Medical-Industrial Hygiene Presentation

Refinery Management Meeting

Houston, Texas

February 13, 1978

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Contents:

SECTION A

Section A: Standards for Toxic and Hazardous Materials

By now we should all be aware that the OSHA regulations contain a general industry standard requiring control of some 400 air contaminants which may be found in the workplace. Exposures to employees are limited to eight-hour time weighted averages with threshold limit values set in parts per million or milligrams per cubic meter of air.

The Occupational Safety and Health Administration and the National Institute of Occupational Safety and Health have been busy formulating specific permanent standards which will replace these general industry standards. Permanent standards are now in existence for some 17 substances.

The following section gives information relative to the present status of the standards as they are being considered by OSHA and NIOSH:

A. Anatomy of OSHA Standards
B. Permanent Standards
C. Recommended or Proposed Standards
D. Draft Technical Standards
E. Criteria Documents

Anatomy of OSHA Standards

While there may be minor differences in content, generally all of the permanent standards will basically be constructed upon a common format. The following summary will indicate requirements one may expect to find as parts to any permanent standard.

ANATOMY OF OSHA STANDARDS

Permissible Exposure Limit

Exposure limits are defined in terms of Threshold Limit Values (TLV) as related to Time Weighted Averages (TWA) for an eight hour work day or in terms of Ceiling Limits greater than preset levels averaged over any 15 minute period during the workday.

Exposure Determinations and Measurements

Requirements for establishing exposure determinations and measurements for the specific substances are conditions of standards.

Methods of Measurement

Provision of the standards regarding methods of measurement of employee exposure are designed to assure that employee exposures are measured according to methods that will produce relatively accurate results.

Compliance Details

Provisions of the standards require that engineering or work practice controls shall be used to reduce exposure to the regulated substances to the permissible exposure limit or below. However, in situations where engineering and work practice controls are not sufficient to reduce exposures to the permissible limit, they shall nonetheless be used to reduce exposures to the lowest level feasable, and shall be supplemented by the use of respirators. The respirator program must comply with specific provisions of compliance.

Respirator Protection

The standards require employers to select NIOSH-MESA approved respirators.

Fire and Safety

The standards require the employer to familiarize himself with the guidelines for the safe handling and use of each regulated substance present in the workplace. The guidelines give chemical and physical data for each regulated substance, information on fire and explosion hazards, and spill, leak, and disposal procedures.

Personal Protective Clothing and Sanitation

The standards contain requirements for the use of protective clothing and equipment and for actions to be taken when a liquid or solid form of a regulated substance comes into contact with either the employee's clothing or skin.

Spills and Disposal

When applicable, the standards contain procedures for the cleanup and disposal of spills of the regulated substances. The purpose of these procedures is to prevent fires, explosions, or dispersion of the substances into the workplace in such a manner as to cause the permissible exposure limit to be exceeded.

Training and Information

The standards contain requirements for the employer to provide an annual training program for employees to present information contained in Substances Safety Data Sheets, to review the signs and symptoms of exposure and medical conditions which may be aggravated by exposure to the regulated materials, and to instruct employees to report any such signs, symptoms, or medical conditions to the employer. Employees must also be trained in the safe use of the regulated substances, emergency procedures, and correct use of protective equipment.

Housekeeping and Sanitation

The standards require employers to ensure that appropriate action is taken to maintain a clean workplace and that employers provide appropriate washing facilities and emergency eye wash facilities.

Medical Surveillance

The standards prescribe medical programs appropriate for the materials found in the workplace. These programs include such provisions as: preplacement histories and examinations, laboratory tests which may be very inclusive for testing the conditions and abilities of employees, and annual medical examinations.

Recordkeeping

The standards require the employer to maintain written records of exposure determinations, measurements of employee exposures, tests of mechanical ventilation systems (where such systems constitute engineering controls), annual training sessions, and records required by employee medical surveillance provisions. Duration of maintenance of records is established for each substance.

Access to Records

The standards provide for access to records of exposure measurements by employees, former employees or their representatives, and access to medical records by physicians designated by employees or former employees.

Observation of Measurement

The standards require that employers give affected employees or their representatives an opportunity to observe any measuring of employee exposures to any of the regulated substances conducted pursuant to these regulations.

Appendixes

The information contained in the three appendixes is advisory in nature and is not intended, by itself, to create any additional obligations not otherwise imposed by the standard or to detract from any existing obligation.

Appendix A, the "Substance Safety Data Sheet," is geared to the employee. It explains, in simple language, the substance identification, health hazards associated with the regulated substance, emergency first aid procedures, protective clothing and equipment to be used in working with the regulated substance, and precautions for the safe use, handling, and storage of the regulated substance.

Appendix B, the "Substance Technical Guidelines," is meant to aid the employer in complying with the requirements of the proposed standards. It includes physical and chemical data, fire and explosion hazard data, details of cleanup and disposal of spills, and information on how to take air samples.

Appendix C, the "Medical Surveillance Guidelines," is intended for the examining physician. The employer is required to provide this to the physician when employees are undergoing required medical examinations. Because a physician cannot be expected to be knowledgeable about all of the chemical substances used in industry, and in many instances the usual medical libraries lack the necessary information, Appendix C assures that the physician has adequate information to conduct a meaningful examination.

Permanent Standards

There are 16 substances for which permanent standards are in existence. All of these came into existence by OSHA utilizing the Emergency Standard process and include asbestos, vinyl chloride, and 14 carcinogens. Benzene was declared to be a suspected carcinogenic substance and a Temporary Emergency Standard was declared effective May 21, 1977. Benzene is under temporary stay pending court action. Noise, a physiological stress, is controlled in a standard effective on August 27, 1971, under Part 1910.95, 1910 Subpart G of the OSHA Regulations.

The following summary lists these substances and stresses along with a list of the 14 carcinogens which are permanent standards.

