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MINING TARGET ENVIRONMENTAL SURVEILLANCE STUDY:NITROPROPANE SENSITIZED AMMONIUM NITRATE BLASTING AGENTS

NATIONAL INST. FOR OCCUPATIONAL SAFETY AND HEALTH, MORGANTOWN, WV

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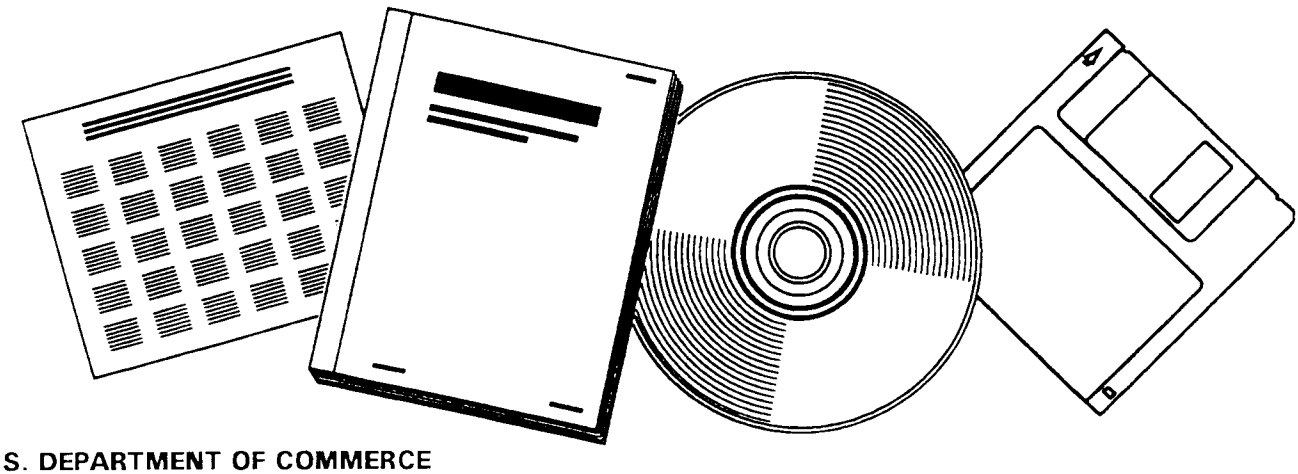

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Nitropropane sensitized ammonium nitrate blasting agents are being field tested at several locations so that they may be routinely used in the future. This report is an initial evaluation of potential health hazards resulting from use in the field.

Sampling for 1-nitropropane and methanol was conducted at one surface bulk loading operation and worker exposures were well below those levels currently considered acceptable by both NIOSH and MSHA. 1-Nitropropane samples were also analyzed for 2-nitropropane and levels were found to be below the detectable limit. Under similar operating conditions overexposure is unlikely. As with all systems, poor work practices can lead to overexposure.

An evaluation of work practices at the facility surveyed revealed that poor work practices resulted in unnecessary exposure to 1-nitropropane and methyl alcohol. Recommendations were made to reduce this unnecessary exposure. As a result of this survey, NIOSH sampling and analysis method S-59 for methyl alcohol was tested and determined to be unsuitable for field use. Direct reading indicator tubes were found to be a good method of screening to ensure low exposure levels are being maintained.

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PREFACE

The Federal Mine Safety and Health Act of 1977 gave NIOSH the responsibility of conducting occupational health research in the mining industry. The NIOSH research program includes surveillance projects in which initial evaluations are made of certain materials or agents to determine if they are potentially toxic in the manner in which they are found or used in mines. Several current investigations in the surveillance effort are characterizations of worker exposure to environmental contaminants resulting from the use of explosives and blasting agents in mines. This report, which is an estimate of the potential health hazard resulting from use of nitropropane sensitized ammonium nitrate blasting agents is part of these surveillance efforts.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

ABSTRACT

Nitropropane sensitized ammonium nitrate blasting agents are being field tested at several locations so that they may be routinely used in the future. This report is an initial evaluation of potential health hazards resulting from use in the field.

