NIDSH

CRITERIA FOR A
RECOMMENDED STANDARD....

OCCUPATIONAL EXPOSURE TO

- n-ALKANE MONO THIOLS
- CYCLOHEXANETHIOL
- BENZENETHIOL



U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

criteria for a recommended standard....

OCCUPATIONAL EXPOSURE TO

n-ALKANE MONO THIOLS, CYCLOHEXANETHIOL, and BENZENETHIOL



U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

Center for Disease Control

National Institute for Occupational Safety and Health

September 1978

DISCLAIMER

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

DHEW (NIOSH) Publication No. 78-213

PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and provide for the safety of workers occupationally exposed to an ever-increasing number of potential hazards. The National Institute for Occupational Safety and Health (NIOSH) evaluates all available research data and criteria and recommends standards for occupational exposure. The Secretary of Labor will weigh these recommendations along with other considerations, such as feasibility and means of implementation, in promulgating regulatory standards.

NIOSH will periodically review the recommended standards to ensure continuing protection of workers and will make successive reports as new research and epidemiologic studies are completed and as sampling and analytical methods are developed.

The contributions to this document on thiols by NIOSH staff, other Federal agencies or departments, the review consultants, the reviewers selected by the Society of Toxicology and the American Industrial Hygiene Association, and Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, are gratefully acknowledged.

The views and conclusions expressed in this document, together with the recommendations for a standard, are those of NIOSH. They are not necessarily those of the consultants, the reviewers selected by professional societies, or other Federal agencies. However, all comments, whether or not incorporated, were considered carefully and were sent with the criteria document to the Occupational Safety and Health Administration for consideration in setting the standard. The review consultants and the Federal agencies which received the document for review appear on pages v and vi.

J. Michael Lane, M.D.

Acting Director, National Institute for Occupational Safety and Health

The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health (NIOSH), had primary responsibility for development of the criteria and recommended standard for thiols. David J. Brancato of this Division served as the criteria manager. Equitable Environmental Health, Inc. (EEH) developed the basic information for consideration by NIOSH staff and consultants under contract CDC 210-77-0148.

The Division review of this document was provided by J. Henry Wills, Ph.D. (Chairman), Richard A. Rhoden, Ph.D., Bryan D. Hardin (Division of Biomedical and Behavioral Science), Loren L. Hatch, D.O., Ph.D. (Division of Technical Services), and Clara H. Williams, Ph.D.

REVIEW CONSULTANTS

Dennis I. Chamot, Ph.D.
Assistant to the Executive Secretary
Council of AFL-CIO Unions for
Professional Employees
Washington, D.C. 20006

Gerald W. Grawey, M.D. Caterpillar Tractor Company Peoria, Illinois 61629

Harry L. Markel, Jr. NIOSH, Region VI Dallas, Texas 75202

Russel K. Tanita DOL/OSHA Washington, D.C. 20210

Dennis A. Tyler Phillips Petroleum Company Bartlesville, Oklahoma 74004

J. Drake Watson Pennwalt Corporation King of Prussia, Pennsylvania 19406

FEDERAL AGENCIES

Department of Agriculture
Agricultural Research Service

Department of Defense
Office of Deputy Assistant Secretary for
Energy, Environment, and Safety

Department of the Air Force
Office of the Surgeon General
Aerospace Medicine Division, Inspection and Safety Center
Occupational and Environmental Health Laboratories

Department of the Army
Army Environmental Hygiene Agency

Department of the Navy
Bureau of Medicine and Surgery
Navy Environmental Health Center

Department of Energy
Division of Operational and Environmental Safety

Department of Health, Education, and Welfare
Food and Drug Administration
National Institutes of Health
National Cancer Institute
National Institute of Environmental Health Sciences
National Institute of Neurological and Communicative Disorders
and Stroke