PERMANENT STANDARDS

Asbestos

14 Carcinogens

4-Nitrobiphenyl
Alpha-Naphthylamine
4,4-Methylene bis(2-Chloraniline)
Methyl Chloromethyl Ether
3,3-Dichlorobenzidine (and its salts)
bis-Chloromethyl Ether
Beta-Naphthylamine
Benzidine
4-Aminodiphenyl
Ethyleneimine
Beta-Propiolactone
2-Acetylamino Fluorene
4-Dimethylaminoazobenzene
n-Nitrosodimethylamine

Vinyl Chloride

Noise

Benzene (Emergency Temporary Standard under temporary stay)

Recommended or Proposed Standards

A number of substances have been recommended or proposed for consideration for permanent standards. The status of these will be varied throughout the standard completion system. Some will have been completed to the extent that NIOSH has presented them for consideration by OSHA and these will have appeared in the Federal Register and are being considered in public hearings; others will have been proposed to OSHA but they will not have been considered in the Federal Register for public hearings; yet others may be in Technical Draft Forms where OSHA and NIOSH are jointly working on them.

A mechanism also used by NIOSH is production of information in detailed documented form called a "Criteria for a Recommended Standard" for the occupational exposure to the particular substance being considered.

The following summaries list the various substances relative to the standard completion system. This information may include substances appearing in multiple standard completion status relative to the information available in the Industrial Hygiene Office of the Medical Division.

RECOMMENDED OR PROPOSED STANDARDS

Acetylene
Acrylamide
Alkanes:
  Pentane
  Hexane
  Heptane
  Octane
Alkyl Benzenes:
  p-Tert-Butyltoluene
  Cumene
  Ethyl Benzene
  Alpha-Methyl Styrene
  Styrene
  Vinyl Toluene
Allyl Chloride
Ammonia
Arsenic

Beryllium
Boron Trifluoride

Carbaryl
Carbon Dioxide
Carbon Tetrachloride
Chlorine
Chloroform
Chromium
Coke Oven Emissions
Crystalline Silica
*Cyclohexane

Dioxane

Epichlorohydrin
Ethylene Dibromide
Ethylene Dichloride

Fibrous Glass
Formaldehyde

Hydrogen Cyanide
Hydrogen Fluoride

Inorganic Nickel
Isopropyl Alcohol

*Ketones:
  Camphor
  Mesityl Oxide
  5-Methyl-3-Heptanone

*Proposed along with Alkyl Benzenes.

VMD 723060

Ketones
  2-Butanone
  Methyl n-Amyl Ketone
  Ethyl Butyl Ketone
  Hexone (Methyl Isobutyl Ketone)
  Cyclohexanone
  2-Pentanone

Lead

Methyl Alcohol
Methyl Parathion
Methylene Chloride

Nitric Acid

Oxides of Nitrogen
*Ozone

Phenol
Phosgene
Polychlorinated Biphenyls

Sodium Hydroxide
Sulfuric Acid
Sulfur Dioxide

1,1,2,2-Tetrachloroethane
Tetrachloroethylene (Perchloroethylene)
Toluene
1,1,1-Trichloroethane (Methyl Chloroform)
Trichloroethylene

Xylene

Zinc Oxide

DRAFT TECHNICAL STANDARDS - INDEX

Furfural - Set C, Part I

Glycidol - Set F, Part I

Heptane - Set G, Part I
Hexachloronaphthalene - Set H, Part II
Hexone - Set C, Part I
Hydrogen Bromide - Set L, Part II
Hydrogen Fluoride - Set L, Part II
Hydroquinone - Set E, Part II

Isoamyl Acetate - Set D, Part II
Isoamyl Alcohol - Set E, Part II
Isobutyl Acetate - Set D, Part II
Isobutyl Alcohol - Set E, Part II
Isopropyl Acetate - Set E, Part II
Isopropyl Alcohol - Set E, Part II
Isopropyl Glycidyl Ether - Set F, Part II

Mesityl Oxide - Set B
Methylal - Set F, Part II
Methyl Acetate - Set D, Part II
Methyl Alcohol - Set E, Part II
Methyl Acralate - Set D, Part II
Methyl Cellosolve - Set F, Part II
Methyl Cellosolve Acetate - Set D, Part II
Methylcyclohexane - Set G, Part I
5-Methyl-3-Heptanone (Ethyl Sec-Amyl Ketone) - Set B
Methyl Iodide - Set H, Part II
Methyl (n-Amyl) Ketone (2-Heptanone) - Set B
Methyl Isobutyl Carbinol - Set E, Part II
Methyl Metharyclate - Set E, Part II
Molybdenum Compounds, Soluble - Set M

Naphtha (Coal Tar) - Set G, Part I
n-Amyl Acetate - Set E, Part I
n-Butyl Glycidyl Ether - Set F, Part I

Octane - Set G, Part II
o-Dichlorobenzene - Set J, Part II
o-Toluidine - Set L, Part II
Ozone - Set B

Pentane - Set G, Part II
2-Pentanone - Set C, Part II
Petroleum Distillates (Naphtha) - Set G, Part II
Phenol - Set L, Part II
Phenyl Glycidyl Ether - Set F, Part II
Phenyl Hydrazine - Set L, Part II
Phosphoric Acid - Set M
Pival (Pivalyl-1,3-Indadione) - Set B

Platinum Soluble Salts - Set M
p-Nitroaniline - Set B
Propyl Alcohol - Set E, Part II
Propylene Dichloride - Set G, Part II
p-Tert-Butyltoluene - Set C, Part I
Pyridine - Set L, Part II

Rhodium Metal Fume & Dusts - Set M
Rhodium Soluble Salts - Set M

Sec-Amyl Acetate - Set D, Part I
Sec-Butyl Acetate - Set D, Part I
Sec-Butyl Alcohol - Set E, Part I
Sec-Hexyl Acetate - Set D, Part II
Stoddard Solvent - Set G, Part II
Styrene - Set C, Part II
Sulfuric Acid - Set L, Part II