Sampling for 1-nitropropane and methanol was conducted at one surface bulk loading operation and worker exposures were well below those levels currently considered acceptable by both NIOSH and MSHA. 1-Nitropropane samples were also analyzed for 2-nitropropane and levels were found to be below the detectable limit. Under similar operating conditions overexposure is unlikely. As with all systems, poor work practices can lead to overexposure.

An evaluation of work practices at the facility surveyed revealed that poor work practices resulted in unnecessary exposure to 1-nitropropane and methyl alcohol. Recommendations were made to reduce this unnecessary exposure.

As a result of this survey NIOSH sampling and analysis method S-59 for methyl alcohol was tested and determined to be [illegible]able for field use. Direct reading indicator tubes were found to be a good method of screening to ensure low exposure levels are being maintained.

During field tests at one location workers have complained of various symptoms related to exposure. It is recommended that MSHA notify NIOSH of any future operations where workers exhibit symptoms so a medical evaluation of the health hazard can be made.

I. INTRODUCTION

A. Purpose. This report is an estimate of the potential health hazard resulting from use of nitropropane (NP) sensitized ammonium nitrates (AN) blasting agents in mines. The purpose of this estimate is to provide NIOSH with sufficient background information to make qualified decisions on the degree of resources to be allocated to further research efforts in the field and to assist NIOSH, MSHA, and operators in the evaluation of the health hazard at similar operations.

B. Scope. This report is limited in scope to consist of information obtained from a background literature search and sampling conducted at one facility.

C. Historical Data. NIOSH initiated this surveillance study in December 1980 as a result of a letter from MSHA expressing concern over possible health hazards resulting from worker exposure to "new field mixtures" such as nitropropane sensitized ammonium nitrate. (Reference 6)

There are currently two nitropropane based blasting agents commercially available for use in mining, NP-X and COMSOL*. COMSOL is available in both bulk form and wet packs while NP-X is available only in bulk form. Table 1, below contains information on their chemical makeup and examples of typical field formulations.

TABLE 1

NAME, CONSTITUENTS, AND TYPICAL FIELD FORMULATIONS
OF NITROPROPANE BASED AMMONIUM NITRATE BLASTING AGENTS

Product Name	Constituents of Fuel	Typical Field Formulations
NP-X	The fuel which is referred to as NPN is composed of 50% NiPar S-10* (1-nitropropane), and 50% methyl alcohol by volume	87% ammonium nitrate, 13% NPN by weight
COMSOL*	Composed of 70-85% NiPar S-10* (1-nitropropane) and 15-30% fuel, such as fuel oil, by volume	90% ammonium nitrate, 10% COMSOL, by weight

COMSOL*, and NiPar S-10* are registered trademarks of IMC Corporation.

Use of trademarked names does not constitute endorsement by the National Institute for Occupational Safety and Health but is used only to assist in the identification of a product.

Representatives of NIOSH, MSHA, and IMC Corporation, the sole manufacturer of nitropropanes in the United States met in Denver, Colorado on April 10, 1981 to discuss the possibility of NIOSH conducting sampling at a mine where NP sensitized AN blasting agents were being used. NIOSH decided to sample at a location where bulk NP-X was being used during summer months. Bulk NP-X operations were chosen over operations where wet packs or bulk COMSOL formulations were used because of the higher estimated exposure levels at bulk loading operations and the additional potential exposure to methyl alcohol at NP-X loading operations.

At the time of this meeting no domestic mines currently used bulk NP-X on a routine basis. There were, however, a number of mines where the product was being field tested and the product was expected to be used in the future. One such mine, the Cleveland Cliffs Iron Company's Empire Mine in Palmer Michigan had field tested the product and found it economical to use as a substitute for aluminized ammonium nitrate fuel oil. Field testing was suspended at the Empire Mine prior to the April 10th meeting in response to worker concerns over alleged health hazards resulting from exposure to the product. Specifically, workers complained of headaches, skin rash, throat burns, chest and stomach pains, and sexual impotence. The symptoms were not medically substantiated and the exposure levels at the time of the complaints were not documented.