Department of Interior Fish and Wildlife Service

Department of Labor
Mine Safety and Health Administration

Department of Transportation Materials Transportation Bureau

Consumer Product Safety Commission

Environmental Protection Agency
Office of Research and Development

National Aeronautics and Space Administration

CONTENTS

		Page
PREFACE		iii
REVIEW (CONSULTANTS	v
FEDERAL	AGENCIES	vi
I.	RECOMMENDATIONS FOR A THIOL STANDARD	1
	Section 1 - Environmental (Workplace Air) Section 2 - Medical Section 3 - Labeling and Posting Section 4 - Personal Protective Equipment and Clothing Section 5 - Informing Employees of Hazards from Thiols	1 2 4 7 8
	Section 6 - Work Practices Section 7 - Sanitation Practices Section 8 - Monitoring and Recordkeeping Requirements	11 14 14
II.	INTRODUCTION	16
III.	BIOLOGIC EFFECTS OF EXPOSURE	17
	Extent of Exposure Historical Reports Effects on Humans Odor Threshold Studies Epidemiologic Studies Animal Toxicity Metabolic Studies Correlation of Exposure and Effect Carcinogenicity, Mutagenicity, Teratogenicity, and Effects on Reproduction	17 19 22 26 33 33 54 61
IV.	Environmental Data Environmental Data Sampling and Analytical Methods Engineering and Administrative Controls	67 67 67 71
٧.	WORK PRACTICES	75
	Training Protective Clothing and Equipment Emergency and First-Aid Practices	75 77 78

CONTENTS (CONTINUED)

		Page
	Material Handling Sanitation	78 80
VI.	DEVELOPMENT OF STANDARD	82
	Basis for Previous Standards Basis for the Recommended Standard	82 83
VII.	RESEARCH NEEDS	92
	Sampling and Analytical Studies Epidemiologic Studies Long-Term Animal Exposure Studies Carcinogenicity Studies Mutagenicity Studies Teratogenic and Related Reproductive Effects Electroencephalographic Studies Skin Effects Metabolic Studies Personal Protective Equipment	92 92 93 93 93 94 94 94
VIII.	REFERENCES	95
IX.	APPENDIX I - Analytical Method for Butanethiol	107
х.	APPENDIX II - First Aid for Eyes Contaminated with Benzenethiol	117
XI.	APPENDIX III - Material Safety Data Sheet	119
XII.	TABLES	127

I. RECOMMENDATIONS FOR A THIOL STANDARD

NIOSH recommends that employee exposure to thiols in the workplace be controlled by adherence to the following sections. The recommended standard is designed to protect the health and provide for the safety of employees for up to a 10-hour workshift, in a 40-hour workweek, during a working lifetime. Compliance with all sections of the recommended standard should prevent adverse effects of exposure to thiols on the health of employees and provide for their safety. Techniques recommended in the standard are valid, reproducible, and available to industry and government agencies. Sufficient technology exists to permit compliance with the Although NIOSH considers the recommended workplace recommended standard. environmental limits to be safe levels based on current information, employers should regard them as the upper boundaries of exposure and make every effort to maintain exposures as low as is technically feasible. criteria and recommended standard will be reviewed and revised as necessary.

These criteria and the recommended standard apply to exposure of employees to selected monofunctional organic sulfhydryl compounds, specifically, the 14 n-alkane thiols having the general molecular formula $C_nH_{2n}+1SH$ (where n = 1, 2...12, 16, and 18), the aliphatic cyclic thiol, cyclohexanethiol, and the aromatic thiol, benzenethiol; hereinafter they may be referred to as "thiols." Synonyms for thiols include mercaptans, thioalcohols, and sulfhydrates.

Because of systemic effects, absorption through the skin on contact, and possible dermal irritation, "occupational exposure to thiols" is defined as work in any area where thiols are produced, processed, stored, or otherwise used. If thiols are handled or stored in intact, sealed containers, eg, during shipment, NIOSH recommends that only Sections 3, 5(a), and 6(g) of this proposed standard apply. If exposure to other chemicals also occurs, provisions of any standard applicable to the other chemicals shall be followed.