Terphenyls - Set C, Part II
Tert-Butyl Acetate - Set D, Part I
Tert-Butyl Alcohol - Set E, Part I
1,1,2,2-Tetrachloro-1,2-Difluoroethane - Set I, Part II
1,1,1,2-Tetrachloro-2,2-Difluoroethane - Set I, Part II
1,1,2,2-Tetrachloroethane - Set I, Part II
Tetrahydrofuran - Set F, Part II
1,1,2-Trichloro-1,2,2-Trifluoroethane - Set I, Part II
1,2,3-Trichloropropane - Set I, Part II
Trifluoromonobromomethane - Set I, Part II
Turpentine - Set G, Part II

Vinyl Toluene - Set C, Part II

Xylidine - Set L, Part II

DRAFT TECHNICAL STANDARDS - INDEX

SET B

Camphor
Chloroacetaldehyde
Alpha-Chloroacetophenone (Phenacyl Chloride)
Ethyl Butyl Ketone (3-Heptanone)
Mesityl Oxide
5-Methyl-3-Heptanone (Ethyl Sec-Amyl Ketone)
Methyl (n-Amyl) Ketone (2-Heptanone)
p-Nitroaniline
Ozone
Pival (Pivalyl-1,3-Indadione)

SET C - PART I

Acrolein
p-tert-Butyltoluene
Cumene (Isopropyl Benzene)
Cyclohexane
Cyclohexanone
Diphenyl (Biphenyl)
Ethyl Benzene
Furfural
Hexone

SET C - PART II

Alpha-methyl Styrene
2-Pentanone
Styrene
Terphenyls
Vinyl Toluene

SET D - PART I

Sec-Amyl Acetate
Tert-Butyl Acetate
Sec-Butyl Acetate
Butyl Acetate
2-Ethoxyethylacetate
Ethyl Acrylate
Ethyl Formate

SET D - PART II

Sec-Hexyl Acetate
Isoamyl Acetate
Isobutyl Acetate
Methyl Acetate
Methyl Acrylate
Methyl Cellosolve Acetate
Methyl Methacrylate
Di-Sec-Octyl Phthalate

SET E - PART I

n-Amyl Acetate
Cyclohexanol
Sec-Butyl Alcohol
Tert-Butyl Alcohol
Butyl Alcohol
Diacetone Alcohol

SET E - PART II

Hydroquinone
Isoamyl Alcohol
Isobutyl Alcohol
Isopropyl Acetate
Isopropyl Alcohol
Methyl Alcohol
Methyl Isobutyl Carbinol
Propyl Alcohol

SET F - PART I

2-Butoxy Ethanol
n-Butyl Glycidyl Ether
Cyclohexene
Dipropylene Glycol Methyl Ether
Ethyl Ether
Glycidol

SET F - PART II

Isopropyl Glycidyl Ether
Methyl Cellosolve
Methylal
Phenyl Glycidyl Ether
Tetrahydrofuran

SET G - PART I

Butadiene
Dioxane
Heptane
Methylcyclohexane
Naphtha (Coal Tar)

SET G - PART II

Octane
Pentane
Petroleum Distillates (Naphtha)
Propylene Dichloride
Stoddard Solvent
Turpentine

SET H - PART I

Benzyl Chloride
Bromoform
Chlorobromomethane
1,2-Dichloroethylene
Difluorodibromomethane

SET H - PART II

Ethyl Bromide
Hexachloronaphthalene
Methyl Iodide

SET I - PART II

1,1,2,2-Tetrachloro-1,2-Difluoroethane
1,1,1,2-Tetrachloro-2,2-Difluoroethane
1,1,2,2-Tetrachloroethane
1,1,2-Trichloro-1,2,2-Trifluorethane
1,2,3-Trichloropropane
Trifluoromonobromomethane

SET J - PART I

Arsine
Carbon Tetrachloride
Diazomethane
o-Dichlorobenzene
Diethylamine
Dimethylamine

SET L - PART I

Acetic Anhydride
Acetonitrile
Cresol
Dimethylaniline

SET L - PART II

Hydrogen Bromide
Hydrogen Fluoride
Phenol
Phenylhydrazine
Pyridine
Sulfuric Acid
o-Toluidine
Xylidine

SET M

Copper Dusts and Mists
Soluble Molybdenum Compounds
Phosphoric Acid
Platinum Soluble Salts
Rhodium Metal Fume and Dusts
Rhodium Soluble Salts

CRITERIA DOCUMENTS AS OF JANUARY 1, 1978

Acetylene 1976
Alcohol, Isopropyl 1976
Alcohol, Methyl 1976
Alkanes 1977
Allyl Chloride 1976
Ammonia 1974
Arsenic, Inorganic 1973
Arsenic, Inorganic
(New Criteria - 1975)
Asbestos 1972
Benzoyl Peroxide 1977
Benzene 1974
Beryllium 1972

Cadmium 1976
Carbaryl 1976
Carbon Disulfide 1977
Carbon Monoxide 1972
Chlorine 1976
Chloroform 1974
Chromic Acid 1973
Coke Oven Emissions 1973
Crystalline Silica 1974

Ethylene Dichloride 1976

Fibrous Glass 1977

Hot Environments 1972
Hydrogen Cyanide & Cyanide Salts 1976
Hydrogen Fluoride 1976
Hydrogen Sulfide 1977

Lead, Inorganic 1972

Mercury, Inorganic 1973
Methyl, Parathion 1976
Methylene Chloride 1976

Nickel, Inorganic 1977
Nitric Acid 1976
Noise 1973

Organotin Compounds 1976

Phenol 1976
Phosgene 1976

Sodium Hydroxide 1975
Sulfur Dioxide 1974
Sulfuric Acid 1974

Toluene 1973
Toluene Diisocyanate 1973
Tetrachloroethylene-1,1,2,2 1976
Trichloroethylene 1973

Ultraviolet Radiation 1972

Waste Anesthetic Gases & Vapors 1977

Xylene 1975

Zinc Oxide 1975

SECTION B

Section B: Potential Petroleum Refining Stresses

There are specific and potential chemical and physical stresses which are known to be generally associated with petroleum refining. The following section summarizes these in association with the various standard refining units. This can serve as a basis for the institution of a Toxic and Hazardous Material Abatement Program.

