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# Current Safety Topics in the PETROLEUM INDUSTRY

*as presented in sessions of the Petroleum Section at the 42nd National Safety Congress*

VR 20

Industrial Hygiene in the Petroleum Industry *(A. C. Pabst)* . . . 4

Safe Handling of Insecticides *(F. R. Willsey)* . . . 9

Safe Handling of Farm Fuels *(Dr. Norval J. Wardle)* . . . 10

Human Side of Safety *(E. C. Martin)* . . . 12

Safe Handling of Electrical Equipment on the Farm *(W. L. Ulich)* . . . 14

The Drilling Contractor's Job in Safe Operations *(Harry H. Hillman)* . . . 16

*(Continued on next page)*

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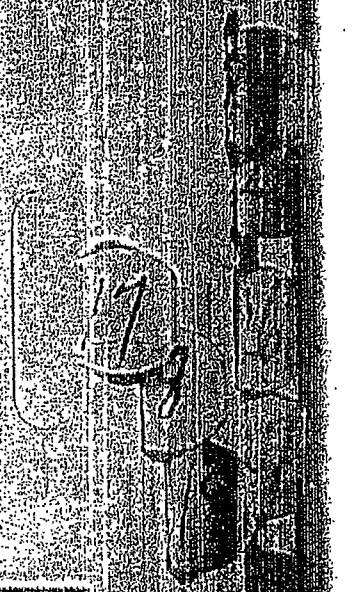
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1954 TRANSACTIONS VOLUME 17

# Current Safety Topics in the MINING INDUSTRY

*as presented in sessions of the Mining Section at the 42nd National Safety Congress*




Limiting Factors in Dust Control and Ventilation *(C. S. Gibson)* 5

The Unwatering of the Osceola Lode (A Symposium) ..... 10

The General Project *(C. A. Campbell)* ..... 10

Character of the Water and Associated Problems *(R. J. Marcotte)* ..... 12

Engineering Problems *(P. H. Ostlender)* ..... 17

Use of the Camera in Accident Prevention *(Seymour B. Fleming)* 21

Noise *(M. C. M. Pollard)* ..... 23

Practical Noise Control in Quarries and Mines *(A. B. Hoftiezer)* 25

Safety Practices in Sinking the Peterson "A" Shaft *(Peter F. Torreano)* ..... 27


*(Continued on next page)*

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# Industrial Hygiene in the Petroleum Industry

By A. C. PABST
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Industrial hygiene is a field that is closely interwoven with industrial safety. In fact, it can be regarded as a medical engineering phase of safety.

Unfortunately, many people do not know what industrial hygiene is and the functions of an industrial hygienist. The reason for this is that industrial hygiene is a comparatively new science and practically unknown twenty years ago.

Today there are only about 800 industrial hygienists in the United States, and a large number of this group are not in industry, but working for the federal government or state departments. Usually, people hearing the word "hygiene" recall they had a hygiene course in high school which dealt with personal habits such as bathing, cleaning the fingernails, teeth, and so forth and immediately jump to the conclusion that an industrial hygienist in industry must be interested in keeping employees clean.

In my initial visit to many refineries, it seemed that the first place I was taken was to locker rooms to inspect shower and lavatory facilities. In some degree, industrial hygienists are interested in the employee's cleanliness, but only so far as it is necessary to protect his health. We are more interested in keeping an employee's lungs, skin, and other organs clean and free from hazardous gases, liquids, and other harmful substances.

Hygiene is defined as that branch of medical science that relates to preservation of health. Therefore, industrial hygiene may be defined as the science of prevention and control of occupational illness. It resolves itself into the problem of finding factors or conditions in work places that may cause or contribute to the illness or serious discomfort of employees, and of devising methods and means of eliminating or controlling such conditions. Another term that may best describe industrial hygiene might be industrial medical engineering.

The industrial hygienist has done much toward bringing medicine and safety engineering into close cooperation partly because his interests overlap these two fields.

The typical industrial hygienist usually started out as a chemist or chemical engineer who became interested and studied toxicological effects of chemicals on man. Consequently, he has a good background of chemistry and engineering combined with some medical knowledge—a sort of one-third doctor, one-third engineer, and one-third chemist. His objectives are protection and improvement of health and safety of workers in industrial environments from all manner of harmful exposures related to occupation.