It was then decided that the Empire Mine would be suitable for the study. A survey was eventually conducted during a specially arranged loading of NP-X on June 2-4, 1981. Survey results are contained in a report by this office entitled "Industrial Hygiene Assessment of the Use of Nitropropane-Methanol Sensitized Ammonium Nitrate Blasting Agent at the Empire Mine, Palmer, Michigan", October 8, 1981. Information contained in the referenced report serves as the basis for this study.

D. Occupational Health Guidelines for 1-Nitropropane. The NIOSH/OSHA Occupational Health Guidelines for 1-nitropropane, Reference 10, have been reproduced and are attached as Appendix A.

COMMENTS: (1) The results of sampling conducted as part of this survey indicate that odors similar to those of 1-nitropropane can be noticeable at about 5 ppm. This indicates that the threshold of odor is substantially lower than the 80 ppm no-detection limit reported in the guideline under the section entitled "warning properties".

(2) Sampling and analysis for 1-nitropropane can be performed by NIOSH P&CAM 272, Reference 7, or by use of a direct reading instrument such as a portable gas chromatograph. A method of measurement was not available at the time of publication of the guideline.

E. Occupational health guidelines for methyl alcohol. The NIOSH/OSHA Occupational Health Guidelines for methyl alcohol, Reference 10, have been reproduced and are attached as Appendix B.

COMMENT: As a result of sampling conducted as part of this study, a stability study of methyl alcohol on silica gel was undertaken (Reference 12). Based on results of the stability study NIOSH concluded that severe breakthrough can occur when sampling for methanol with standard size silica gel tubes (NIOSH Method S59). Therefore, when reading the section of Occupational Health Guidelines for Methyl Alcohol in Appendix B entitled "Monitoring and Measure Procedures" note should be taken to the fact that standard size silica gel adsorbent tubes should be avoided and NIOSH Method P&CAM 247 should be used in lieu of NIOSH Method S59.

II. FINDINGS AND DISCUSSION

A. Description of the Operation Surveyed. It is believed that equipment, accessories and practices followed at the operation surveyed are similar to those found at bulk NP-X and COMSOL loading operations at other open pit mines. Results of the survey which follow can be used to assist in making preliminary estimations of the degree of health hazard resulting from use of these products at other mines.

Six truckloads of NP-X and six truckloads of ammonium nitrate fuel oil (ANFO) were unloaded during the three day survey. Two truckloads of each type of blasting agent were unloaded each day which is representative of normal workload. It took approximately two hours to unload each truck.

A typical shot pattern consisted of approximately eighty 12 1/2 inch diameter holes of 50 foot depth. Three shot patterns were loaded during this survey. Initially, the bottom 15 feet of each hole was filled with NP-X. The AN truck followed and loaded each hole with approximatey 30 feet of ANFO. Finally 7 feet of stemming was pushed into each hole by a front end loader. Polyethylene bag liners were used on some holes to prevent contamination of the blasting agents with water. It took approximately 1-3 minutes to load each blasting agent into each hole.

Workers potentially exposed to 1-nitropropane and methyl alcohol at the operation surveyed include:

(1) NP-X Truck Driver

(2) NP-X Taper (Measures to insure NPN loaded to proper depth in borehole)

(3) Booster Loader (Loads primer into borehole during NPN loading)

(4) NP-X Bag Holder (Holds polyethylene liner opening up to auger spout during loading)

(5) AN Prill Truck Driver

(6) AN Taper (Measures to insure AN prills loaded to proper depth in borehole)

(7) AN Bag Holder (Holds polyethylene liner opening up to auger spout during loading)

B. Environmental Sampling and Analysis. Sampling for 1-nitropropane, 2-nitropropane, and methyl alcohol was conducted at the Empire Iron Mine to assist in the determination of exposure levels at similar operations. Results are believed to represent worst case exposure levels under "optimal operating conditions."

