

HEALTH HAZARDS AND OCCUPATIONAL DISEASES

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Action of Hazardous Substances

1. Irritants
2. Asphyxiants
3. Volatile drugs and druglike substances
 - a. Primary irritants
 - b. Primary anesthetics
 - c. Anesthetics with systemic effects on the liver and kidneys
 - d. Anesthetics with systemic effects on the blood-forming organs
 - e. Anesthetics with systemic effects on the nervous system
 - f. Substances whose anesthetic action is observed by more severe systemic effects
4. Inorganic and organometallic substances
 - a. Acute poisons
 - b. Chronic poisons

HEALTH HAZARDS AND OCCUPATIONAL DISEASES - outline continued

Preventive Measures

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2. Process and Operations Study
3. Materials Study
4. Sampling and Measurements
5. Using Results of the Survey
 - a. Do exposures exist in the plant?
 - b. What is the significance of the exposures?
 - c. What can we do about them?

The Survey as a Basis for Controls

They must -

1. Protect the man
2. Not interfere with his work
3. Be acceptable to the worker
4. Be reasonable and practical
5. Not cost too much.

Several basic control techniques are. -

1. Isolation
2. Substitution
3. General ventilation
4. Local exhaust ventilation
5. Personal protective equipment

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HEALTH HAZARDS AND OCCUPATIONAL DISEASES - outline continued

Emergency Action

1. Remove victim to fresh air
2. Give proper first aid
3. Take care of the eyes
4. Proper treatment of clothing

Conclusion

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Action of Hazardous Substances

Hazardous substances encountered in the petroleum industry can cause local irritation, systemic poisoning or occasionally both. Some are sensitizers and a few have or have been suspected to have carcinogenic properties. Damage to health may result if a person is exposed to a sufficient quantity of any of these substances for a sufficient time. In acute poisoning, the quantity is usually relatively large and the exposure time short. In chronic poisoning, the exposure time is generally long and repeated while the quantity is relatively low, often being so low that the individual may be unaware of any exposure at the time. With most sensitizers, the first few exposures may cause no reaction; but once a person becomes sensitized, reactions may occur from contact with very small quantities for very short periods of time.

The wide variety of hazardous substances used or handled permits only a very broad classification of their toxic or hazardous properties. Factors other than inherent toxicities often determine the type and severity of their effects. For example, acute benzene poisoning has a different clinical picture than chronic poisoning by this same chemical.

And while ethyl alcohol is somewhat more toxic than methanol, the latter is much more dangerous when ingested because of its slow rate of metabolism. Sometimes the physical state and physical properties of a substance determine to a large extent the nature and severity of its action on the body. Most skin irritants are liquids and in many cases the degree of local irritation has no relation to their systemic toxicities as is the case with kerosine. Differences in viscosities sometimes are the determining factor in the type of injury. The aspiration hazard from a low viscosity substance like kerosine is quite different and more severe than that from a higher viscosity product like medicinal mineral oil. The solubility of an irritant gas influences to a large extent the part of the respiratory tract that is affected. Ammonia, which is very soluble in water irritates the nose and throat primarily while nitrogen dioxide, being much less soluble, acts mainly on the tissues in the lungs.

Various classifications of hazardous substances have been proposed but none are completely satisfactory. Henderson and Haggard developed a classification for gases and volatile liquids which is based to a large extent on the acute effects of inhalation with less emphasis on chronic effects. The matter of skin absorption, skin and eye irritation, carcinogenicity, sensitization, allergic reactions, were purposely excluded. Henderson and Haggard grouped gases and volatile substances into these four categories:

1. Irritants are substances which when inhaled produce injury to the air passages or lungs, or both. Some irritant gases and vapors also are systemic poisons but their local effects overshadow any systemic effects that may occur after exposure. The more soluble ones can also be expected to cause eye irritation. Examples are: ammonia, chlorine, sulfur dioxide, ozone, phosgene, acrolein.

2. Asphyxiants exert their action in one of three ways: by reducing the amount of oxygen available for breathing, by preventing oxygen transport by the blood, or by preventing utilization of oxygen by the tissues. The quantities of these gases necessary for them to act varies widely. Large volumes of gases such as nitrogen, hydrogen, methane, must be present before the oxygen content of the air becomes sufficiently low to be unsafe to breathe. Such gases are classed as simple asphyxiants. With other gases such as carbon monoxide and the cyanogen compounds, particularly hydrogen cyanide, only very small amounts are needed to cause asphyxiation. These gases are called chemical asphyxiants. Carbon monoxide reduces the amount of oxygen available to the tissues because of its much greater affinity for hemoglobin as compared to that of oxygen. The cyanogens prevent the tissues from using oxygen, even though it may be delivered to them in adequate amounts.