SPECIFIC AND POTENTIAL CHEMICAL AND PHYSICAL STRESSES WHICH MAY BE ASSOCIATED WITH PETROLEUM REFINING UNIT OPERATIONS

Crude Oil Treatment - Desalting and Dehydration

The potential stresses associated with operation of the dehydration or demulsification processes include the various hydrocarbon fractions, particularly the low-boiling compounds which can be generated and released by some of the initial processing of crude oil, as well as various inorganic impurities inherent in the crude oil streams. Most significant of these inorganic compounds are the sulfides, which could result in release of hydrogen sulfide. This is a particular problem in the dehydrating processes which utilize elevated operating temperatures for processing of sour crude oil having high hydrogen sulfide content.

Airborne particulate contaminants to which workers can be exposed in dehydrating operations include the various dry chemicals which may be added to the feedstock and the diatomaceous earth employed in the filtration method. Diatomaceous earth sometimes can contain significant amounts of crystalline silica (cristobalite) formed during the calcining of the diatomaceous earth. The silica content and the small particle size of diatomaceous earth materials make this substance a potentially hazardous one in some petroleum refinery operations.

Desulfurization

Potential stresses arising out of desulfurization processes can be of either a chemical or physical nature and are dependent upon the concentration generated and the likelihood of exposure of the workers.

In the sulfuric acid treatment of distillates, the major potential airborne contaminants are the acid and alkaline mists.

The major potential contaminants associated with catalytic desulfurization are hydrogen sulfide and hydrogen.

Phenol and furfural, the relatively non-volatile materials used with the solvent extraction process, are seldom present in significant concentrations in the process areas except in the event of leaks or spills. The major industrial hygiene problem is general surface contamination and the consequent potential for direct contact with the skin. However, release of these contaminants into the air can be associated with the final stripping of the raffinate where the major purpose of the steam is to remove any residual solvent.

Primary Distillation

The potential health stresses associated with primary distillation processes are hydrogen sulfide, olefinic, paraffinic, naphthenic, and aromatic hydrocarbons, and carbon (coke) as chemical stresses and heat and noise as potential physical stresses.

Vacuum Flashing

The potential stresses associated with vacuum flashing include olefinic, paraffinic, naphthenic, and aromatic hydrocarbons as well as heat and noise.

Catalytic Cracking

The major potential stresses associated with catalytic cracking are the various hydrocarbons (olefinic, paraffinic, and aromatic) as well as hydrogen sulfide, carbon monoxide, the various catalysts used, noise and heat. High boiling (approximately 700°F) aromatic oils produced can be extremely potent skin irritants and potentially carcinogenic.

Hydrogenation - Hydrogen Treating and Hydrocracking

The potential health stresses associated with hydrogenation processes include hydrogen (fire and explosion), catalyst dusts, metal carbonyls, hydrogen sulfide, aromatic hydrocarbons, paraffinic hydrocarbons, olefinic hydrocarbons, carbon, noise and heat.

Catalytic Reforming

The potential stresses associated with the operation of a catalytic reforming unit are both chemical and physical in nature and vary only marginally with respect to changes in the nature of the crude oil being processed. The major chemical and physical stresses associated with catalytic reforming include hydrogen sulfide, carbon monoxide, aromatic hydrocarbons (benzene, toluene, xylene, etc.), aliphatic hydrocarbons, hydrogen, catalysts, noise and heat.

Alkylation - Sulfuric Acid Processes and Hydrofluoric Acid Processes

The potential health stresses associated with the various alkylation processes include hydrocarbons (olefinic and paraffinic), sulfuric acid, hydrofluoric acid, heat and noise.

Aromatic Recovery - Fractional Distillation, Azeotropic Distillation, Solvent Extraction, Solid Absorption, Crystallization

The potential hazards encountered in the operation of an aromatic recovery facility are quite similar to those in a catalytic reforming unit. A major area of concern, however, is the exposure of repair and maintenance personnel during operational malfunctions or designed modification to existing facilities. The major chemical hazards associated with aromatic recovery operations are aromatic hydrocarbons and aliphatic hydrocarbons. The physical hazards associated with aromatic recovery are noise and heat.

Polymerization

The potential health hazards associated with polymerization processes include olefinic and paraffinic hydrocarbons, sulfuric acid, phosphoric acid, catalyst dust, noise and heat.

Isomerization

The potential health stresses associated with isomerization processes may include any or all of the following: aromatic, olefinic and paraffinic hydrocarbons, aluminum chloride, hydrogen chloride, antimony trichloride, catalyst dust, hydrogen, noise and heat.

Gasoline Treating and Blending

The greatest risk is faced by maintenance personnel who may be required to encounter potential hazards for sustained periods. Potential stresses which may arise from gasoline treating and blending include the various hydrocarbon components as well as the additives, EDC, EDB, tetraethyl lead being the most toxic encountered in the blending processes.

Lubrication Oil and Wax Manufacture

Contaminants which are potentially hazardous when present in sufficient concentration or where exposures may be of sufficient duration include the following: aromatic thiophosphates, benzene, toluene, calcium phenolate, chlorinated hydrocarbons, dichloro-dibenzyl-disulfide, isobutylene, phenol, furfural, propane, methyl ethyl ketone (MEK), and sulfurized terpenes. It is particularly important to minimize or eliminate the potential for direct skin contact with the formulated oils.

Grease Manufacture

Potential airborne contaminants which may pose a hazard when present in high enough concentrations or when the contact time is of sufficient duration include the various alkali and metallic salts, oil mists, alkaline mists, and heat stress. It should be kept in mind that a variety of additives, many of them proprietary in nature, are used in the manufacture of oils and greases.

