediation should be undertaken if future sampling results exceed criteria he specified.

METHODS

Medical Survey

NIOSH conducted telephone and on-site interviews with miners who were concerned that exposures to Solcenic HL might be putting them at risk for sinusitis, rhinitis, adult onset occupational asthma, and dermatitis, especially during periods of atypical exposure such as when working around large spills.

We administered a medical-work history questionnaire on October 18, 19, and 20, 2000. Its purpose was to assess the prevalence of various respiratory and skin disorders and symptoms. The questionnaire requested demographic data, a brief work history, and possible workplace exposures and included questions designed to identify individuals with sinusitis (nasal), breathing, and dermal (skin) disorders. Because Solcenic HL is only used at the longwall, workers were grouped as either “longwall miners” (potentially exposed individuals) or “nonlongwall workers” (minimally exposed or nonexposed individuals). The minimally exposed group includes some miners who occasionally assisted with relocation and maintenance of the longwall equipment. There were 85 respondents out of 250 current employees representing an estimated 100 percent of the longwall workforce and 25 percent of the “nonlongwall” workforce. Appendix B contains the questionnaire.

Environmental Survey

During the initial site visit on February 14, 2000, NIOSH conducted a visual inspection of the longwall and the hydraulic system. Bulk samples were taken of water on the mine floor, fresh water line leakage from the wetdown hose, emulsion from #45 shield ram-jack leakage, emulsion from #35 shield valve bank leakage, emulsion from #45 shield leakage on the floor, emulsion near the pump area on the floor, and Solcenic HL concentrate from the 8000-gallon capacity surface storage tank. These samples were analyzed for pH (to assist in determination of the potential for dermal (skin) irritation and to assist in the analyses of the fate of triazine which decomposes to formaldehyde in the presence of acids).

Chemical Evaluation

Limiting dermal exposure is critical to preventing allergic and irritant skin disorders related to metalworking fluid exposure. The method used during this survey to assess dermal exposure was to observe situations where exposures may occur (such as leaks and spills) and base recommendations for

corrective action on good industrial hygiene practice (e.g., minimize potential dermal exposures through maintenance, recovery of emulsion during longwall moves, oversight of emulsion concentration, etc.). Observation-based corrective action is preferred to sampling-based corrective action because:

- dermal exposures are difficult to quantify;
- when dealing with leakage in a coal mine environment, exposures are expected to be highly variable, making sample results difficult to interpret;
- there are numerous ingredients in a dilute emulsion and toxicological data on them and their interaction is sparse; and
- it is good industrial hygiene practice to minimize leakage or spills of any chemical.

Miners have the potential to be exposed to formaldehyde, and other products from decomposition of the triazine biocide, and to the triazine biocide itself. Although it would have been useful to have conducted direct air sampling for triazine, it is not currently practical.

Because sampling methods for the triazine in air do not exist, we used standard NIOSH methods to sample for formaldehyde, a decomposition product of triazine. On June 13-14, 2000, formaldehyde samples were taken with SKC silica gel 2,4-dinitrophenyl hydrazine sorbent tubes at one liter per minute (L/min) for 120 minutes. Samples were collected at four locations:

- Above ground at outside air intake;
- Underground at longwall headgate; this location was upstream from the shearer.
- Underground along the shearer path; samples were collected while moving with the shearer. Interferences from dust suppression sprays on the shearer were possible.
- Underground at longwall tailgate; this location was downstream from the shearer.

The samples were analyzed by DataChem Laboratories, Inc., Salt Lake City, Utah, using NIOSH Method 2016 (NIOSH, 1998b).

Bulk samples were also taken for analyses by gas chromatography - mass spectrometry (GC-MS).

On August 25, 2000, formaldehyde samples were taken during a longwall move (teardown and setup). In addition, air samples for formaldehyde-containing dusts were taken on 25-mm polyvinyl chloride filters using a modified NIOSH Method 5700 (NIOSH, 1994a). The original sample extracts were adjusted to a pH of 2 with concentrated hydrochloric acid and reinjected into the gas chromatograph.

NIOSH also sampled the shearer spray water, Solcenic HL emulsion, rock dust, and leakage from the mine floor. The samples were analyzed by GC-MS to screen for basic chemical composition. In addition, a bulk sample rock dust was soaked in the emulsion, filtered and analyzed by GC-MS using a RTX-5 amine column.

On October 12, 2000, MSHA submitted an independent set of bulk samples for analysis of the Solcenic HL concentrate, Solcenic HL emulsion, and a mixture of Solcenic HL and rock dust. The emulsion and the mixture samples were extracted with methanol, filtered, and analyzed. The raw Solcenic HL was analyzed directly.

Bacteria and fungi

On June 13-14, 2000, samples for bacteria and fungi in air were collected on 0.2 micrometer (μm) polyethersulfone filters using open-faced 37-millimeter (mm) cassettes at four locations. Air was drawn through the filters at a rate of 2.5 L/min for either 3 or 5 minutes. The filters were washed, serially diluted, and then cultured onto malt extract agar (MEA) for fungal count and speciation, or cultured onto trypticase soy agar (TSA) for bacteria counts and speciation. In addition, bacteria and fungi were collected in ViaTrap® mineral oil with an SKC BioSampler™ at 6.5 L/min at each of the four locations. The sampling time was approximately two hours. Samples were analyzed for culturable fungi

and bacteria counts and speciation by plating onto MEA and TSA.

Four bulk samples were collected for microbial analyses: Solcenic HL concentrate from the above-ground storage tank; water from the nozzle of the shearer dust suppression system; Solcenic HL emulsion from the underground recycle loop; and Solcenic HL emulsion leaking from the #4 shield. Samples were cultured for fungi and bacteria counts and speciation on MEA, TSA, and R2A. Total coliform and *Escherichia coli* (*E. coli*) were analyzed by SM 9222B on m-Endo broth.

Identification and speciation of *Mycobacterium* was done on Mitchison 7H11 media. Culturable *Legionella* identification and enumeration was done using CDC "Procedures for the Recovery of *Legionella* from the Environment" (1992). All of the microbiological analyses were conducted by P & K Microbiology Services, Inc., Cherry Hill, New Jersey.

RESULTS

Medical

There were 85 respondents out of approximately 250 workers at this mine. The mean age of the respondents was 50 (range 38-63); 99 percent (84/85) were male; and 96 percent were Caucasian. The respondents' work areas were:

- longwall (33),
- continuous miner (15),
- belt (5),
- other or rover (18),
- underground maintenance shop (2),
- and surface (12).