COMMENT: By the term optimal working conditions it is meant that trucks were maintained, and leakage was sealed. The term worst case infers that sampling was conducted only during periods of actual exposure, results were not time weighted over 8-hours; and that good industrial hygiene practices which would have minimized unnecessary exposure were not followed.

C. Sample Results. Results of sampling are summarized below. The method of sampling and results of analyses are discussed in greater detail in Reference 11.

1. Grab Samples Analyzed for Methyl Alcohol.

Six breathing zone grab samples were collected and analyzed with an AID Portable Gas Chromatograph with a flame ionization detector on Thursday, June 4. Peak exposure to methyl alcohol while loading lined boreholes was approximately 40 mg/m^3 for both the primer loader and the liner holder. Corresponding adsorbent tube sampling by NIOSH indicated exposures averaged over an 85 minute period where a series of boreholes were loaded were 16.8 and 8.5 mg/m^3 respectively. IMC Corporation reported concentrations of 22.2 and 12.9 mg/m^3 for their concurrent samples. Results of other grab samples taken during the same period showed peak concentrations to range from less than 5 mg/m^3 for the liner holder on two occasions, to 30 mg/m^3 for the primer loader taken while loading unlined holes.

(2) Grab Samples Analyzed for 1-nitropropane.

Results of six short term breathing zone grab samples taken for 1-nitropropane show peak concentrations to range from less than 5 mg/m^3 to 45 mg/m^3. Corresponding adsorbent tube samples taken by IMC Corporation over an 85 minute period when a series of boreholes were loaded ranged from 8.3 to 29.6 mg/m^3. Results of NIOSH long term adsorbent tube samples taken during the same period (sample run 6) are not available due to laboratory problems encountered in the analyses.

(3) Adsorbent tube samples analyzed for methyl alcohol.

Twenty four adsorbant tube breathing zone samples and one general area sample were analyzed for methyl alcohol (see Reference 11 for results). Methyl alcohol was sampled and analyzed using NIOSH Method No. S59 (Reference 7). When this method was validated, the effects of humidity were not taken into consideration. Migration and possibly breakthrough occurred on 18 of the 25 samples taken. The amount of analyte adsorbed ranged from 0.04-0.38 mg per standard size silica gel tube (100 mg front section, 50 mg backup section). IMC Corporation conducted concurrent sampling on larger silica gel tubes (520 mg front section, 260 mg backup section) and reported detectable quantities on their backup section in two of twenty five samples.

The IMC sampling differed from NIOSH's in that they (1) packed their samples on dry ice immediately after sampling, (2) used larger silica gel tubes and (3) analyzed their samples within one week (vs four weeks for NIOSH). Concentrations of methyl alcohol in air reported by IMC Corporation ranged from 3.3 to 87.5 mg/m^3. The NIOSH results ranged from 2.1 to 90.13 mg/m^3.

(4) Adsorbent tube samples analyzed for 1 and 2 nitropropanes.

In summary, 19 breathing zone samples and one general area sample were analyzed for 1- and 2-nitropropanes (see Reference 11 for results). Airborne concentrations of 1-nitropropane were within levels currently considered acceptable by NIOSH, MSHA, and the American Conference of Governmental Industrial Hygienists. NIOSH results ranged from 2.2 mg/m^3 to 24.8 mg/m^3. IMC Corporation sample results ranged from 2.5 to 46.1 mg/m^3. 2-nitropropane was not detected on any of the samples analyzed by NIOSH. The level of detection was 0.01 mg per adsorbant tube, which corresponded to concentrations ranging from less than 1.3 to less than 6.0 mg/m^3 or less than 0.36 to less than 1.67 parts per million (PPM).

D. Discussion.

(1) Odors were noticeable during most loading operations even at low concentrations (i.e., about 5 ppm 1-nitropropane and 20 ppm methanol as measured with an AID portable GC). These odors, which resembled that of 1-nitropropane were objectionable to some workers, especially during the loading of lined holes.

(2) Exposure levels were higher at holes where polyethylene liners were used. One worker, who held the liner up to the auger while the hole was being filled, potentially receives a higher exposure than most of the other workers. However, all levels observed were below the permissible exposure level. This exposure could easily be reduced by securing the liner to the auger and removing the worker from the loading area during loading.