De-asphalting and Asphalt Manufacture

Contaminants associated with asphalt production which may pose potential health stresses when present in sufficient concentration include hydrogen sulfide, sulfur dioxide, hydrocarbons (aromatic and polycyclic aromatics), ferric cyanide, and phosphorus pentoxide.

Bulk Loading and Packaging

The potential health stresses associated with bulk loading and packaging of petroleum products encompass a wide range of possibilities, obviously including all products and major intermediate chemicals of the plant. Noise is of particular concern in highly automated canning operations or similar activities where sustained contact of metal on metal is required.

Coking

The contaminants emitted by coking operations which are potential stresses when present in sufficient concentrations are mainly gases. Because of the desulfurization reactions which occur, a large amount of hydrogen sulfide can be generated. The potential for generation of excessive levels of coke dust, polycyclic aromatics, carbon monoxide, phenol, and products of combustion warrants careful attention to the process.

Sulfur Recovery

Particulates generated by sulfur recovery processes include compounds of sulfur, arsenic, vanadium, and bauxite. Gaseous contaminants which may be emitted from the processes include hydrogen sulfide, sulfur dioxide, sulfur oxide, carbon disulfide, carbonyl sulfide, carbon monoxide, and carbon dioxide. The generation of aerosols containing potentially hazardous materials is possible when oxidizing vessels using air injection are opened to the atmosphere.

Steam Generation

The major potential stresses associated with the operation of a boiler are considered to be heat and noise. However, a number of chemical hazards are possible depending on the types of process operations and the boiler design. These include hydrogen sulfide, sulfur dioxide, carbon monoxide, hydrocarbons, and water treatment chemicals such as chlorine, algicides, chromates and dichromates, arsenates, and organophosphates.

Waste Disposal Treatment

The potential stresses encountered in various waste disposal treatment operations can be gases or particulates and include the full spectrum of potential stresses associated with petroleum refining operations. In addition to those materials which are considered products of the refinery, these potential stresses include acids, alkalis, alumina, metallic salts, "zeolites", siliceous dusts, chlorine, chlorine dioxide, carbon monoxide, carbon dioxide, ozone, alcohols, aldehydes, hydrogen sulfide, heat, and noise.

Maintenance Activities

Potential hazards which maintenance workers may encounter vary as to the particular unit operation involved. Depletion of oxygen in vessels by wetted activated carbon is a main cause of development of an atmosphere within the vessel that does not support life.

Toxic substances can be introduced into the interior of a vessel during the course of maintenance activities. Cleaning within a vessel with solvents as well as welding, grinding, and relining operations are prime examples of such activities. Metal fume fever has resulted from such activities on monel and stainless steel vessels. The interior of many high-corrosion process vessels are leaded, the linings for which must be installed manually in sheets (bonding) or by homogenous lead lining techniques.

Exterior maintenance operations aside from the welding and grinding activities include the removal and installation of insulation to process lines and vessels. Asbestos contained in old insulation materials may pose a source of potential exposure.

Service Shops

The spectrum of environmental stresses to which workers in the various service shops are potentially exposed includes all chemical and physical stresses encountered in the various unit operations since it is conceivable that various component pieces of equipment could be worked on in one or more of the area shops. Most service shops incorporate, to some extent, operations which present potential exposures to carbon monoxide, various hydrocarbons, metal fumes and dusts, asbestos, and various solvents used primarily for degreasing operations (usually chlorinated hydrocarbons). Potential physical stresses include heat, cold, noise, and ionizing radiation.

Cooling Towers

Potential stresses in cooling tower operations arise mainly from the contamination of the cooling water by process materials or by the various water treatment chemicals used.

Additives and inhibitors used in cooling towers are generally nonvolatile and potential problems associated with these materials are related to handling of the materials per se. Chlorine, particularly where used in large amounts, can pose a significant hazard if not handled properly. Other chemical additives include algicides, chromates and dichromates, arsenates, and organophosphates.

SECTION C

Section C: Monitoring Programs

The following section summarizes the present status of the various refinery monitoring programs. As a matter of convenience, these are listed as follows:

Continuous Programs - All refineries are aware of the Asbestos Standard and have programs which monitor, in a limited manner, for asbestos exposure. Paramount Refinery, as an exception, maintains a scheduled monitoring program for asbestos workers since the Mastics Plant is in operation at this location. The Lake Charles Refinery is meeting the requirements of the Vinyl Chloride Standard for their dock workers through a cooperative monitoring program with the Lake Charles Chemical Plant. Because hydrogen sulfide is a problem in the type of crude oil being refined at the Billings Refinery, the air is continuously monitored by area monitors and limited personal monitoring is done. Since phenol is associated with the delayed coking operation in the Lake Charles Refinery, the air is periodically monitored. No personal monitoring has been done for employees working at the cokers although Industrial Hygiene recommendations have been made for such to be done. Medical surveillance is established for persons working in areas covered by the Asbestos and Vinyl Chloride Standards and recommendations have been made for the other areas listed.

Appropriate programs for monitoring for radioactive materials are established at the Billings, Lake Charles, Ponca City, and Wrenshall Refineries.

Non-Continuous Programs - The Ponca City Refinery has selected from the list of proposed standards a number of candidate substances for general survey. No continuous program has been established for periodic monitoring and no personal monitoring has been done in any of the areas.

Semi-Continuous Programs - The Billings Refinery has been active for a number of months with a program which periodically looks at air contaminants. Monitoring is done with the Drager indicator tube system and indicator badges. Personal dosimeters are used for monitoring noise exposures.

In general, surveys for benzene have been made throughout the plants, but no personal monitoring has been done.

SECTION C

MONITORING PROGRAMS - PRESENT STATUS

Continuous Program

Asbestos - All refineries.
Vinyl Chloride - Lake Charles Refinery Docks.
Hydrogen Sulfide - Paramount and Billings.
Phenol - Lake Charles Coking Units.
Radiation - Billings, Lake Charles, Ponca City, and Wrenshall Refineries.