The 33 respondents whose reported work area was the longwall represent most of the longwall workers, based on 10-15 miners working the longwall per shift for two shifts per day and five working the longwall on swing shift. The miners who reported working areas other than the longwall represent about 25 percent of the nonlongwall workforce.

Table 1 lists the number of miners, by primary work area, who sought medical intervention for nasal/sinus and dermal symptoms and who reported breathing symptoms.

Nasal/sinus symptoms

Ninety percent (77/85) of the respondents reported nasal and sinus symptoms (i.e., persistent stuffy or blocked nose, nasal discharge, running nose or drainage, episodes of sneezing, nose bleeds, or sinus headaches or face pains). Of those, 45 percent (35/77) sought medical intervention for sinusitis or sinus symptoms. The miners who sought medical intervention attributed "Solcenic," "dust," and "longwall" as factors that exacerbate symptoms.

Breathing symptoms (including asthma)

The breathing questionnaire was designed to identify miners experiencing lower respiratory system breathing symptoms in the preceding 12 months. Seventy-eight percent (66/85) of the respondents had one or more breathing symptoms. Six individuals had been diagnosed with asthma, with three of the six diagnosed between 1994 and 1997 when Solcenic 2 and 3, B Series hydraulic fluid was used at the mine. Two of six with adult onset asthma were diagnosed in or after 1997, the year Solcenic HL was introduced into the mine environment. Of the 66 respondents reporting respiratory symptoms, 59 claimed their breathing symptoms occurred after 1989. In descending order of importance, "Solcenic" and "dust" were named as the materials or chemicals that exacerbated lower respiratory symptoms.

Dermal symptoms

The skin rash or dermal questions ascertained that 48 percent (41/85) of respondents self-reported some sort of a dermal complaint on their hands, arms, or body. Eighty-eight percent (36/41) reported that they noticed a rash as early as 1990. Twenty (49 percent) (20 of the 41) stated it was necessary to seek medical

treatment for their condition. Exposures to the head and feet were also self-reported. Miners, when asked to explain their condition, listed the following as anecdotal descriptions: redness, dry skin with scaling, itching, burning, prickling and stinging, and pain.

Environmental

During the initial site visit on February 14, 2000, NIOSH conducted a visual inspection of the longwall and the hydraulic system. Hydraulic fluid emulsion leakage was observed at multiple points along the longwall with the most leakage near the tailgate. We also observed drippage of small amounts of emulsion onto miners' clothing. Because the face area is confined, miners intermittently walk through small puddles of leaked emulsion, providing additional opportunities for dermal contact. A mild chemical odor was detected in the vicinity of the leakage. Several miners reported that failures of the high pressure lines sometimes results in breaks that spray a fine mist of hydraulic fluid emulsion into their breathing zone and onto their faces and clothing.

The longwall face area was wet, making conditions conducive for microbial growth.

During a previous NIOSH investigation into the use of a wetting agent at the Robinson Run Mine [NIOSH (Hewett), 1995], water samples were collected on December 19, 1994, and analyzed for copper. All sample results were below the limit of quantification of 20 micrograms per liter. Because an algae bloom requiring treatment had not occurred immediately prior to this survey, copper sulfate had not been recently added to the holding pond, and analyses for copper was not conducted.

Bulk samples from February 14, 2000

The pH of samples taken on February 14, 2000, is shown in Table 2.

Bulk samples from June 13-14,

2000

Solcenic HL concentrate from the 8000-gallon above ground tank

Legionella, *Escherichia coli* (*E. coli*), other coliforms, other bacteria, and fungi were not detected in the sample taken on June 13, 2000. Triazine and oxazoladine biocides were present but not quantified in the concentrate (the GC-MS method was used to identify components such as triazine and oxazoladine and not to accurately quantify them).

Solcenic emulsion from Shield #4 leak

Legionella, *E. coli*, other coliforms, and other bacteria were not detected in the sample taken on June 13, 2000. Trace amounts of triazine and oxazoladine were present in the emulsion. Four CFU/ml of basidiomycetes were detected.

Solcenic emulsion from recycle tank

Legionella, *E. coli*, other coliforms, and other bacteria were not detected in the sample taken on June 13, 2000. Two CFU/ml of an unidentified fungus were detected in the sample. This sample was not analyzed for triazine and oxazoladine.

Shearer nozzle water

Low concentrations of the fungus *Trichoderma koningii* were detected in the shearer water (2 CFU/ml). *Legionella* was not detected in the bulk sample. There were 8 CFU of *E. coli*/100 ml. The total coliform level was 8 CFU/100 ml. Total bacteria concentration was 3.2×10^3 CFU/ml. The species *Burkhoderia cepacia* constituted approximately half of the bacteria with *Brevendimonas diminuta*, *Chromobacterium violaceum*, and gram-negative bacteria making up the remainder.

Bulk samples from August 25, 2000

Figures 1-3 are total ion chromatograms from the mass spectral analyses of the Solcenic HL concentrate from the 8000-gallon aboveground storage tank (Figure 1), the emulsion from the hydraulic lines (Figure 2), and the leakage taken from the mine floor (Figure 3).

Shearer nozzle water

No organic compounds were detected.

“Rock dust” extract

No organic compounds were detected.

Solcenic HL emulsion

Ethanolamine, a glycol ether compound, a series of aliphatic oxy-compounds (possibly alcohols), and a series of unresolved aliphatic hydrocarbons (typical pattern of a mineral oil type constituent) were detected in the sample.

Leakage on the mine floor

Ethylene glycol, a glycol ether compound, aliphatic oxy-compounds, and aliphatic hydrocarbons were the main compounds detected. A trace amount of morpholine was also detected.

Leakage around the hydraulic fluid recirculation pump

A glycol ether compound was detected. Trace amounts of several other components were also detected including ethylene glycol, diethylene glycol, dipropylene glycol isomers, acetic acid, hexanal, and some nitrogen compounds.

Bulk samples submitted by MSHA on October 12, 2000

Solcenic HL concentrate

Ethanolamine, a glycol ether compound, aliphatic alcohols, aliphatic hydrocarbons, oxazolidine, and triethanoltriazine were detected.

Solcenic HL emulsion

Ethanolamine, a glycol compound, aliphatic alcohols, and aliphatic hydrocarbons were detected. Traces of oxazolidine were present.

Mixture of Solcenic HL and rock dust

Ethanolamine, a glycol compound, aliphatic alcohols, and aliphatic hydrocarbons were detected. Traces of oxazolidine and triethanoltriazine were present.

Air Samples from June 13-14, 2000

Table 3 summarizes the results of air sampling for fungi.