(3) Poor work practices observed during this survey tended to produce unnecessary exposure. Two examples are given below:

(a) The AN prill truck was positioned downwind of the NP-X truck roughly one half of the time during which odors emanating from the NP-X loading area were noticeable in the AN prill loading area.

(b) Workers sometimes positioned themselves in areas of high potential exposure, such as on the downwind side of a hole during loading. There did not appear to be any operational reason for them to be downwind; they could have repositioned themselves upwind without interfering or impeding operations.

(4) Company safety representatives sampled the worker breathing zone for methyl alcohol with direct reading indicator tubes. This method of screening to determine if further action is required has the advantages of being simple, rapid, convenient, and inexpensive. It provides an excellent means of screening to ensure levels of methyl alcohol (and 1-nitropropane by rough correlation) are being maintained well within safe limits.

Methyl alcohol is not present at bulk COMSOL loading operations. Use of a combustible gas meter calibrated for 1-nitropropane would provide a quick and easy screening method for estimating worker exposure levels. Interferences from fuel oil would result in higher readings providing an added margin of safety. An advantage of using this method is that operators and workers can see immediate results of sampling.

III. Conclusions.

A. Based on the results of long term adsorbant tube sampling conducted as part of this survey, worker exposures to 1-nitropropane were below the MSHA permissible and NIOSH Recommended Limits. Under similar environmental and operating conditions, overexposure to this agent is unlikely. As with all systems, poor work practices can lead to overexposure.

B. Conclusions based on NIOSH sampling for methyl alcohol performed as part of this survey cannot be made because of migration and possible breakthrough on silica gel adsorbant tubes. Based on the results of NIOSH short term grab samples analyzed on an AID GC and on results of IMC Corporation concurrent sampling (reference 8) NIOSH concludes that worker exposure to methyl alcohol was below the MSHA permissible and NIOSH recommended limits. Under environmental and operating conditions similar to those encountered during this survey, overexposure to methyl alcohol is also unlikely. As with all systems, poor work practices can lead to overexposure.

C. Although overexposure is unlikely, unnecessary exposure can be reduced by following good industrial hygiene practices.

D. NIOSH Method No. S59 is not valid for sampling for methyl alcohol in the field.

IV. Recommendations.

A. Users.

1. Sample the worker breathing zone for levels of methyl alcohol in air with direct reading indicator tubes at NP-X loading operations when the operation starts, and where workplace conditions indicate increased potential for exposure. This would include operations where visible leakage is present, where workers exhibit symptoms of exposure, and where poor work practices are observed. If results of worker breathing zone sampling indicate increased exposure (approaching levels considered unsafe) then control should be implemented to reduce exposure (i.e., alter work practices, repair leaks) or other methods of sampling for both 1-nitropropane and methyl alcohol should be conducted to quantitate exposure levels.

2. At bulk COMSOL loading operations sampling for levels of 1-nitropropane in worker breathing zone should be conducted soon after start-up and when changes in working conditions warrant reevaluation. Use of direct reading instruments, such as a combustible gas meter calibrated for 1-nitropropane, is the preferred method of sampling.

3. Ensure that proper work practices which minimize unnecessary exposure are being followed, specifically:

(a) Workers should be instructed to position themselves in areas where potential for exposure is minimal such as areas upwind of loading sites.

(b) Bag liners should be mechanically attached to auger trucks while loading NP-X.

B. MSHA - Notify NIOSH of instances where workers exhibit symptoms of exposure to these agents and of results of sampling conducted during inspections.

C. NIOSH:

1. Conduct an HHE (to include a medical evaluation) of any operation where workers exhibit symptoms of exposure.

2. Assess the usage patterns of NP sensitized AN blasting agents at the end of FY82.

V. REFERENCES

1. Sax, N. I. Dangerous Properties of Industrial Materials, 4th Edition, Van Nostrand Reinhold Co., NY 1975.

2. E. I. Dupont de Nemours and Co. (Inc.). Blasters Handbook, Wilmington, Delaware, 16th Ed., 1980.

3. ACGIH, Committee on Threshold Limit Values: Documentation of the Threshold Limit Values for Substances in Workroom Air, ACGIH, Cincinnati, OH, 1980.