Section 1 - Environmental (Workplace Air)

(a) Concentration

(1) Occupational exposure shall be controlled so that no employee is exposed to benzenethiol at concentrations in excess of 0.5 milligrams per cubic meter (mg/cu m) of air (0.1 ppm in air by volume) determined as a ceiling concentration for any 15-minute period.

- (2) Occupational exposure to aliphatic thiols shall be controlled so that employees are not exposed at concentrations greater than the limits, in milligrams per cubic meter of air, shown in Table I-l as a ceiling concentration for any 15-minute period.
- (3) Occupational exposure to mixtures of thiols shall be controlled so that no employee is exposed at an equivalent concentration for the mixture greater than that calculated by the formula given in 29 CFR $1910.1000 \, (d)(2)(i)$.

(b) Sampling and Analysis

Procedures for the collection and analysis of workroom air samples shall comply with those given in Appendix I or with any method shown to be at least equivalent in precision, sensitivity, and accuracy.

Section 2 - Medical

Medical surveillance shall be made available as outlined below to all workers occupationally exposed to thiols.

(a) Preplacement examinations shall include at least:

- (1) Comprehensive medical and work histories with special emphasis directed to symptoms and signs of disorders of the central and autonomic nervous systems, the cardiovascular system, and the skin.
- (2) Physical examination giving particular attention to the nervous and cardiovascular systems. For workers subject to occupational exposure to benzenethiol, eye examinations shall be included in addition to the above-mentioned systems.
- (3) An evaluation of the worker's ability to use positive pressure respirators. Criteria should include the presence of significant obstructive or restrictive pulmonary disease or cardiopulmonary impairment.
- (4) White blood cell counts (WBC's) (total and differential), hematocrit, hemoglobin concentration in whole blood, total bilirubin, and urinalysis. The value of estimations of fecal urobilinogen in distinguishing jaundice due to hemolytic anemia from that due to other common causes should be kept in mind.
- (b) Periodic examinations shall be made available at least annually to any workers who have been occupationally exposed to thiols and shall include:

(1) Interim medical and work histories.

TABLE I-1
RECOMMENDED EXPOSURE LIMITS FOR ALIPHATIC THIOLS

Thiol	Ceiling Concentration Limits		
	mg/cu m	Approximate ppm Equivalents	
l-Methanethiol	1.0	0.5	
l-Ethanethiol	1.3	0.5	
1-Propanethiol	1.6	0.5	
l-Butanethiol	1.8	0.5	
l-Pentanethiol	2.1	0.5	
l-Hexanethiol	2.4	0.5	
1-Heptanethiol	2.7	0.5	
l-Octanethiol	3.0	0.5	
l-Nonanethiol	3.3	0.5	
l-Decanethiol	3.6	0.5	
l-Undecanethiol	3.9	0.5	
l-Dodecanethiol	4.1	0.5	
l-Hexadecanethiol	5.3	0.5	
l-Octadecanethiol	5.9	0.5	
Cyclohexanethiol	2.4	0.5	

- (2) Physical examination as described in (a)(2) above.
- (3) Laboratory examinations as described in (a)(4) above.
- (4) Referral for a more detailed diagnostic workup if signs or symptoms of neurologic abnormalities are discovered in workers occupationally exposed to these substances.
- (c) Employees and prospective employees having medical conditions, such as fainting spells, neuromuscular weakness, and cardiopulmonary impairment, that could be directly or indirectly aggravated by exposure to thiols shall be counseled on the increased risk to their health from exposure to the substances.
- (d) Medical personnel should be aware of the possibility of delayed systemic effects such as fainting spells, neuromuscular weakness, and/or cardiopulmonary impairment. Persons requiring medical attention as a result of exposure to thiols may require observation for up to 72 hours. Medical examinations as described in (a) 2 shall be then made available if warranted.
- (e) Pertinent medical records shall be maintained by the employer for all employees occupationally exposed to thiols. Such records shall be retained for at least 30 years after employment ends. These records shall be made available to the designated medical representatives of the Secretary of Labor, of the Secretary of Health, Education, and Welfare, of the employer, and of the employee or former employee.