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3. Volatile drugs and druglike substances have one physiological effect in common, that of inducing anesthesia, although with some the action may be obscured by some other systemic effects. Some of them are also irritating to surface tissues. Depending on the concentration present, the depth of anesthesia will range from mild symptoms to complete loss of consciousness and death. In very high concentrations death may be due to asphyxiation. Henderson and Haggard subdivided these substances into six subclasses:

a. Primary irritants. Those with sufficiently strong irritant properties to prevent absorption of any appreciable amounts or to obscure the effects of absorption. Some of the ketones, ethers, alcohols, and esters are in this subgroup.

b. Primary anesthetics. No marked effect other than anesthesia and no serious systemic effects from prolonged exposure. Examples are hydrocarbons of the paraffin, olefin, and acetylene series, nitrous oxide, ethers.

c. Anesthetics with systemic effects on the liver and kidneys. The chlorinated hydrocarbons belong to this subgroup.

d. Anesthetics with systemic effects on the blood-forming organs. Of the aromatics and alkyl aromatics, benzene is the only one that affects the blood-forming organs. It has been established that the alkyl aromatics such as toluene and the xylenes do not have this effect.

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e. Anesthetics with systemic effects on the nervous system. Included in this subgroup are ethyl alcohol, methyl alcohol, esters of organic acids, carbon disulfide.

f. Substances whose anesthetic action is observed by more severe systemic effects. These are substances whose predominant action is the "nitrite effect" like the alkyl nitrites and alkyl nitro-substitution products or those which convert oxyhemoglobin to methenoglobin with relatively little "nitrite effect" such as nitrobenzene, aniline and toluidine.

4. Inorganic and organometallic substances.

In this group there is a large number of substances with a wide variety of compositions and actions which do not fit into any of the other three groups. Examples which show this wide variance are mercury vapors, tetraethyl lead, nickel, iron, and cobalt carbonyls, and hydrogen sulfide. This latter gas also has irritant properties resembling those of chlorine though less intense. Immediate death from hydrogen sulfide is due, however, to its systemic action. The occasional delayed death one or two days after exposure to this gas may be the result of its irritant action on the respiratory passages.

Preventive Measures

Selection of the proper preventive measures to avoid health damage requires a detailed knowledge of the handling or use methods of the hazardous substance as well as a knowledge of

its physical and toxicological properties. Today, containers of many hazardous substances have precautionary labels. An adequate label will name the hazardous component, state the toxicological effect, outline the preventive measures and the emergency action to be followed in the event of exposure. All precautionary instructions on such labels should be followed.

A detailed description of the precautionary measures for all hazardous substances is not feasible in this general review. However, a summary of the more common ones that relate to the various types of potential exposure follows:

1. Job Study and Analysis

The kind of work a man does is certainly important in relation to environmental factors that may influence his health. Many times in the course of a periodic survey a job study and analysis must be done. This is necessary to determine exposure time, work habits, and related items. In some situations a mere change in work procedure may mean the difference between exposure and no exposure. Intermittent operation of a process and accompanying job requirements may be important in terms of exposure time, and ultimately in the kind of control measures required.

2. Process and Operations Study

Closely related to the job study is the study of process or operations. A good working knowledge of all operations in the plant is essential. This includes both manufacturing or process as well as mechanical work. This information tells us the source of those factors of concern to health. We must know

the materials that go into a process, what happens to them, and how they may come in contact with the worker. The same general information must be developed for physical factors, such as noise and radiation.

A process study is necessary also in terms of how controls can be applied. Many times these involve engineering features which may influence or limit design of controls.

3. Materials Study

The majority of environmental exposures result from process or related materials being liberated into the plant atmosphere. Therefore, information on the physical, chemical, and toxicological properties of these is of great importance.

In the periodic survey, all materials for each operation should be listed. The chemical and physical properties should be studied. If the process is one in which chemical reactions can occur, new or side products should be studied in the same fashion.

The toxic properties of a material is of even greater importance. If an exposure to a material is to be evaluated, its toxicity must be known. Without this information there is little ground for a quantitative appraisal of exposure.

4. Sampling and Measurements

In order to put the evaluation of an exposure on a quantitative basis, we must know actual levels of exposure. In other words, "How much of this material is the man taking into

his body by inhalation?" Therefore, it becomes necessary to measure, as accurately as possible, the amounts of those gases, vapors, dusts, mists, and the like which are in the air the worker is breathing. From this information his daily "dose" can be determined.