4. ACGIH, TLV's: Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1980. ACGIH, Cincinnati, OH.

5. DHHS (NIOSH) Publication No. 80-142, Health Hazard Alert - 2-Nitropropane, NIOSH, October 1, 1980.

6. Letter, dated 2/21/80, to Mr. William Palmer, Industrial Hygienist, NIOSH from Mr. Claude Reich, MSHA, Subject: Health Hazards Associated with the Use of Explosives.

7. NIOSH Manual of Analytical Methods, 2nd Ed., D. Taylor Coordinator - Cincinnati, Ohio, April 1977.

8. Report, dated 7/6/81, to R. B. Kayser, IMC Corporation from R. F. Purcell, IMC Corporation, Subject: AN Sampling - Empire Mine, Palmer, Michigan.

9. DHEW (NIOSH) Publication No. 72-210, NIOSH/OSHA Pocket Guide to Chemical Hazards, NIOSH, September 1978.

10. DHHS (NIOSH) Publication No. 81-123, Occupational Health Guidelines for Chemical Hazards, NIOSH, January 1981.

11. NIOSH Report dated 10/8/81, Industrial Hygiene Assessment of the Use of Nitropropane-Methanol Sensitized Ammonium Nitrate Blasting Agent at the Empire Mine, Palmer, Michigan.

12. Letter dated August 6, 1981, to MRSB Sample Coordinator, MRSB Sample Coordinator, Subject: Stability Study of Methanol on Silica Gel.

Occupational Health Guideline for 1-Nitropropane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3CH_2CH_2NO_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1-nitropropane is 25 parts of 1-nitropropane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 90 milligrams of 1-nitropropane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for 1-nitropropane from 25 ppm to 15 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1-Nitropropane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1-Nitropropane causes irritation of the eyes and respiratory tract, headache, nausea, vomiting, and diarrhea.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1-nitropropane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1-nitropropane at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1-nitropropane exposure.

—Chronic respiratory disease: 1-Nitropropane causes respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1-nitropropane might cause exacerbation of symptoms due to its irritant properties.

—Liver disease: 1-Nitropropane causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 1-Nitropropane causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

1-Nitropropane vapor is an eye irritant and in animals causes mild respiratory irritation and severe liver damage. Rabbits died from exposure to 5,000 ppm for 3 hours, but 10,000 ppm for 1 hour was not lethal. Effects were conjunctival irritation, lacrimation, slow respiration with some rales, muscular incoordination, ataxia, and weakness. Autopsy of animals exposed to lethal concentrations revealed severe fatty infiltration of the liver and moderate kidney damage. Human volunteers exposed to over 100 ppm noted eye irritation. There are no reports of systemic effects in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1. Molecular weight: 89.1
2. Boiling point (760 mm Hg): 131.6 C (268 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of 1-nitropropane): 3.1
5. Melting point: −108 C (−162 F)
6. Vapor pressure at 20 C (68 F): 7.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.4
8. Evaporation rate (butyl acetate = 1): 0.8

• **Reactivity**

1. Conditions contributing to instability: Overheating in closed containers may cause violent explosion.
2. Incompatibilities: Even though no detonation of 1-nitropropane has been reported, contact with amines, strong acids, and alkalies may cause 1-nitropropane to become unstable. Contact with strong oxidizers may cause fires and explosions. Mixtures of 1-nitropropane and hydrocarbons (or other combustible materials) are highly flammable. Contact with some metal oxides may cause decomposition and development of pressure.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving 1-nitropropane.
4. Special precautions: Liquid 1-nitropropane will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 35.6 C (96 F) (closed cup)
2. Autoignition temperature: 420.6 C (789 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: Data not available
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: The AIHA *Hygienic Guide* states that "the odor (of nitropropane) is detectable at 300 ppm but not at 80 ppm."
2. Eye Irritation Level: Grant states that "tests of nitropropane vapor on human volunteers have established that a sensation of eye irritation is noted at a concentration of 150 ppm in air."
3. Evaluation of Warning Properties: Since the odor and irritation thresholds of nitropropane are not within three times the permissible exposure limit, it is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

At the time of publication of this guideline, no measurement method for 1-nitropropane had been published by NIOSH.