Section 3 - Labeling and Posting

All labels and warning signs shall be printed both in English and in the predominant language of non-English-reading workers. Workers unable to read the labels and signs provided shall receive information regarding hazardous areas and shall be informed of the instructions printed on labels and signs.

(a) Labeling

All bulk containers that hold thiols shall carry, in a readily visible location, a label that bears the trade name or other common name of the product and information on the effects of exposure to the compound on human health. The information shall be arranged as in the example below for all the thiols except benzenethiol.

SPECIFIC THIOL (Trade or Common Name) DANGER COMBUSTIBLE

MAY BE HARMFUL IF ABSORBED THROUGH SKIN,
INHALED, OR INGESTED
MAY CAUSE IRRITATION OF SKIN
KEEP CONTAINERS CLOSED WHEN NOT IN USE

For methanethiol, ethanethiol, propanethiol, butanethiol, pentanethiol, and cyclohexanethiol, the word FLAMMABLE shall be used instead of COMBUSTIBLE in the above example and the following caution shall be added to the label: Exposure to vapor from large spills may produce unconsciousness.

For benzenethiol, the information shall be arranged as in the example below:

BENZENETHIOL
(Trade or Common Name)
DANGER
COMBUSTIBLE

MAY BE FATAL IF ABSORBED THROUGH SKIN,
INHALED, OR INGESTED
MAY CAUSE IRRITATION OF EYES AND SKIN
KEEP CONTAINERS CLOSED WHEN NOT IN USE

On all labels, the following information shall be included as in the example below:

Do not get on skin, in eyes or mouth, or on clothing.
Avoid breathing vapor.
Use only with adequate ventilation.
Keep containers closed when not in use.
Wash hands and face thoroughly before eating, drinking, smoking, or using toilet.

<u>First Aid:</u> Remove victims to fresh air immediately. Give artificial respiration if needed. Give oxygen if breathing is impaired. Call a physician.

In case of skin contact, immediately flush with copious quantities of water, then wash with soap and water. In case of eye contact with benzenethiol or with mixtures that contain benzenethiol, the affected

eye shall be treated with not more than two drops of 0.5% silver nitrate (AgNO₃), applied from a bougie or other previously sealed container, and then flushed with copious quantities of water. Eyes contacted by thiols other than benzenethiol shall be flushed with copious amounts of water. A physician should be consulted promptly about any eye contact with solid or liquid thiols.

(b) Posting

In areas where exposure to thiols can occur, signs containing appropriate health hazard warning statements shall be posted in readily visible locations. Such information for the n-alkane monothiols and cyclohexanethiol shall be arranged as in the example below:

DANGER! COMBUSTIBLE

THIOL PRESENT IN AREA (THIOL NAME OR NAMES)

MAY BE HARMFUL IF ABSORBED THROUGH SKIN, INHALED, OR INGESTED

MAY BE IRRITATING TO SKIN

Do not get on skin, in eyes or mouth, or on clothing.

Do not breathe vapor.

Keep containers closed when not in use.

For methanethiol, ethanethiol, propanethiol, butanethiol, pentanethiol, and cyclohexanethiol, the word FLAMMABLE shall be used in place of COMBUSTIBLE in the above example.

For benzenethiol, the information shall be arranged as in the example below:

DANGER! COMBUSTIBLE

BENZENETHIOL PRESENT IN AREA
MAY BE FATAL IF ABSORBED THROUGH SKIN,
INHALED, OR INGESTED

MAY BE IRRITATING TO EYES AND SKIN

Do not get on skin, in eyes or mouth, or on clothing.

Do not breathe vapor.

Keep containers closed when not in use.

In an emergency involving thiols, all affected personnel shall be provided with immediate first aid, followed by prompt medical evaluation and care. In the event of skin or eye contact with liquid thiols, skin and eyes shall be flushed with copious amounts of water. In case of eye contact with benzenethiol or with a mixture including benzenethiol, the affected eye shall be treated with no more than two drops of a 0.5% solution of silver nitrate (AgNO $_3$), applied from a bougie or other previously sealed container, and then flushed with copious quantities of water. For further discussion, see Appendix II.