Non-Continuous Program

Ponca City Refinery (General Survey Mainly With Detector Tubes)

Ammonia	Benzene	Carbon Tetrachloride
Chlorine	Cresol	Ethyl Mercaptan
Furfural	Hydrogen Fluoride	Hydrogen Sulfide
MEK	Petroleum Distillates	Phenol
Phosphoric Acid	Propane	Sulfur Dioxide
Toluene	Xylene	

Semi-Continuous Program

Billings Refinery (Detector Tube-type Surveys)

Acetone	Alcohol	Ammonia
Benzene	Carbon Dioxide	Carbon Disulfide
Carbon Monoxide	Carbon Tetrachloride	Chlorine
Hydrogen Chloride	Hydrogen Fluoride	Hydrogen Sulfide
Lighting	Mercaptans	Mercury
Noise Dosimetry	Phenol	Sound Levels
SO_2	Tetraethyl Lead	Trichloroethane

SECTION D

Section D: Industrial Hygiene Recommendations

In view of the preceding quick survey covering Standards for Toxic and Hazardous Materials, Potential Refinery Stresses, and The Present Status of Refining Monitoring Programs, it is recommended that a Toxic and Hazardous Exposure Abatement Program be instituted for all refineries.

The following section summarizes the important areas which would need to be considered in order for the most desirable program to be effective.

As a part of this program, it is emphasized that the Industrial Hygiene Recommendations for Safe Practices in Handling High Boiling Aromatic Oils in Refineries, which was sent to all plants in August, 1976, should become a part of this program. A copy of these recommendations is attached to this section.

TOXIC AND HAZARDOUS MATERIALS EXPOSURE ABATEMENT PROGRAM

I. Objective

The objective of a Toxic and Hazardous Materials Exposure Abatement Program is to reduce employee exposure to all chemicals, materials and substances used in or as a part of the manufacturing processes within the plant. Although it is by OSHA regulations that employee exposure to toxic and hazardous materials be reduced, it is of utmost importance that plant management strive towards reducing exposure to all chemicals, materials and substances, regardless of whether or not they are currently considered to be toxic or hazardous.

II. Implementation

In order for an abatement program to succeed, plant management will need to give its full support to the program and should take whatever means necessary to reduce employee exposure. However, the proper share of the responsibility will be required of the supervisory personnel working in all unit areas of the plant. The program will need to be thoroughly explained to all supervisory personnel. It must also be understood that the full cooperation from all personnel will be expected.

The responsibility for coordinating and carrying out the program should be placed with the plant Safety Department.

III. Written Surveys

A. Initial Written Surveys

Each department or unit should initially and annually conduct a written survey of chemicals, substances or materials used or stored within their working area. These surveys should determine the chemicals present, the types and amounts of probable exposure to workers, the work practices and other controls in use, and further controls that are needed.

In conducting the survey, a "Usage Inventory" sheet should be prepared for each chemical, substance or material. Blank forms of the sheet should be provided by the plant Safety Department.

Following completion of the survey, the results should be reviewed by the respective department or unit supervisor for completeness and accuracy. Following this review, a similar review should be performed by the Safety Department. In each case, incomplete or inaccurate work should be returned for correction and resubmitted within 30 days.

After completion of the review of survey sheets and corrections are made, the Safety Department should develop a file, by department or unit, for each material in the plant. Material Safety Data Sheets will also be filed for each material.

B. New Chemicals

Prior to the purchase of any new material, the Plant Buyer should request a Material Safety Data Sheet from the supplier. When the sheets are received, the buyer should forward them to the Safety Supervisor who should retain them on file and should send a copy to the appropriate department who will be using the material.

In turn the using department should retain the data sheets in their "Material Hazard Reference Books" and should conduct a survey of the materials within 30 days after the material is put into use.

IV. Monitoring

The Safety Department should be responsible for conducting an effective, on-going monitoring program. What materials to monitor will be determined by the types and amounts of exposures. (See V.)

A. Methods

Methods for long-range use in monitoring should be defined by the Safety Department.

B. Equipment

Equipment necessary for an effective monitoring program should be obtained and upgraded as dictated by the materials present in the plant and by those materials which may be purchased at some later date.

C. Actual Monitoring

Sampling should be done in such a way as to give a clear picture of the potential or actual exposure to workers in the respective areas in relationship to the materials present in the workplace. It is desirable that sampling cover an eight hour work period or that it be done in such a way that valid construction can be made for eight hour exposures.

V. Hazard Classification

The Safety Department should classify all known plant materials by hazard type, in order of priority.

A. Carcinogenic Materials

B. Materials Causing Severe Damage

This category would include materials that produce chronic disorders, acute systemic disorders, nervous system disturbances, respiratory effects other than irritation, blood disturbances, and genetic and/or fetal changes.

C. Materials Producing Irritation

This category includes materials that produce irritation to the eyes, nose, throat, upper respiratory system, lungs and skin.

D. Low Risk Health Effect Materials

For priority purposes, the amount of probable (or known) exposure may also be considered:

1. Exposure Above the Established Limits

Where exposure limits are set, efforts should be directed toward reducing exposures to below "Action Levels." Minimum acceptable performance should be reduction to below the "Threshold Limit Value" (TLV).

2. Exposure Causing Discomfort

Where conditions exist that cause personal discomfort, effects will be directed toward reducing exposures to levels that eliminate such discomfort.

3. No Exposure

In cases where exposure hazards are absent, abatement activity should be minimal.

VI. Training

A. Respirators

A respirator training program should be given by the Safety Department to all personnel whose work requires the use of such equipment. This training should be directed at accomplishing the requirements of the OSHA General Industry Standards on Respiratory Protection, 29 CFR 1910.134, and Chapter XII, OSHA Standard Method for Determination of Respiratory Protective Acceptability.