Outdoors

Cladosporium was the predominant fungal genus found at the intake to the mine. *Cladosporium* is commonly found in the outdoor air. Total fungi concentrations ranged from below the level of detection to 1.5×10^4 CFU/m³. Bacteria levels in the outdoor air were below the detection level of the sampling method.

Formaldehyde concentrations ranging up to 0.006 ppm were detected in outdoor air on June 13-14, 2000.

Headgate Area

Basidiomycetes (mushroom spores) and *Penicillium chrysogenum* were the most commonly recovered fungi at the headgate area. Concentrations ranged from 980-4100 CFU/m³, depending upon the activities in the headgate area (e.g., shearer at headgate versus shearer and tailgate). *Actinomyces* were the most commonly recovered bacteria in the headgate samples (from below the limit of detection to 1.4×10^5 CFU/m³).

Formaldehyde concentrations ranging up to 0.006 ppm were detected in the headgate area on June 13-14, 2000.

Mid-gate Area

The predominant groups of fungi in the mid-gate area were *Penicillium chrysogenum*, basidiospores and *Cladosporium*. Concentrations ranged from 740-9500 CFU/m³. The highest concentrations were measured during shearing activities. *Actinomyces* and *Rhodococcus* were the most commonly found bacteria in the shearer location. *Actinobacter* and *Pseudomonas* were recovered at the shearer on the second day when the sampling basket was placed on the shearer. Total bacterial concentrations ranged from below the limit of detection to 2.4 x 10⁴ CFU/m³.

Crosscut near beltline

One sample was taken at this location. The fungal concentrations were 6400 CFU/m³. *Actinomyces* concentrations were 1.5 x 10⁴ CFU/m³.

Formaldehyde concentrations ranging up to 0.027 ppm were detected in the mid-panline area on June 13-14, 2000.

Tailgate Area

The predominant groups of fungi found in the tailgate area were *Penicillium chrysogenum* and basidiospores. Concentrations ranged from 250-4000 CFU/m³. The majority of the samples were below the limit of detection for bacteria in air.

Formaldehyde concentrations ranging up to 0.016 ppm were detected in the tailgate area on June 13-14, 2000.

Air samples from August 25, 2000

During longwall teardown and set-up

Formaldehyde concentrations in air up to 0.02 ppm were measured at the teardown area. The measured formaldehyde concentrations in air at the setup area ranged to 0.009 ppm.

Formaldehyde concentrations on mine dust were below the limit of detection (LOD, 0.01 ppm per sample). When the sample extracts were adjusted to a pH of 2 with concentrated hydrochloric acid and

reinjecting into the gas chromatograph (to estimate if triazine could be converted to formaldehyde), the formaldehyde concentrations were found to be between the limit of detection and the limit of quantification (LOQ) (0.03 ppm). Three of four pH adjusted field blanks also had detectable levels of formaldehyde between the LOD and the LOQ.

DISCUSSION

Medical

The prevalence of self-reported sinus or nasal symptoms that required medical attention was 24 percent (8/33) among longwall miners versus 48 percent (24/52) among miners whose primary work areas were other areas of the mine. Because the rate of symptoms was higher in the nonexposed group, there appears to be an inverse relationship between the routine use of Solcenic HL and nasal/sinus symptoms. However, self-reporting bias is a possible explanation for the higher rate of symptoms in the nonexposed group; those without symptoms may not have been motivated to respond to the questionnaire. Exposure misclassification is another possible explanation; some of the “minimally exposed workers” may have experienced acute exposures to Solcenic HL during their temporary assignments to work on the longwall. During longwall moves (teardown and set-up), some miners reported working in and around large puddles of emulsion during which atypical exposure occurred. Miners reported that on the latest move (January 2001) the emulsion was recovered and the potential for exposure was greatly reduced.

The prevalence of self-reported asthma with onset after 1990 was 6 percent (2/33) among longwall miners and 6 percent (3/52) among nonlongwall miners. [For comparison, McWhorter *et al.* (1989) estimated the prevalence of self-reported asthma among U.S. adults to be 2.6 percent]. Of the five self-reported cases, two worked on the longwall, two worked throughout the mine including the longwall, and one worked on a continuous mining section. Four of the five, including the continuous mining

section worker, claimed that “Solcenic” or “hydraulic fluid” exacerbated their asthma symptoms. Self-reporting bias and misclassification are concerns, and we can neither establish nor rule out a relationship between exposure to Solcenic HL and self-reported adult onset asthma.

Miners may have had other exposures that contributed to these symptoms such as a wetting agent that was in use at the Robinson Run mine during the 1994-1995 time-frame [NIOSH (Hewett), 1995].

The prevalence of self-reported dermal symptoms that required medical treatment was 21 percent (7/33) for longwall miners and 25 percent (13/52) for other miners. Once again, self-reporting bias and misclassification are concerns, and we can neither establish nor rule out a relationship between exposure to Solcenic HL and self-reported mine-related dermatitis. Reported anecdotal histories from miners indicate that dermal contact with emulsion results from intermittent splashing, breaking of hydraulic hoses, spills, and inability to clean up after exposure.

Thoracic Particulate Mass

Solcenic HL emulsion is similar in composition to a water emulsifiable metalworking fluid. The NIOSH metalworking fluid method for thoracic particulate mass is not applicable to longwall miners who are potentially exposed to hydraulic fluids because of interferences from the relatively high thoracic coal dust concentrations on longwall sections (downstream of the shearer).

Triazine and Formaldehyde (a breakdown product of triazine)

Some miners felt that exposures to Solcenic HL emulsion resulted in sensitization and bleeding in the upper respiratory tract. Of the major components of Solcenic HL, we hypothesized that the triazine biocide was a plausible causal agent [Detwiler-Okabayashiet *et al.* (1996)]. Based on an assumed maximum triazine concentration ranging from 1000-

2000 ppm in the hydraulic fluid emulsion (the concentration recommended for removal of heavy fungal contamination from a metal working fluid), the maximum triazine concentration in the leakage is estimated to be in the 0.1-0.2 percent range. Triazine has been found to be sensitizing in some individuals (Angus Chemical Co., 1997). In early studies reviewed by Rycroft (1978), patch testing in occupational groups exposed to triazine (as Grotan BK) resulted in sensitization rates ranging from 0 to 8 percent; tested concentrations ranged from 0.1 to 1 percent triazine. Pre-existing eczematous dermatitis may have increased the likelihood of sensitization in some test subjects. In a more recent study, a 1 percent concentration of triazine (as Grotan BK) produced positive sensitization reactions in 1 percent of 1772 patients with suspected allergic contact dermatitis (Schnuch *et al.*, 1998). Therefore the review data support the hypothesis that sensitization to a small number of miners is possible at dilutions used in mining.