(c) When respirators are permitted under Section 4(c), the following statement shall be added in large letters to the signs required in Section 3(b):

RESPIRATORY PROTECTION REQUIRED IN THIS AREA

(d) In any area where emergency situations may arise, by Section 3(b) shall be supplemented with signs giving emergency first-aid instructions and procedures, the and first-aid supplies and emergency equipment, and the location οf location of emergency showers and eyewash fountains.

Section 4 - Personal Protective Equipment and Clothing

Engineering controls shall used when needed be οf thiols or below the recommended concentrations airborne at environmental limit and to minimize skin and eye contact. addition, employers shall provide protective equipment and clothing to employees when necessary.

(a) Eye Protection

Safety glasses with side shields shall be worn whenever there is occupational exposure to thiols. Chemical safety goggles and face shields (8-inch minimum) meeting the requirements of 29 CFR 1910.133 and ANSI Z87.1-1968 shall be provided and worn in any operation in which there is a reasonable possibility that thiols may be splashed into the eyes.

(b) Skin Protection

Depending on the operations involved and the probable or likely extent of dermal exposure, protective clothing and equipment, including gloves, aprons, suits, boots, and face shields (8-inch minimum) with goggles, shall be worn to prevent skin contact with particulate or splashed liquid thiols.

(c) Respiratory Protection

- (1) Use of respiratory protective equipment shall be permitted only in the following circumstances to protect employees from exposure to airborne thiols at concentrations that may exceed the recommended environmental limit:
- (A) During the time necessary to install and test the controls required in Section 6(b).
- (B) For nonroutine operations, such as maintenance or repair activities.
 - (C) In emergencies.
- (2) When use of respirators is permitted, the respirator shall be selected and used pursuant to the following requirements:
- (A) Employers shall establish and enforce a respiratory protective program meeting the requirements of 29 CFR 1910.134.
- (B) Employers shall provide respirators in accordance with Tables I-2 I-3 and shall and ensure that employees use the respirators when necessary. The respiratory protective devices provided in conformance with Tables I-2 and I-3 shall comply with the standards jointly approved by NIOSH and the Mine Safety and Health Administration (formerly by the Mine Enforcement and Safety Administration and the Bureau of Mines) as specified under the provisions of 30 CFR 11.
- (C) Employers shall ensure that respirators are properly cleaned and maintained and that employees are trained and drilled at least annually in the use of respirators assigned to them and in ways to test for leaks.
- (D) Respirators shall be easily accessible, and employees shall be informed of their location.

Section 5 - Informing Employees of Hazards from Thiols

- (a) Employees occupationally exposed to thiols shall be verbally informed of the hazards of such exposure, the symptoms associated with such exposure, appropriate emergency procedures, and proper procedures for the safe handling and use of thiols.
- (b) A continuing education program, conducted at least annually by qualified health and safety personnel, shall be instituted to ensure that employees whose jobs may involve exposure to thiols, including those engaged in maintenance and repair, have

TABLE I-2
RESPIRATOR SELECTION GUIDE FOR BENZENETHIOL

Concentration Range	Respirator Type Approved under Provisions of 30 CFR 11
Less than or equal to 5 mg/cu m	 Chemical cartridge respirator with half-mask facepiece and organic vapor cartridge Supplied-air respirator operated in demand (positive pressure) mode with full facepiece
Less than or equal to 25 mg/cu m	 Gas mask with chin-style or front- or back-mounted organic vapor canister with full facepiece Supplied-air respirator in demand (positive pressure) mode with full facepiece Self-contained breathing apparatus operated in demand (positive pressure) mode with full facepiece
Greater than 25 mg/cu m	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand mode (2) Combination supplied-air respirator with full facepiece and auxiliary self-contained air supply operated in the pressure-demand mode
Emergency (entry into area of unknown concentration for purposes such as firefighting)	(1) Self-contained breathing apparatus with full facepiece, operated in pressure-demand mode (2) Combination supplied-air respirator with full facepiece and auxiliary self-contained air supply, operated in the pressure-demand mode