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Clothing wet with liquid 1-nitropropane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1-nitropropane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1-nitropropane, the person performing the operation should be informed of 1-nitropropane's hazardous properties.

• Any clothing which becomes wet with liquid 1-nitropropane should be removed immediately and not reworn until the 1-nitropropane is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid 1-nitropropane may contact the eyes.

SANITATION

• Employees who handle liquid 1-nitropropane should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1-nitropropane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a thinner and solvent for cellulose compounds, lacquers, and dopes; in vinyl resins for industrial coatings and printing inks; in synthetic finish removers,; and for oil- and spirit-soluble dyes of molded plastics	Process enclosure; local exhaust ventilation; personal protective equipment
Use as an extraction solvent for purification, separation, recrystallization, and recovery for natural and synthetic resins, tars, coating materials, fats, and oils	Local exhaust ventilation; personal protective equipment
Use as a reaction medium in polymer technology, as a catalyst, initiator, and solvent	Local exhaust ventilation; personal protective equipment
Use in organic chemical synthesis for preparation of amines, nitrated alcohols, and acids, and chloronitroparaffins	Local exhaust ventilation; personal protective equipment
Use in manufacture of explosives	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid 1-nitropropane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid 1-nitropropane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid 1-nitropropane soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1-nitropropane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid 1-nitropropane has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If liquid 1-nitropropane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels and burn in a suitable combustion chamber which allows burning in an unconfined condition and is equipped with an appropriate effluent gas cleaning device. Large quantities can be collected, diluted in fuel oil, and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Liquid 1-nitropropane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Liquid 1-nitropropane may be disposed of by diluting in fuel oil and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR 1-NITROPROPANE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
150 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1250 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2300 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Methyl Alcohol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3OH
- Synonyms: Methanol; wood alcohol; Columbian spirits; carbinol
- Appearance and odor: Colorless liquid with a characteristic, pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methyl alcohol is 200 parts of methyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 260 milligrams of methyl alcohol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 200 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 800 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Methyl Alcohol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methyl alcohol can affect the body if it is swallowed, is inhaled, or comes in contact with the skin or eyes.

- **Effects of overexposure**

1. Short-term Exposure: Swallowing methyl alcohol or breathing very high concentrations of methyl alcohol may produce headache, weakness, drowsiness, lightheadedness, nausea, vomiting, drunkenness, and irritation of the eyes, blurred vision, blindness, and death. A person may get better and then worse again up to 30 hours later.

2. Long-term Exposure: Prolonged exposure to higher concentrations of methyl alcohol may result in headaches, burning of the eyes, dizziness, sleep problems, digestive disturbances, and failure of vision. Repeated or prolonged skin exposure may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methyl alcohol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methyl alcohol at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, and eyes should be stressed.

—Skin disease: Methyl alcohol is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be susceptible to the effects of this agent.

—Liver function tests: Methyl alcohol may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Although methyl alcohol has not been proven to be kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Eye disease: Because methyl alcohol may cause optic atrophy and blindness, those with pre-existing eye diseases may be at increased risk from exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. In addition, anyone developing the above-listed conditions or who has been splashed in the eyes with,

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

has ingested, or otherwise has been exposed to methyl alcohol should be placed under medical surveillance.