B. Hazardous Materials Education

A Hazardous Materials Education Program should be given to all plant employees. Each department should conduct its own program within the guidelines developed by the Safety Department.

VII. Personal Protective Equipment

Each department, with the help of the Safety Department, should establish personal protective equipment requirements for hazardous materials handling within the respective department. The Safety Department should also assist in the determination of protective equipment compliance.

Inspection and servicing of respiratory equipment should be done by the Safety Department.

VIII. Material Disposal and Substitution

Wherever possible, chemicals and materials not in use should be disposed of. Substitutes should be found for those materials whose use results in exposures above acceptable levels.

IX. Medical Examination and Treatment

Medical examination and treatment of employees suspected by the Company to have been made ill because of exposure to materials in the workplace will comply with corporate medical guidelines in all cases.

X. Toxic and Hazardous Material Labeling

A Toxic and Hazardous Material Labeling Program, aimed at adequate warning to all users of toxic and hazardous materials, should be proposed by the Safety Department.

XI. Records and References

The Safety Department should assume the prime responsibility for program recordkeeping and for the provision of appropriate references. This should include:

A. Chemical Card Files

A simple chemical, substance and material card file should be established for all known plant materials.

B. Chemical Reference Files

One file should be established for each material and should be used to contain pertinent health information concerning the chemical and exposure controls in use.

C. Monitoring Records Files

Appropriate files should be established for the purpose of maintaining monitoring results.

D. Material Safety Data Sheets

Complete files for Material Safety Data Sheets should be established. Information contained in these should be revised and updated as changes are made.

E. Material Hazard Reference Books

Material Hazard Reference Books should be prepared for each department by the Safety Department. The books should include the results of chemical surveys (see III above), the results of classification (see V above), Material Safety Data Sheets (see XI-D above), and other appropriate information. After the initial issue, the responsibility for future filing will rest with the respective departments.

XII. Program Reviews

A. Department Reviews

The head of each department should conduct a complete review of its Toxic and Hazardous Materials Exposure Abatement efforts once a year.

B. Plant Review

The Plant Manager, all department heads, along with the plant Safety Director should conduct a review of all plant Toxic and Hazardous Materials Exposure Abatement plans and projects once a year. This should follow the Departmental Reviews.

Toxic and Hazardous Materials Exposure Abatement Program

Long Range Goals

1. Strive for no hazardous exposure.
2. Where exposure hazards exist, abatement priorities should be:
   a. Engineering Controls - first priority.
   b. Work Practices Controls - second priority.
   c. Personal Protective Equipment Controls - third priority.
3. Equipment and process changes and installations are adequately reviewed for compliance with law and standards, including CONOCO standards. No change or installation should be allowed which is illegal or below standard.
4. Medical surveillance and treatment are appropriate to needs.
5. All toxic and hazardous materials are clearly labeled for the benefit of all users.
6. All personal protective equipment is adequate, functional, and used correctly.
7. All general reference data, including standards, lists of toxic and hazardous materials and Material Safety Data Sheets are maintained current.

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INDUSTRIAL HYGIENE RECOMMENDATIONS FOR SAFE PRACTICES IN HANDLING HIGH BOILING AROMATIC OIL IN REFINERIES

In 1973 NIOSH issued a criteria document for a Recommended Standard for Occupational Exposure to Coke Oven Emissions. This same agency has attempted to place many other potential sources of polynuclear aromatic compounds, such as those from petroleum distillation, in the same classification as coal derivatives. Even though this proposed interpretative rule is being contested, there is some likelihood that coking or other high temperature operations involving petroleum could be covered by the Coke Oven Emission Standard. This proposed standard will attempt to cope with the PNA exposure problem, principally through prescribed work practices and personal protection. Some of the proposed rules concerning respiratory protection, personal hygiene, and medical follow-up may possibly be applied to petroleum coking operations.

Recent communications have been made and meetings have been held with the industrial hygiene and medical personnel of the Exxon Company dealing with industrial hygiene problems for safe practices for workers handling high boiling aromatic oil. The results of these indicate the advisability that recommendations be made relative to the industrial hygiene practices which should be followed concerning these materials.

Attached are recommendations which are felt minimal in view of the questions, relative to the chemistry and toxicology of these materials, which are not answered at the present time. These recommendations should allow programs to be established in the refineries which will integrate control with good personal hygiene and plant housekeeping as are needed to handle all hydrocarbons safely.

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VMD 723092

RECOMMENDED INDUSTRIAL HYGIENE PRACTICES FOR WORKING WITH HIGH BOILING AROMATIC OILS

I. Oils from operations containing more than 10 percent of fractions boiling at or above 700°F should be considered to be high boiling aromatic oils.
If these oils are allowed to remain in contact with the skin, they may cause skin irritation.
In general, these oils may be identified as follows:

A. Heavy cycle gas oil, clarified oil and slurry oil from catalytic cracking units.
B. Coker heavy gas oil and coker bottoms.
C. Hydrocracker bottom streams.
D. Any other oils, which may be purchased, blended or of unknown identity, boiling at or above 700°F.

II. General Hygiene Practices - Minimize Exposure

A. In order to avoid spills and leakage of these materials, precautions should be taken when loading, unloading, or when obtaining samples. Any spills should be promptly cleaned up and care should be exercised to avoid skin contact or inhaling vapors.
B. Employees who are working with these materials or who are working on equipment which contains these materials, should wear appropriate protective clothing. The circumstances will dictate the degree of protection needed. This may require only a pair of rubber gloves and safety goggles or rubber shoes and rubber suit might be required.
C. In case that ordinary work clothes, including shoes, become grossly contaminated with these oils, they should be promptly changed. Emergency clothing should be made available. The contaminated clothing should not be re-used until the contamination has been removed. This type of clothing should be cleaned and laundered by the refinery.
D. In the event that the skin becomes contaminated with these materials, it should be washed with soap and water promptly. If the employee experiences any skin irritation, he should report to the Medical Department or Safety Department.
E. In order to minimize the inhalation of vapors, employees should exercise care in opening equipment or taking samples. Working on the windward side of such operations will aid in alleviation of exposure to such materials. It may be necessary to wear air-supplied breathing equipment when performing such operations as cleaning drums, tanks or when working in other closed spaces.