The qualitative concentration of the triazine biocide in the emulsion samples taken from the longwall panel varied from “none detected” to “trace amounts of triazine.” Although triazine was not found in all of the samples, its degradation products (oxazoladine and ethanolamine) were found in all of the emulsion bulk samples (in trace amounts). The absence of and/or presence of only trace amounts of triazine in the emulsion is an indicator that contact with acidic microbial waste products in the emulsion result in the decomposition of triazine and the release of formaldehyde.

Likewise emulsion leakage that comes into contact with acidic mine water or acidic water from the wetdown hose (Table 2) may also release formaldehyde.

Area sampling for formaldehyde measured concentrations up to 0.027 ppm over the two sampling trips with the highest levels measured at the tailgate (downstream of areas where leakage was observed) and in a crosscut near the recirculation pump (an area with poor ventilation). Although these results are two orders of magnitude lower than the PEL and one order of magnitude lower than the

TLV concentration, they demonstrate that above background and REL concentrations of formaldehyde are possible.

Appendix C contains guidance on how much leakage can occur before REL concentrations of formaldehyde along the longwall face are possible. This guidance can assist in the determination of situations where concentrations are likely to be below the REL for formaldehyde and of situations when sampling for formaldehyde is warranted. It is a conservative estimate, that is purposely designed to be protective of workers and should not be used to estimate formaldehyde exposure.

pH

The pH of the concentrate and emulsion leakage ranged from 8 to greater than 10 (Table 2). As such they are bases, may irritate the eyes and skin, and should be kept away from strong oxidizers.

Evaluation Criteria

A discussion of the evaluation criteria used in this report is found in Appendix D.

The formaldehyde air sampling results are compared to the NIOSH REL, the MSHA PEL, and the ACGIH TLV.

- NIOSH REL: While the formaldehyde concentrations approached or slightly exceed the REL, the samples were area samples. Personal samples are a better measure of actual exposure. The results demonstrate the potential for personal exposures above NIOSH REL concentrations and the need to implement controls to minimize unnecessary exposure. The NIOSH policy on the hierarchy of controls is to give priority to elimination of hazards through substitution where feasible. It may be feasible to reduce the possibility of exposures to formaldehyde vapors that exceed the REL by using the technical basis for hydraulic fluid performance to

determine if triazine biocides in Solcenic HL could be used at greater dilutions. If substitution is not feasible, engineering and administrative controls such as improved maintenance to control leaks and recycling of the emulsion during longwall moves should be implemented.

- MSHA PEL: Sampling indicates that the MSHA PEL of 2 ppm (ceiling) is unlikely to be exceeded during routine operations. The likelihood of exceeding the MSHA PEL when working around spillage in poorly ventilated areas or around large spills is unknown.
- ACGIH TLV: The current TLV, 0.3 ppm (ceiling) has A2 (Suspected Human Carcinogen) and SEN notations (SEN refers to the confirmed potential for worker sensitization as a result of dermal contact and/or inhalation exposure). To comply with the TLV, dermal contact with formaldehyde releasing emulsions should be avoided. Sampling indicates that the ACGIH TLV of 0.3 ppm (ceiling) is unlikely to be exceeded during routine operations. The likelihood of exceeding the ACGIH TLV when working around spillage in poorly ventilated areas or around large spills is unknown.

One hypothesis that was tested and rejected was that miners may be indirectly exposed to formaldehyde via rockdust (calcium carbonate) that is used to soak-up spilled emulsion. Traditional adsorbent tube sampling methods will not accurately assess formaldehyde exposure via this route. In this scenario, the basic pH of the rockdust prevents the triazine in the emulsion from degrading to formaldehyde. Mine activity causes the rock dust on the mine floor to become resuspended in air and deposit in the upper respiratory tract. Depending on the pH of the mucosal membranes and/or the presence of bacteria in these membranes, the triazine in the rockdust could degrade to formaldehyde. The laboratory experiments with a mixture of rock dust and Solcenic HL concentrate demonstrated that this pathway is unlikely

Microbial Sampling

Sampling for airborne bacteria and fungi in the mine environment was problematic. Sampling method options were limited by pump permissibility (the pumps certified for use in potentially explosive mine environments do not have the sufficient flow rate capacities needed for sampling bioaerosols).

The concentrations of airborne fungi could not be accurately quantified due to the brief sampling times (3 or 5 minutes), potential interferences from coal dust and shearer sprays, and potential negative bias from filter transfers and low air flows through the Biosampler.

Microbial content of shearer sprays

Drinking water standards for *E. coli* and total coliforms may apply because some of the inhaled bacteria will end up ingested due to mucociliary activity in the respiratory tract. Therefore, it would be prudent to prevent possible inhalation and ingestion of contaminated mine water sprays either by limiting water spray exposures and/or by decreasing the microbial contamination in the spray water. NIOSH recommends that water sprays from surface sources be treated so that they are free of fecal coliforms and *E. coli*. (NIOSH HETA 93-968, 1993)

Fungi in the emulsion

The low levels of fungi found in the emulsion (4 CFU/ml basidiomycetes and 2 CFU/ml unidentified fungus) may have originated from contact with equipment surfaces during sampling and indicate that the biocide in the emulsion was effective.

Airborne bacteria and fungi

Although these data cannot be linked to any specific health effect, they do serve to clarify several issues. The predominant fungi found in the mine environment (*Penicillium*) were different than that found outside the mine at the intake (*Cladosporium*)

which indicates that there may be reservoirs of fungi within the mine (Table 3). The concentration of fungi in the shearer water was low (2 CFU/ml) which suggests that there are other fungal reservoirs. For example, some of the miners reported mushroom growth inside the mine. Based upon the results of our sampling protocol, fungal reservoirs could not be definitively identified. Activity level (e.g., shearer on) and location (e.g., upwind or downwind of the shearer) affected recovery of species and concentrations of airborne bacteria and fungi. At the Midgate and Headgate locations, actinomycetes were recovered in 55 percent of the filter samples. Airborne exposures to thermophilic actinomycetes have been associated with hypersensitivity pneumonitis (Kotimaa, 1984). The species of bacteria recovered in air were not similar to the species recovered in the suspected reservoir (i.e., the shearer water). This may be a limitation of the sampling methodology or there may be other potential bacterial reservoirs.