• Summary of toxicology

Ingestion of methyl alcohol is a well-known cause of optic neuropathy and may be lethal. Severe acidosis may result from ingestion or high exposures. Animals exposed to vapor concentrations above 8000 to 10,000 ppm show narcotic effects progressing from lethargy, to ataxia, to prostration and death in a state of profound acidosis due in part to the metabolic formation of formaldehyde and formic acid. Occupational exposure to high concentrations of methyl alcohol vapor has been reported to cause death or blindness, usually from working in a confined space. A woman died after exposure for 12 hours to vapor concentrations calculated at 4000 to 13,000 ppm. Chronic poisoning manifested by marked diminution of vision and enlargement of the liver has been reported in a workman exposed at levels of 1200 to 8000 ppm for a period of 4 years. Direct skin contact with methy alcohol may cause dermatitis, erythema, and scaling.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 32
2. Boiling point (760 mm Hg): 64.5 C (148 F)
3. Specific gravity (water = 1): 0.8
4. Vapor density (air = 1 at boiling point of methyl alcohol): 1.1
5. Melting point: −98 C (-144 F)
6. Vapor pressure at 20 C (68 F): 97 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): 5.9

• Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide and formaldehyde) may be released in a fire involving methyl alcohol.
4. Special precautions: Methyl alcohol will attack some forms of plastics, rubber, and coatings. It may also react with metallic aluminum at high temperatures.

• Flammability

1. Flash point: 11 C (52 F) (closed cup)
2. Autoignition temperature: 385 C (725 F)
3. Flammable limits in air, % by volume: Lower: 6.7; Upper: 36
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• Warning properties

1. Odor Threshold: May and Summer report that the odor threshold of methyl alcohol (methanol) is 5900 ppm. The AIHA *Hygienic Guide* states that the odor is faint at 2000 ppm.
2. Eye Irritation Level: The *Hygienic Guide* states that irritation occurs only at high concentrations. Grant states that "external contact of methanol with the eye has been alleged to have caused corneal opacities, but this must be far from the rule . . . . By exposure of cats to methanol vapors an attempt has been made to induce vacuoles in the corneal epithelium similar to those produced by other solvents, but this has been unsuccessful."

Browning reports that concentrations ranging from 7500 ppm to 69,000 ppm irritate mucous membranes.

3. Evaluation of Warning Properties: Methyl alcohol (methanol) has poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methyl alcohol. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of methyl alcohol in an adsorption tube containing silica gel, followed by desorption with water, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methyl alcohol may be used. An analytical method for methyl alcohol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the

process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methyl alcohol.

• Clothing wet with liquid methyl alcohol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methyl alcohol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methyl alcohol, the person performing the operation should be informed of methyl alcohol's hazardous properties.

• Any clothing which becomes wet with liquid methyl alcohol should be removed immediately and not reworn until the methyl alcohol is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methyl alcohol may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methyl alcohol should be promptly washed or showered to remove any methyl alcohol.

• Eating and smoking should not be permitted in areas where liquid methyl alcohol is handled, processed, or stored.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methyl alcohol may occur and control methods which may be effective in each case:

Operation	
Liberation during application of surface coatings such as shellac, wood dyes, nitrocellulose lacquers, water-proofing formulations, and phenolic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent for rotogravure inks, aniline dyes, and duplicator fluids	General dilution ventilation
Liberation during manual application of methanol as a cleaner for coated surfaces, leather, gloves, and metal and resins surfaces prior to further treatment	General dilution ventilation; personal protective equipment
Liberation during manufacture of formaldehyde by oxidation or dehydrogenation	Local exhaust ventilation; general dilution ventilation
Use in plastics industry to produce plasticizers, softening agents, and acrylic resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use as an intermediate in the preparation of methacrylates, methyl chlorides, methyl ethers, dimethyl sulfate, methyl formate, and methyl bromide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during application as an extractant in industrial chemical processes such as refinery gasoline and oils and purifying pharmaceuticals such as steroids and hormones	Local exhaust ventilation; general dilution ventilation
Use as a solvent in rubber industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If methyl alcohol gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If methyl alcohol gets on the skin, promptly flush the contaminated skin with water. If methyl alcohol soaks through the clothing, remove the clothing immediately and flush the skin with water. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of methyl alcohol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When methyl alcohol has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If methyl alcohol is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Methyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Methyl alcohol may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber.

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• Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies – Methyl Alcohol*, New York, 1970.

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
10,000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25,000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 25,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

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