From a technical standpoint these measurements involve the collection of various samples and the analysis of these in the laboratory. Physical factors must also be measured. This phase of the periodic survey is time consuming, requires considerable instrumentation, but actually is the heart of any such survey.

5. Using Results of the Survey

Generally plant surveys should answer three important questions:

- a. Do exposures exist in the plant?
- b. What is the significance of the exposures?
- c. What can we do about them?

The existence of exposures can be determined by relating data from measurements to various standards or reference points and to past experience with the situation at hand. Basically, the same procedure is followed in judging the significance of an exposure. The most common reference points are the MAC values. In passing, it should be pointed out that often more confidence is written into these values than was the intent when they

were established. They are basically set up as bench marks for control purposes and this should be recognized in making use of them.

What can be done about exposures falls into the category of controls, which we should discuss separately.

The Survey as a Basis for Controls

When exposures have been defined by survey techniques, the next basic problem is how they can be controlled. For control procedures to be acceptable they must meet certain requirements, such as --

They must 1. Protect the man.

2. Not interfere with his work.

3. Be acceptable to the worker.

4. Be reasonable and practical.

5. Not cost too much.

There are several basic techniques which can be used in controlling exposures. They are -

1. Isolation.

2. Substitution.

3. General ventilation.

4. Local exhaust ventilation.

5. Personal protective equipment.

The United States of America Standards Institute through its Committee on Acceptable Concentrations of Toxic Dusts and Gases has also published standards in this area. Formerly these

standards gave only one value. The USASI standards now recognize that there are other factors such as a relation between duration of exposure and concentration. Where applicable for a particular substance, values are given for ceiling concentrations, eight-hour time-weighted average concentrations, levels to avoid sensory responses, "peaks" and the duration thereof above the acceptable concentration for continuous exposure.

The reviews in this series contain the ACGIH and the USASI values, if such exist, for the substance under consideration. These values should be used and interpreted subject to the limitations in the first paragraph of this section. In addition, it should be kept in mind that because of the wide variation in individual susceptibility, exposures of an occasional person, even below the values may cause discomfort, aggravation of a pre-existing condition or even an occupational disease.

Emergency Action

If because of the failure or inadequacy of the preventive measures, acute effects occur from exposure to a hazardous substance a medical emergency may exist. Then the immediate application of emergency procedures is necessary. This is not necessary for cases of chronic poisoning.

When a person has been overcome by a toxic gas or vapor, he should be immediately removed to an uncontaminated atmosphere. Rescuers should not attempt to do this unless they have adequate respiratory protection. If natural breathing has

been interrupted artificial respiration should be started immediately after removal from the contaminated atmosphere. The various methods of administering artificial respiration are described in API Publication 2017, First Aid Training Guide. The victim should be kept warm and completely at rest.

Eye contact with irritating substances, particularly liquids, requires emergency action. The eyes should be immediately flushed with water for at least 15 minutes and medical attention obtained immediately thereafter. The use of neutralizing solutions, for example, dilute acetic acid in the case of alkali burns of the eye, is inadvisable. Valuable time may be lost while looking for the bottle of the neutralizing chemical, the strength may have changed from long standing, and sometime the solution may do more harm to the eye than the original irritant. Flushing is best done using an eye fountain but if such a fixture is not available, water from a tap or hose should be used. If there are no sources of water at hand, the person can immerse his head in a bucket of water so that his eyes are in contact with the water. Needless to say, the eyes should be kept open during the flushing operation. Often this will require the assistance of a fellow worker. It is advisable to train all employees in the proper technique of flushing the eyes.

Substances which can cause corrosion or immediate irritation to the skin or systemic effects by reason of skin absorption should be removed from the skin immediately. The skin should be flushed with copious amounts of water. Safety showers for this purpose should be provided in all areas where there is likelihood of exposure to these substances. Time should not be taken to remove clothing or footwear before getting under the shower; it should be removed while the affected person is being flushed with water. If a shower is not available, water from a hose can be used. Agents other than water may be more effective in removing some substances but water is useful in any case because its direct mechanical action will remove even water insoluble substances to a large extent. In addition, water is usually readily available.

Conclusion

An adequate program for the protection of the health of employees includes both industrial hygiene control and medical supervision. Industrial hygiene procedures include evaluation of the work environment by surveys and inspection, selection of the proper control measures, and periodic surveys and studies to ascertain if operations have changed and if control equipment is functioning properly. Medical supervision includes preplacement physical examinations in order to avoid

possible exposure of persons with certain pre-existing conditions to certain hazardous substances. Periodic physical examinations at proper intervals should be made to detect early symptoms of occupational disease and to determine the adequacy of existing control methods.

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APPENDIX I. Group I. Solvents.