CONCLUSIONS

The hypothesis that miner exposures to Solcenic HL emulsion caused or exacerbated the reported health effects in some workers was not supported by questionnaire and sampling data. A relationship can neither be established nor ruled out based upon the low response rate and sampling limitations.

Exposure to formaldehyde vapors is possible during atypical events such as large spills.

Pathogenic microbial species were found in both the shearer spray and the mine air, but their relationship to the reported symptoms is unknown.

The hypothesis that miner exposures to both the emulsion (specifically formaldehyde from the triazine biocide) and/or bioaerosols could have caused or exacerbated the reported health effects in some workers cannot be established or ruled out.

RECOMMENDATIONS

The following recommendations are based on information derived from studies of metal working fluid exposed workers. Based on best work practices, it would be prudent to:

- Follow appropriate health and safety guidelines in the NIOSH Metalworking Fluids Criteria Document.
- Evaluate substitutes to Solcenic HL or components of Solcenic HL that may be used at dilutions that minimize the risk of nasal/sinus, respiratory, and dermal symptoms for technical feasibility.
- Implement a preventive maintenance program for the longwall hydraulic system, with the goal of minimizing leakage and spillage of the Solcenic HL emulsion. Monitor the volumetric rate of consumption of Solcenic HL to identify system failures and to trigger preventive actions. Include routine recovery of the hydraulic fluid during longwall moves, rather than allowing it to spill out into the work area.
- Ensure that the manufacturer's instructions are followed to maintain the concentrations of the triazine biocide above levels necessary to prevent microbial growth in the emulsion, yet below the level that could cause miners to experience dermal effects and/or respiratory irritation.
- Implement a program to avoid skin contact with Solcenic HL and its emulsion.
- Provide an occupational medical monitoring program for all miners who routinely have skin contact with Solcenic HL emulsion or who experience symptoms suggestive of sensitization. Consider implementing a program similar to that outlined in the NIOSH Metalworking Fluids Criteria Document.

- Provide all miners with appropriate education and training, particularly with respect to self-referral for medical valuation if they develop symptoms suggestive of asthma, hypersensitivity pneumonitis, other respiratory conditions, or dermatitis.
- Sample for formaldehyde in air during atypical events such as large spills.
- Provide additional filtration or microbial treatment for the feed water supply to the shearer sprays.

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Table 1
Results of Medical/Work History Questionnaire for Robinson Run Miners
HETA 2000-0098

Location	N	Sinus & Nasal Symptoms* Nasal/Sinus	Asthma since 1990	Breathing Symptoms	Dermal Symptoms*
Longwall	33	8 (24%)	3 (9%)	25 (76%)	7 (21%)
Continuous Miner	15	10 (67%)	1 (7%)	12 (80%)	5 (33%)
Belt	5	3 (60%)		4 (80%)	1 (20%)
UG maintenance	2	0		2 (100%)	0
Surface	12	6 (50%)		10 (83%)	3 (25%)
Other or Rover	18	8 (44%)	2 (11%)	13 (72%)	4 (22%)
	85	35	6	66	20

* respondents sought medical intervention for symptoms

Table 2
The pH of samples taken at the Robinson Run Mine on February 14, 2000
HETA 2000-0098

Sample location	pH
Solcenic HL concentrate	>10
#45 shield emulsion leakage from ground	8-8.5
pump area leakage from ground	8-8.5
emulsion from #35 shield valve bank leak	>10
emulsion from #45 shield ram-jack leak	>10
fresh water line leak from wetdown hose	5-5.5
mine water	6.5

Table 3
Results of Air Sampling for Fungi at the Robinson Run Mine
HETA 2000-0098

Location	Geometric mean of culturable fungi concentration (range) CFU/m ³	Predominant fungal species identified
Outside at Intake	3.6 x 10 ³ (0 - 1.5 x 10 ⁴)	<i>Cladosporium</i>
Headgate/no shearing activity	1.4 x 10 ³ (9.8 x 10 ² - 2.9 x 10 ³)	<i>Penicillium chrysogenum</i>
Headgate during shearing	3.1 x 10 ³ (1.2 x 10 ³ - 4.1 x 10 ³)	<i>Penicillium chrysogenum</i>
50 yards downwind of shearer	1.3 x 10 ³ (7.4 x 10 ² - 2.0 x 10 ³)	<i>Cladosporium</i>
Corridor near belt line	6.4 x 10 ³ (1 sample)	<i>Penicillium aurantiogriseum</i> , basidiospores
Headgate side at shearer	6.0 x 10 ³ (4.4 x 10 ³ - 7.5 x 10 ³)	<i>Penicillium chrysogenum</i> , basidiospores, <i>Cladosporium</i>
Tailgate side at shearer	8.1 x 10 ³ (6.9 x 10 ³ - 9.6 x 10 ³)	<i>Penicillium chrysogenum</i> , basidiospores, <i>Cladosporium</i>
Tailgate	1.2 x 10 ³ (2.5 x 10 ² - 4.0 x 10 ³)	<i>Penicillium chrysogenum</i> , basidiospores

Solcenic HL Concentrate

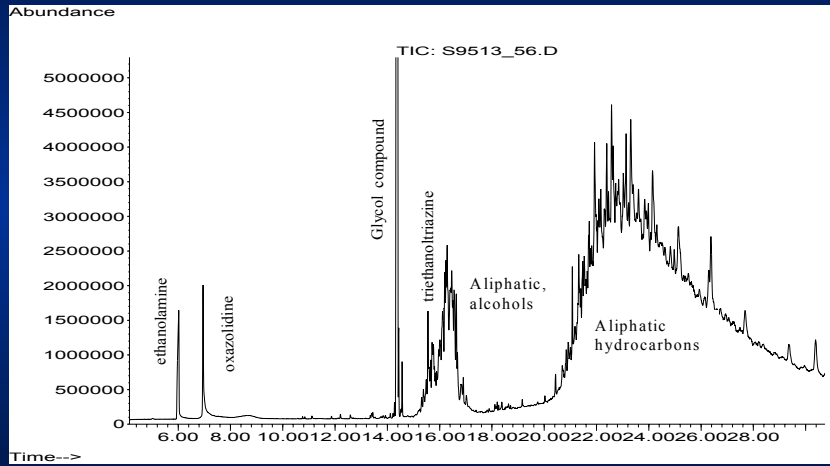


Figure 1: Composition of Concentrate from the 8000-gallon aboveground storage tank.