TABLE I-3

RESPIRATOR SELECTION GUIDE FOR n-ALKANE THIOLS (C1-C12, C16, C18)

AND CYCLOHEXANETHIOL

Concentration Range	Respirator Type Approved under Provisions of 30 CFR 11
Less than or equal to 5 ppm	 Chemical cartridge respirator with half-mask facepiece and organic vapor cartridge Supplied-air respirator operated in demand (positive pressure) mode with half-mask facepiece
Less than or equal to 25 ppm	(1) Gas mask with chin-style or front- or back-mounted organic vapor canister with full facepiece (2) Supplied-air respirator in demand (positive pressure) mode with full facepiece (3) Self-contained breathing apparatus operated in demand (positive pressure) mode with full facepiece
Greater than 25 ppm	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand mode (2) Combination supplied-air respirator with full facepiece and auxiliary self-contained air supply operated in the pressure-demand mode
Emergency (entry into area of unknown concentration for purposes such as firefighting)	 Self-contained breathing apparatus with full facepiece, operated in pressure-demand mode Combination supplied-air respirator with full facepiece and auxiliary self-contained air supply, operated in the pressure-demand mode

current knowledge of job hazards, proper maintenance procedures, and cleanup methods.

Employees shall be informed of the general nature of the medical surveillance program and of the advantage of participation in the program. Each employee shall be told about the availability of the required information that shall include, as a minimum, that prescribed in paragraph 5(c).

- (c) Required information shall be recorded on the US Department of Labor form OSHA-20, Material Safety Data Sheet, shown in Appendix III, or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.
- (d) Each employee shall be informed of the location of the information described in paragraph 5(c). This information shall be kept on file at each establishment or department and shall be readily accessible to all employees occupationally exposed to thiols.
- (e) In an emergency involving thiols, all affected personnel shall be provided with immediate first aid, followed by prompt medical evaluation and care. In the event of skin or eye contact with liquid thiols, skin and eyes shall be flushed with copious amounts of water. In case of eye contact with benzenethiol or with a mixture including benzenethiol, the affected eye shall be treated with no more than two drops of a 0.5% solution of silver nitrate (AgNO₃), applied from a bougie or other previously sealed container, and then flushed with copious quantities of water. For further discussion, see Appendix II.

Section 6 - Work Practices

(a) Protective clothing and equipment, as set forth in Section 4, shall be worn by all employees who work where there is the possibility of skin or eye contact with particulate thiols.

(b) Emergency Procedures

For all work areas, emergency procedures as specified below, as well as any other procedures appropriate for a specific operation or process, shall be formulated in advance and employees shall be instructed in their implementation.

(1) The plan shall include pertinent information for obtaining emergency medical care and transportation to the hospital of injured workers.

- (2) Firefighting procedures shall be established implemented. These shall include procedures for emergencies involving the In case of fire, thiol sources shall be shut οf thiol vapor. off, flared (methanethiol), removed. or controlled by special Containers shall be removed or cooled with water spray. instructions. Chemical foam, carbon dioxide, or dry chemicals shall be used for fighting fires. proper respiratory protection and protective and clothing shall be worn.
- (3) Approved eye, skin, and respiratory protection as specified in Section 4 shall be used by personnel essential to emergency operations.
- (4) Nonessential employees shall be evacuated from exposure areas during emergencies. Perimeters of hazardous exposure areas shall be delineated, posted, and secured.
- (5) Personnel adequately protected against the attendant hazards shall shut off sources of thiols, clean up spills, and immediately repair leaks. Personnel shall flare methanethiol rather than shut off its source.