<u>Solvent</u>	<u>TLV (ppm)</u>	<u>Evpn. rate</u>	<u>ER/TLV ratio</u>
n- Amyl alcohol	100	34	0.34
Butylcellosolve	50	6	0.12
o- & p- Cresol	5	1	0.20
Diacetone alcohol	50	14	0.28
o- Dichlorobenzene	50	15	0.30
Diisobutyl ketone	50	18	0.35
Ethyl alcohol	1,000	340	0.34
Isoamyl acetate	100	12	0.12
Methylcyclohexanol	100	2	0.02
Methylcyclohexanone	50	17	0.34
Phenol	5	0.8	0.16

APPENDIX I. Group II. Solvents.

<u>Solvent</u>	<u>TLV (ppm)</u>	<u>Evpn. rate</u>	<u>ER/TLV ratio</u>
Acetone	1,000	1,160	1.16
Amyl acetate	100	62	0.62
Aniline	5	4	0.80
n- Butyl acetate	150	100	0.67
n- Butyl alcohol	100	45	0.45
Chlorobenzene	75	75	1.00
Cyclohexanone	50	23	0.46
Dichloroethyl ether	15	11	0.73
Diethylaminoethanol	10	15	1.50
Ethanolamine	3	1	0.33
Ethylbenzene	100	91	0.91
Heptane	500	386	0.77
Isobutyl acetate	150	174	1.16
Isobutyl alcohol	100	80	0.80
Isopropylbenzene	50	57	1.14
Methylamyl acetate	50	47	0.94
Methylamyl alcohol	25	33	1.45
Methylamyl ketone	100	40	0.40
Methylbutly ketone	100	87	0.87

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APPENDIX I. Group II. Solvents.

<u>Solvent</u>	<u>TLV (ppm)</u>	<u>Evpn. rate</u>	<u>ER/TLV ratio</u>
Methylcyclohexane	500	320	0.64
n- Octane	500	336	0.67
3- Pentanone (diethyl ketone)	200	275	1.38
n- Propyl acetate	200	276	1.38
n- Propyl alcohol	200	110	0.55
Toluene	200	240	1.20
1,2,3, Trichloropropane	50	39	0.78
Xylene	100	63	0.63

APPENDIX I. Group III. Solvents.

<u>Solvent</u>	<u>TLV (ppm)</u>	<u>Evpn. rate</u>	<u>ER/TLV ratio</u>
2- Butanone (MEK)	200	572	2.86
Cyclohexane	300	720	2.40
Cyclohexene	300	597	1.99
Dimethylformamide	10	17	1.70
Dioxane	100	311	3.11
Ethyl acetate	400	615	1.54
Furfural	5	9	1.80
n- Hexane	500	1,000	2.00
Isopropyl acetate	250	500	2.00
Methylisobutyl ketone	100	165	1.65
Nitropropane	100	180	1.80
n- Pentane	1,000	2,860	2.86
2- Pentanone	200	320	1.60
Perchloroethylene	100	280	2.80

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APPENDIX I. Group IV. Solvents.

<u>Solvent</u>	<u>TLV (ppm)</u>	<u>Evpn. rate</u>	<u>ER/TLV ratio</u>
Acetic anhydride	5	46	9.20
Acetonitrile	40	579	14.50
Allyl alcohol	2	100	50.0
Benzene	25	630	25.2
Carbon disulfide	20	2,260	113.0
Carbon tetrachloride	10	1,280	128.0
Chloroform	50	1,160	23.2
1,2 Dichloroethylene	200	1,656	8.2
Diethylamine	25	1,596	63.8
Dimethyl sulfate	1	4,151	4,151.0
Ethyl bromide	200	4,557	22.8
Ethylenediamine	10	1,015	101.5
Ethylene dibormide	25	656	26.2
Ethylene dichloride (1,1)	50	1,160	23.2
Ethyl ether	400	3,300	8.3
Methyl acetate	200	1,180	5.9
Methyl alcohol	200	610	3.1
Methyl chloroform	350	1,577	4.5
Methylene chloride	500	2,750	5.5
Methyl formate	100	4,080	40.8

APPENDIX I. Group IV. Solvents.

<u>Solvent</u>	<u>TLV (ppm)</u>	<u>Evpn. rate</u>	<u>ER/TLV ratio</u>
1- & 2- Nitropropane	25	125	5.0
Propylene dichloride	75	530	7.1
Pyridine	5	158	31.6
1,1,2,2, Tetrachloroethane	5	65	13.0
Tetrahydrofuran	200	800	4.0
Triethylamine	25	451	18.0
Trichloroethylene	100	620	6.2