Solcenic HL Emulsion

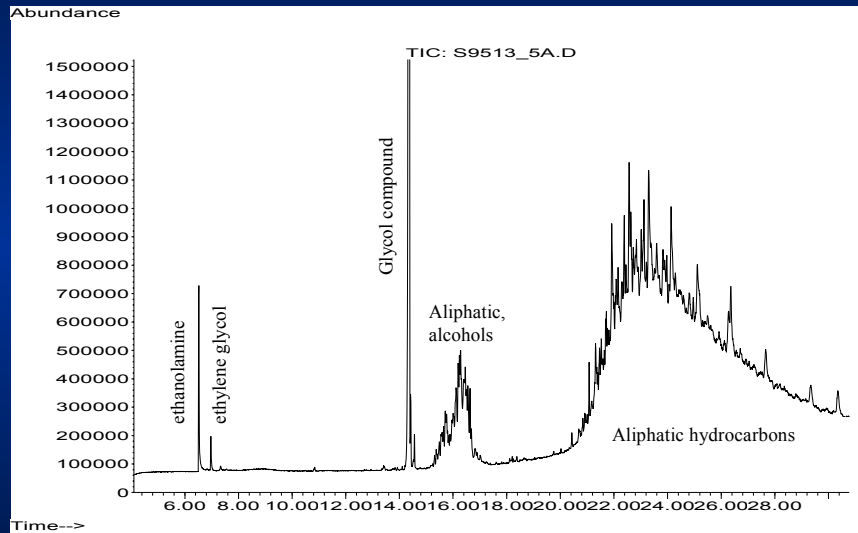


Figure 2: Composition Results for Emulsion from the hydraulic lines.

Leakage from Mine Floor

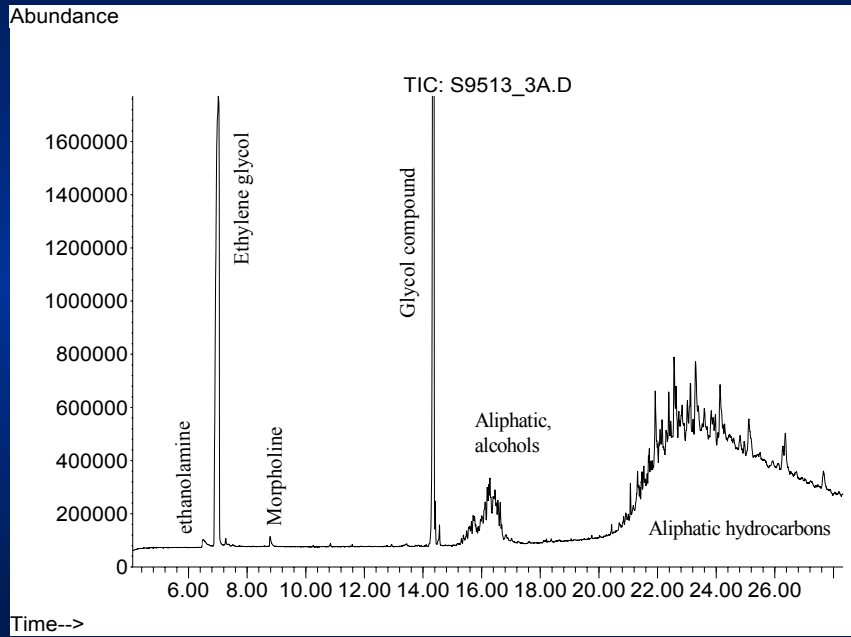


Figure 3: Composition Results for Leakage from the mine floor.

APPENDIX A
MSDS FOR SOLCENIC HL

APPENDIX B

Sample Medical / Work History Questionnaire

APPENDIX C

A Guide for Formaldehyde Sampling

The following calculation provides guidance on how much leakage can occur before the formaldehyde concentration could exceed the NIOSH REL along the longwall panel. It can be used to assist in a determination of when concentrations are likely to be BELOW the REL for formaldehyde and situations where sampling for formaldehyde is warranted.

This estimate assumes that in the presence of acidic bacterial waste products in the emulsion, triazine decomposes through the intermediate oxazoladine to ethanolamine and formaldehyde. In situations where the emulsion leakage is mixed with acidic mine drainage, most of the triazine in the leakage will convert to formaldehyde. Because some of the triazine in the emulsion is likely to have converted to formaldehyde and reacted with organic matter prior to leaking into the mine environment, this estimate has a built-in safety factor.

This is a conservative estimate, purposely designed to be protective of workers and should not be used to estimate formaldehyde exposure.

Assumptions

- all the triazine in the emulsion is immediately converted to formaldehyde in a room the size of all the air that passes over the longwall panel.
- based on a typical metalworking fluid, the biocide is assumed to be formulated to a 0.1 percent (0.001) dilution in the emulsion.
- based on MSDSs for triazine, the biocide is 78.5 percent triazine (specific gravity = 1.16, gram molecular weight or gmw = 219).
- 60,000 cubic feet per minute (1700 cubic meters per minute) constant ventilation.
- 24.45 liters per gram mole.
- gmw of formaldehyde = 30 and 3 moles of formaldehyde per mole of triazine.
- Acceptable concentration = REL = 0.1 parts per million as a ceiling (a concentration that should not be exceeded at any time).

Calculation of the amount of emulsion leakage that could result in REL ceiling concentrations

The volume of formaldehyde released per minute should be less than 0.1 millionths of the ventilation rate or 0.00017 cubic meters (0.17 liters) per minute. *This value was obtained by multiplying 0.1 parts formaldehyde per 1,000,000 parts air by 1,700 cubic meters of air per minute.*

0.17 liters of formaldehyde is the equivalent of 0.007 gram moles of formaldehyde. *This value was obtained by dividing 0.17 liters by 24.45 liters per gram mole.*

One gallon of emulsion contains up to 0.047 gram moles of formaldehyde. *This value was obtained by multiplying:*

$$\frac{0.001 \text{ gal triazine}}{\text{gal emulsion}} (0.785) \frac{8.34 \times 1.16 \text{ lb triazine}}{\text{gal triazine}} \frac{454 \text{ g triazine}}{\text{lb triazine}} \frac{90 \text{ g formaldehyde}}{219 \text{ g triazine}} \frac{\text{gram mole formaldehyde}}{30 \text{ grams formaldehyde}}$$

The triazine biocide in 0.15 gallons of emulsion, has the potential to release 0.007 gram moles of formaldehyde, therefore if emulsion leakage is kept to below 0.15 gallons per minute (about 10 gallons per hour), REL concentrations of formaldehyde along the longwall panel are unlikely.

Note that these are conservative calculations and that the actual relationships between leakage of emulsion and the REL ceiling should be established through sampling.