(c) Control of Airborne Thiols

Engineering controls shall be used to keep the concentration of thiols at or below the recommended limits. The use of a closed system is an effective method for controlling the escape of vaporized thiols into the air of the workplace. Local exhaust ventilation, used alone or in combination with the closed system, may also be effective. shall be designed to prevent accumulation or recirculation of thiols in the workroom, to keep concentrations within the limits of the recommended standard, and to remove thiols from the breathing zones of workers. Where a fan is located in ductwork and the concentration thiols greater than 25% of the lower explosive limit of the material being handled, the fan rotating element shall be constructed of nonsparking material and the casing shall consist of or be lined with nonsparking material. There shall sufficient clearance be between the fan rotating element and the fan casing to prevent contact between these two structures. Ventilation systems shall be inspected for corrosion shall receive preventive maintenance at least every 3 months. Airflow measurements (face velocities, static pressures, etc) should be included as part of the preventive maintenance program. The cleaning repairing of the ventilation system shall be immediately initiated if sufficient deterioration to indicate imminent development of leaks is found during the physical inspection and preventive maintenance program. This inspection may be required more frequently than every 3 months according to the judgment of an industrial hygienist. Tempered makeup air shall be provided as required to workrooms in which exhaust ventilation is operating.

(d) Storage

Storage of bulk amounts of thiols shall meet the requirements combustible liquid storage as specified in 29 CFR flammable or The C₁ through C₅ alkane thiols IB 1910.106. have the class Hexanethiol octanethiol the class IC designation. and have designation. Heptanethiol, nonanethiol, and higher molecular alkane thiols have the class III designation.

(e) Entry into Confined or Enclosed Spaces

- (1) Entry into confined spaces, such as tanks, pits, tank cars, barges, and process vessels, shall be controlled by a permit system. Permits shall be signed by an authorized representative of the employer and shall certify that preparation of the confined space, precautionary measures, and personal protective equipment are adequate and that precautions have been taken to ensure that prescribed procedures will be followed.
- (2) Before they are entered for repair, modification, or cleaning, confined spaces shall be inspected and tested for oxygen deficiency and for the presence of thiols and other known or suspected contaminants.
- (3) No employee shall enter any confined space that does not have an entry large enough to admit a person wearing safety harness, lifeline, and appropriate respiratory equipment as specified in Section 4(c).
- (4) Confined spaces shall be ventilated while work is in progress to keep the concentration of airborne thiols at or below the ceiling limit, to keep the concentration of other contaminants below dangerous levels, and to prevent oxygen deficiency.
- (5) Anyone entering a confined space shall be observed from the outside by another properly trained and protected worker. The person entering the confined space shall maintain continuous communication with the standby worker.
- (6) Cleaning, maintenance, and repair of tanks, process equipment, and lines shall be performed only by properly trained, adequately protected employees under supervisory control.

(f) Maintenance

Periodic maintenance shall be performed on all equipment and machinery in areas of potential exposure to thiols. Firefighting equipment and other emergency equipment shall be maintained in good working order, as prescribed by local, state, or Federal regulations.

- (g) Spills, Leaks, and Waste Disposal
- (1) If thiols are leaked or spilled, the following steps shall be taken:
 - (A) Evacuate all nonessential personnel from the area.
- (B) Adequately dike the area of the spill or leak to prevent further contamination.
- (C) Collect spilled material for reclamation or absorb in vermiculite, dry sand, earth, activated charcoal, household bleach solution, or other decontaminating material.
- (2) Personnel entering the spill or leak area shall be furnished with appropriate personal protective equipment. All other personnel shall be excluded from the area.
- (3) Water used to flush thiols shall be treated with hypochlorite to convert thiols to disulfides, eg, by addition of household bleach. The disposal method shall conform to applicable local, state, and Federal regulations and shall not constitute a hazard to the surrounding population or environment.

Section 7 - Sanitation Practices

- (a) Plant sanitation shall meet the requirements of 29 CFR 1910.141.
- (b) Clean and well-ventilated change rooms equipped with separate storage facilities for street clothes and work clothing shall be Showers and washing facilities provided. shall be provided accordance with applicable regulations. Employers shall encourage personnel who work with thiols to shower before leaving the workplace at the end of a workshift.
- (c) Employers shall instruct employees who handle thiols to wash their hands thoroughly with soap and water before eating, smoking, or using toilet facilities.
- (d) The storage, dispensing, preparation, and consumption of food, beverages, or tobacco shall be prohibited in work areas containing thiols.