VMD 723093

III. Preparation of Equipment for Maintenance or Mechanical Work

Prior to maintenance or mechanical work care should be taken to insure the complete removal of all aromatic oil from all equipment. This should be the responsibility of the operating supervisors and they should develop whatever cleaning procedures they deem safe and effective to carry out this requirement.

IV. Identification of Equipment

Processing equipment, remote tanks and pumps should be identified, when appropriate, with printed signs which bear the following information:

THIS UNIT NORMALLY CONTAINS HIGH BOILING OIL.
CAUTION: MAY BURN OR IRRITATE THE SKIN. USE APPROPRIATE PROTECTIVE CLOTHING FOR MAINTENANCE WORK AND WHEN OBTAINING SAMPLES - AVOID SKIN CONTACT - IF CONTACT OCCURS, WASH WITH SOAP AND WATER - IF SKIN BECOMES IRRITATED, REPORT TO MEDICAL DEPARTMENT.

V. Precautions for Laboratory Personnel

A. The same general precautions, as previously outlined, should be followed by laboratory personnel when working with these materials.
B. The handling of oils containing aromatic materials, where vapors may be evolved, should be strictly carried out under a well ventilated hood.
C. All samples should be placed in closed leak-proof containers. These should be clearly and properly tagged for positive identification.

VI. Work Clothing

The following recommendations for work clothing for certain workers are based on results of studies done by the Exxon Company which showed significant amounts of potential skin carcinogens in the outer garments of coke handlers.

A. Work clothing (coveralls) should be supplied for all coker process and operating personnel. This should be done on an individual basis so that each person is supplied a clean change of clothing each day.
B. This supplied clothing should be laundered by the plant.
C. Change-shower rooms should be provided and each worker should be provided individual lockers for clean street clothing. Upon starting a day's work, each worker should come to the locker room, change into clean work clothes, leaving his street clothes in his locker. At the end of the work day the worker should proceed to the shower room, remove his work clothes, place them in a special receptacle, shower and proceed to the clean locker area where he will

dress in his personal street clothes. Under no condition should the work clothes be worn into the locker area, placed in the locker with clean clothes, or worn outside the plant.

D. Consideration should be given to supplying mechanical personnel, who are assigned to jobs where clothing will be contaminated with coke or high boiling oils, with work clothing. This could be done on an individual, day-to-day basis. Requirements for changing, handling of soiled clothing, showering and laundering of clothing would be the same as for coker personnel.

VII. General Precautions for All Petroleum Products

The following recommendations are made regarding the general precautions which should be taken for all petroleum products:

A. Any petroleum product which gets on the skin should be removed promptly. Gasoline, naphtha turpentine, or similar solvents should never be used to remove oil and grease from the skin. Soap and water or a waterless hand cleaner followed by soap and water should be used for this purpose.
B. Clean wipe towels and cloths should be used. Dirty wipe cloths should be washed and cleaned frequently.
C. Oil-soaked clothing should be changed and not worn for great lengths of time. Work clothes should be laundered frequently.
D. Hands and arms should be washed before eating and at the end of the work shift.
E. Cuts and scratches should have first aid attention.
F. The breathing of oil mists or solvent vapors should be avoided.
G. The work areas should be kept clean and spilled petroleum products should be cleaned up immediately.
H. Eating of lunches and consumption of beverages should be done only in areas free of oil contamination.

VIII. Medical

A. All coker workers should be offered a pre-placement and annual medical examination which should include a complete physical examination.
B. The pre-placement examination should include a comprehensive medical history and occupational exposure history.
C. The following items should be offered to the workers on all pre-placement and annual medical examinations:
   1) A 14 X 17 inch posterior-anterior chest x-ray.
   2) A medical questionnaire that includes the presence and degree of respiratory symptoms (breathlessness, cough, sputum production, and wheezing). Based on the judgment of the physician as to the significance of results of the questionnaire, a sputum cytology examination should be performed.
   3) A skin examination for preliminary and malignant lesions and evidence of hyperpigmentation or photosensitivity.
   4) A routine urinalysis to include tests for red blood cells.

Table 2. Angiosarcoma of the liver reported among printers, 1964-1974

Printer	Age at death	Years of exposure	Job description	Chemicals	Diagnosis local
1	50	25	Offset pressman	Inks, cleaning fluids	ASL
2	70	?	Offset pressman	Inks, cleaning fluids	ASK
3	84	50	Self-employed printer	Inks, cleaning fluids	ASL
4	71	35	G.P.O. printer	Inks, cleaning fluids	ASL
5	40	24	Linotype operator	Molten lead, inks, cleaning fluids	ASL
6	20	3	Assistant; cleaner	Inks, cleaning fluids	ASL
7	59	3 (25)	Printer (janitor)	Inks, cleaning fluids	ASL
8	61	16 (10)	Printing salesman (solvent mixer)	CCL_4	ASL
9	59	42	Pressman	Inks, benzene cleaning fluids	Malignant fibroxanthoma

"linotype operator," but all were people working in the printing industry.

When we conducted our epidemiologic investigation, we noted right away that some of these people were not really printers. If you look at case numbers six, seven, and eight, case number six was only exposed to these chemicals for 3 years and turned out to be a part-time printer and cleaning assistant in a print shop. Case number seven had been a janitor for the previous 40 years, and was promoted to a blueprint printer the last 3 years before he became ill. He had been exposed extensively to cleaning fluids, but again had only been a printer for 3 years.

Case number eight turned out not to be a printer at all, but a salesman for a print company, having minimal exposure to the printing industry itself, and case number nine was indeed a printer for 42 years, but the