APPENDIX D

Evaluation Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week, for a working lifetime, without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce negative health effects, even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for mining workplaces are:

- NIOSH Recommended Exposure Limits (RELs),
- American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®), and
- U.S. Department of Labor, Mine Safety and Health Administration (MSHA) Permissible Exposure Limits (PELs).

Employers are encouraged to follow the more protective criterion among the MSHA PELs, the NIOSH RELs, and the ACGIH TLVs. Employers should understand that not all hazardous chemicals have specific MSHA exposure limits such as PELs and short-term exposure limits (STELs).

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended STEL or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Metalworking Fluid Guidelines

Solcenic HL emulsion is similar in composition to water emulsifiable metalworking fluids. Therefore the NIOSH metalworking fluid methods and guidelines may be applicable to miners who are potentially exposed to hydraulic fluids.

NIOSH recommends that occupational exposure to metalworking fluid aerosols be limited to 0.4 mg/m³ of air (thoracic particulate mass) as a time-weighted average (TWA) concentration for up to 10 hours per day during a 40-hour workweek, measured according to NIOSH Method 0500 (NIOSH, 1984). Thoracic particulate mass is the portion of the aerosol that penetrates beyond the larynx. This recommended limit is intended to prevent respiratory disorders. It is prudent to keep concentrations below the NIOSH Recommended Exposure Limit (REL) because some workers with conditions such as work related asthma may experience adverse health effects at lower

concentrations. Because of interferences from the relatively high thoracic coal dust concentrations on longwall sections and because of the highly variable and highly intermittent nature of aerosol exposures, sampling by this method is not feasible and would not yield meaningful results.

Limiting dermal (skin) exposure is critical to preventing allergic and irritant skin disorders related to metalworking fluid exposure. In lieu of sampling, the preferred approach is to observe situations where exposures may occur (such as leaks, spills) and take corrective action to minimize potential aerosol and dermal exposures (through maintenance, recycling emulsion during longwall moves, oversight of emulsion concentration, etc.).

Triazine Compound

Triazines are formaldehyde releasing antimicrobial agents commonly found in metalworking fluids. Formaldehyde releasers are usually soluble in water and are more effective against bacteria than fungi.

The triazine is decomposed by acidic bacterial waste products to release formaldehyde (CH₂O), which goes on to attack bacteria. The triazine concentration recommended for removal of heavy fungal contamination from a metal working fluid is 2000 parts per million (ppm) or 0.2 percent [National Toxicology Program (NTP), 1998]. The triazine concentration in the emulsion leakage is believed to be less than 0.2 percent.

NTP review is ongoing. There are concerns that the toxicity of biocides, including triazine, has not been adequately tested. For example, formaldehyde released from triazine biocides and inhalation of oil mists may in themselves be toxic. Triazine has been shown to be positive in the Ames *Salmonella* assay and produced adverse effects in the lungs and stomachs of rats orally exposed for 90 days (NTP, 1998).

No standards or guidelines have been set by MSHA or NIOSH for occupational exposure to triazine. The ACGIH has not recommended a TLV or Biological Exposure Index (BEI) for this compound. The respiratory effects of two synthetic metalworking fluids and their components were evaluated in two inhalation studies; triazine was identified as an irritating component in both fluids. Male Swiss-Webster mice exposed to triazine at 112-351 mg/m³ exhibited signs of both sensory and pulmonary irritation during the 3-hour exposure. In both studies, triazine resulted in deaths of mice at 24 to 72 hours post exposure. The concentrations of triazine capable of evoking a 50 percent decrease in mean respiratory frequency based on pulmonary irritation (RD₅₀P) were calculated as 137 mg/m³ in the study by Krystofiak and Schaper (1996) and as 190 mg/m³ in the study by Detwiler-Okabayashi and Schaper (1996). From these RD₅₀P values the authors proposed respective occupational exposure limits of 2.3 and 3.2 mg/m³.

Formaldehyde

The triazine compound decomposes through the intermediate oxazoladine to ethanolamine and formaldehyde. Formaldehyde is an airways irritant and a recognized cause of occupational asthma (Chan-Yeung and Malo 1993). Formaldehyde exposure from metalworking fluids has not been shown to be significant. Cohen (1995) reported on the analyses of 550 formaldehyde samples of metal working operations. Three hundred were personal samples, and all were below the OSHA action limit of 0.5 ppm for formaldehyde (DOL, 2000a). Cohen did not compare the results to the NIOSH REL of 0.016 ppm, which is a more protective criterion. A brief description of the NIOSH REL, MSHA PEL, ACGIH TLV, and OSHA PEL for formaldehyde follows.

- The NIOSH REL for formaldehyde is 0.016 ppm as an 8-hour time weighted average (TWA) and 0.1 ppm as a ceiling concentration determined in any 15-minute sampling period. The REL value of 0.016 ppm is based on the lowest reliably quantifiable concentration for an air sample at the time (1988). NIOSH recommends that

formaldehyde be handled as a potential occupational carcinogen with substitution of less toxic substances where feasible. Engineering controls and stringent work practices should be employed to reduce occupational exposure to the lowest feasible limit. Exposure to formaldehyde should be kept as low as feasible to reduce the risk of irritation of the eyes and respiratory tract, dermatitis and sensitization of the skin and respiratory tract, and cancer.

- The MSHA PEL (DOL, 2000b), the legally enforceable formaldehyde standard for underground coal mines, is a 2 ppm ceiling concentration that should not be exceeded during any part of the working exposure. It is adopted from the 1972 ACGIH threshold limit values (TLVs) and is not as protective as other guidelines.
- The current TLV (ACGIH, 2001) is 0.3 ppm (ceiling) and has A2 (Suspected Human Carcinogen) and SEN notations. SEN refers to the confirmed potential for worker sensitization as a result of dermal contact and/or inhalation exposure. To comply with the TLV, dermal contact with formaldehyde releasing emulsions should be avoided.
- The OSHA PEL, for formaldehyde exposure, which is not a legally enforceable exposure limit for underground coal mines, is 0.75 ppm. This limit was established to reduce the risk to workers for cancer, eye, nose, and throat irritation, and sensitization.