Section 8 - Monitoring and Recordkeeping Requirements

Employers shall determine by an industrial hygiene survey whether exposure to airborne thiols is in excess of the

environmental limit. Records of these surveys shall be kept, and if that air levels are at or below the environmental employer concludes Surveys shall be repeated at limit, the records shall confirm this. process change. least annually and within 30 days any οf demonstrates that the environmental the industrial hygiene survey thiols exceeds the environmental limit. concentration of following requirements shall apply:

(a) Personal Monitoring

- (1) A program of monitoring shall be instituted to identify occupationally exposed employees and to measure or permit calculation of their exposures to thiols. Source and area monitoring may be used to supplement personal monitoring.
- (2) In all personal monitoring, samples representative of the exposure in the breathing zone of the employee shall be collected. Procedures for sampling and analysis of thiols shall be in accordance with Appendix I.
- (3) For each ceiling limit determination, a sufficient number of samples shall be collected to characterize employee exposures during each workshift. Variations in work and production schedules, as well as employee locations and job functions, shall be considered in decisions on sampling locations, times, and frequencies.
- (4) Each operation shall be sampled at least once every 3 months or as otherwise indicated by a professional industrial hygienist. If an employee is found to be exposed at a level in excess of the environmental limit, the exposure of that employee shall be measured at least weekly, control measures shall be initiated, and the employee shall be notified of the exposure and of the control measures being implemented. Such monitoring shall continue until two consecutive determinations, 1 week apart, indicate that exposures no longer exceed the environmental limit. Quarterly monitoring shall then be resumed.

(b) Recordkeeping

Records of environmental monitoring shall be retained for at least 30 years after employment ends. These records shall include the dates and times of measurements; duties and location of the employees within the worksite; sampling and analytical methods used; number, duration, and results of the samples taken; ceiling concentrations estimated from these samples; type of personal protective equipment used, if any; and employees' names. Records of environmental exposures applicable to an employee shall be included in the employee's medical records. Records of environmental monitoring shall be available to the designated representatives of the Secretary of Labor, of the Secretary of Health, Education, and Welfare, of the employer, and of the employee or former employee.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon that were prepared to meet the need for preventing occupational disease or injury arising from exposure to thiols. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

After reviewing data and consulting with others, NIOSH formalized a system for the development of criteria on which standards can be established to protect the health and to provide for the safety of employees exposed to hazardous chemical and physical agents. The criteria and recommended standards should enable management and labor to develop better engineering controls and work practices resulting in more healthful work environments; mere compliance with the recommended standards should not be regarded as a final goal.

These criteria and recommended standard for occupational exposure to thiols are part of a continuing series of documents published by NIOSH. The proposed standard applies to the manufacture, formulation, processing, storage, and use of thiols. The recommended standard was not designed for the population-at-large, and its application to any situation other than the occupational environment is not warranted. The recommended standard is intended to protect against the development of both systemic toxic effects and local effects on the skin and eyes of employees.

Occupational exposure to thiols in the United States occurs primarily to employees involved in the formulation of thiols and their use as odorants. Inhalation of the vapor is the most common route of occupational exposure. Mucosal irritation, respiratory changes leading to respiratory failure, muscular weakness culminating in paralysis, mild to severe cyanosis, coma, and death are major reasons for concern about employee exposure to thiols.

Several areas in which further research is needed have been identified. For example, studies, including epidemiologic ones, of the long-term health effects of exposure to thiols at concentrations around the recommended environmental limit would aid in assessing the hazards of low-level exposure. Followup examinations of employees who have had skin contact with thiols would help to quantitate the risks of systemic effects from dermal exposure. Investigations of the carcinogenic, mutagenic, and teratogenic potentials of thiols are needed also.