Mineral Oil

Mineral oils (lubricant base oils) refined from petroleum crude oils are complex mixtures of straight- and branched-chain paraffinic, naphthenic (cycloparaffin), and aromatic hydrocarbons. Long-term exposures to unrefined or poorly refined mineral oils used before the 1950s were reported to cause skin cancer on the hands, forearms, and scrotum of workers; however, water-based metalworking fluids similar to Solcenic HL emulsion have not been associated with these effects. Prolonged skin contact may cause irritation and occasionally dermatitis. Due to its low vapor pressure (0.5mm Hg) inhalation of mineral oil vapors from spilled emulsion should not be an issue; however, under pressure, aerosolization and subsequent exposure via inhalation could occur. Mineral oil does, however, serve as a source of nutrition (carbon) for microorganisms that can grow in hydraulic fluid.

Alcohols

Toxicological data on the proprietary alcohols used are sparse and no occupational exposure limit exists for them. Total ion chromatograms from the mass spectral analyses of the Solcenic HL concentrate (Figure 1), emulsion (Figure 2), and spillage (Figure 3) show there to be numerous aliphatic alcohols present. According to Volume 6 of the 2001 edition of Patty's Toxicology (Monohydric Alcohols - C7 to C18, Aromatic and other Alcohols): "A common property of some of the alcohols is to produce local irritation to the skin, eyes, and respiratory tract, and the effect or potency varies with the type of alcohol. Many alcohols produce minimal or no adverse effects in humans, possibly because of the low toxicity potential of the alcohol." The decanols, dodecanols, and tridecanols have a low order of acute toxicity, are not associated with reports of adverse health effects in humans, and have an odor threshold in the part per billion range (Volume 6, Patty, 2001).

Organic Acid Salt

The proprietary organic acid salt is a compound that is used as a water or cooling treatment additive and that, as an undiluted raw material, may cause respiratory tract burns, skin burns, eye burns, and mucous membrane burns.

Repeated or prolonged contact may cause dermatitis (based on the MSDS for the additive). For skin contact with the organic acid salt, the MSDS recommends: *wash skin with soap and water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention if needed. Thoroughly clean and dry contaminated clothing and shoes before reuse.* For occupational release, the MSDS recommends: *Do not touch spilled material. Small spills: Absorb with sand or other non-combustible material. Small dry spills: Collect spilled material in appropriate container for disposal. Keep unnecessary people away, isolate hazard area and deny entry.* The compound is used at dilutions of less than 0.1 percent in the emulsion. The manufacturer has noted that the organic acid salt will not cause burns at the concentrations found in the emulsion (Hart, 2001). That conclusion was based on eye tests in rabbits with Solcenic HL emulsion. The ability of the organic acid salt to cause irritation and/or sensitization at dilutions found in the mine environment is unknown.

A related compound, the benzotriazole derivative, drometizole, CAS No. 2440224, has been used in similar concentrations in consumer products. It is used as an ultraviolet light absorber and stabilizer in plastics, and before 1981, was used in nail polishes and shampoos. Nail polish containing 1 percent dromoetriazole was mildly irritating to rabbit eyes, but nonirritating to rabbit skin. Drometriazole was believed to be the sensitizing agent in five reported cases of allergic contact dermatitis due to cosmetic use. The Cosmetic Ingredient Expert Review Panel concluded that the safety of this ingredient had not been documented and substantiated, but that it is safe for use in cosmetic products until appropriate safety data have been obtained and evaluated (J. Am. Col. of Tox., 1986).

Poly glycol

The proprietary glycol ether listed in the MSDS has no occupational exposure limit. In Volume 7, Patty's Toxicology, Glycol Ethers, the compound is listed as exhibiting low toxicity from a single exposure by any route of administration. It is slightly irritating to the skin. The undiluted material may markedly irritate eyes, although damage was transitory when tested in rabbits (Patty, Volume 7, 2001).

Bacteria and fungi

No standards or guidelines have been set by MSHA, NIOSH, or the ACGIH for culturable or countable bioaerosols. The ACGIH policy is that a general TLV for culturable or countable bioaerosol is not scientifically supportable because:

- Culturable microorganisms and countable biological particles do not comprise a single entity.
- Human responses to bioaerosols range from innocuous effects to serious, even fatal diseases depending on the specific material involved and workers' susceptibility to it.
- It is not possible to collect and evaluate all bioaerosol components using a single sampling method (different methods of collection and analyses may result in different estimates of concentration).
- At present, information relating culturable or countable bioaerosol concentrations to health effects is generally insufficient to describe exposure-response relationships.

“Specific TLVs for individual culturable or countable bioaerosols have not been established to prevent hypersensitivity, irritant, or toxic responses. At present, information relating culturable or countable bioaerosol exposure to health effects consists largely of case reports and qualitative exposure assessments.” (ACGIH, 2000). Therefore, results of airborne bacteria and fungi air sampling should not be used for compliance testing. Air sampling for microbials provide a short-term snapshot which may not be representative of the fungal conditions over the whole work day or under different environmental conditions (e.g., when the shearer is on, versus off). Because of the limitations in air sampling for fungi and bacteria, air sampling results should not be used to prove

a negative case. Microbes in air vary seasonally, diurnally, and with activity level. These data should be used to help characterize the microbial environment of the underground mine rather than to establish relevant exposures. The development of sampling techniques that are appropriate for underground mine environments would aid in the characterization.

Shearer sprays

Sprays from the surface water may contain microorganisms. Health protective standards for occupational inhalation of water sprays do not exist so comparisons are made to the standards for bathing water and drinking water.

The highest acceptable fecal coliform count for bathing water is 200 fecal coliforms per 100 ml of water. The concentrations in the spray water would be acceptable for an outdoor bathing area; however, the bathing standard is intended to provide protection for dermal and ingestion routes of entry, rather than inhalation of aerosolized water, which is a major route of entry from shearer sprays. Because respiratory infection has been shown to occur at lower aerosolized bacterial concentrations than those inducing gastrointestinal or dermal infection (Katzenelson and Teltch 1976), the bathing water standard should not be used to assess safety from inhalation of shearer spray water.

The U.S. Environmental Protection Agency (EPA) drinking water standard is a more protective standard for water quality. EPA has determined that the presence of fecal coliforms or *E. coli* are generally not harmful themselves, but their presence in drinking water is serious because they are usually associated with sewage or animal wastes. The presence of these bacteria in drinking water generally is a result of a problem with water treatment or the pipes which distribute the water and indicates that the water may be contaminated with organisms that can cause disease. EPA has promulgated an enforceable drinking water standard for fecal coliforms and *E. coli* to reduce the risk of adverse health effects. Under this standard all drinking water samples must be free of these bacteria. Drinking water that meets this standard is associated with little or none of this risk and should be considered safe.

**For Information on Other
Occupational Safety and Health Concerns**

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1-800-35-NIOSH (356-4674)
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