Industrial hygienists and safety engineers have pretty much the same objectives and should be regarded as members of the same team. Actually, the functions of each are sometimes so inter-related it is not possible to draw a clear line of separation between the two fields, nor is it necessary to do so for if a man's health is endangered by working conditions it is an important part of his safety picture. In many industries, safety and industrial hygiene are combined in the same department.

In the petroleum industry, however, industrial hygienists are usually attached to the medical department and work as closely as possible with the safety department for the protection of the employees. There is good reason why the petroleum industrial hygienists must lean heavily upon the safety department. In the petroleum industry the concept of industrial hygiene is relatively new as compared to the chemical and other industries, consequently, the number of petroleum industrial hygienists is exceedingly small.

On the other hand, safety departments are well established, well acquainted with and close to every day problems of the petroleum industry. They have considerably more coverage and manpower.

To illustrate, the American Petroleum Institute's roster of safety and fire protection personnel list some 1,200 names, probably not all, in this occupation. Contrasted to this, to the best of my knowledge, there are at present only 17 industrial hygienists

working for petroleum companies—an industry ratio of approximately 70 safety men to one industrial hygienist. Most of the major oil companies now have at least one industrial hygienist and anywhere from 50 to 100 safety men so you can see it is very necessary for us to work with and through our safety people.

Basically, the practices of industrial hygiene in the petroleum industry is the same as in any other industry and it can be boiled down to four general principles:

1. A knowledge of the toxicology of chemicals and materials.

2. A review of all chemicals or materials used and how handled and tabulation of toxic or potentially hazardous substances.

3. Measurement of worker exposure to hazardous substances.

4. If required, recommendation and installation of adequate control measures and evaluation of the effectiveness of such corrective steps.

## Toxicology of Chemicals

In regard to the toxicology of chemicals, it is usually difficult to adequately define a hazardous material because practically anything can be safe or harmful depending upon how it is used or where it is used.

For example, air and water are not regarded as harmful, but both are quite deadly under certain conditions—air if injected into the blood stream and water if introduced into the lungs.

In the same manner, the use of carbon tetrachloride in a process having properly designed ventilation would not be hazardous, while the use of carbon tetrachloride for mopping floors would be quite dangerous. Most safety people are aware that carbon tetrachloride is a hazardous chemical because there has been considerable publicity regarding its toxicological effects, and in some cases, restrictive labeling requirements have been passed, for example, in New York City. Many other chemicals used in the petroleum industry have inherent toxic qualities of the same magnitude, yet are not so well known.

In regard to toxicology, there are three ways in which a substance can cause adverse effects upon man:

1. It can be ingested or swallowed.

2. It can be harmful by direct contact with the skin or parts of the body.

3. It can be inhaled as a gas, vapor, mist or dust.

### Ingestion

Fortunately, petroleum materials are not commonly or intentionally taken internally and therefore, trouble from this is rather rare in a refinery, although it does occasionally occur unknowingly. I recall watching a worker who had been complaining of stomach trouble, whose duties involved the compounding of litharge or lead oxide in a doctor solution. This man proceeded to empty bags of litharge into an outdoor mixing tank and because of the dust and mists generated he correctly wore a respirator. Of course, his hands were covered with lead oxide, and to my amazement, the first thing he did when he came down off the catwalk was to take an orange out of his lunch box which he started to peel and eat—probably one of the most effective ways to get lead poisoning.

Unfortunately, when petroleum products get into the hands of customers, ingestion is more frequent, usually by small children whose parents carelessly leave products within easy reach. You know that every year there are fatalities reported from children drinking kerosene. We have had hurry calls from doctors involving children drinking such products as penetrating oil and fly sprays.

Some times adults are even worse as there are many cases of anti-freeze poisoning, drinking of brake fluid and one I recall of our radiator flush which contains muriatic acid and chlorinated hydrocarbon. However, this product is fully labeled including poison warning with the skull and cross bones.

It should be emphasized that hardly a substance exists that is not capable of producing effects on the human body if taken in sufficient amounts or under the wrong circumstances. Even common table salt if used in sufficient quantities is toxic. It is reported that many years ago the Chinese used table salt as a means of committing suicide. Every chemical substance, therefore, has a non toxic dose for man and a toxic dose for man. This can be well illustrated by the following slide on a widely used commodity:

**Effect of Alcohol Level in Blood***

| Ounces of Whiskey Consumed in 1 Hr. or less | Percent Alcohol in Blood | Behavior |
|---|---|---|
| ¼ | 0.01 | Normal |
| 1 | 0.02 | Feeling of warmth, pleasant social behavior, judgment blunted. |
| 2 - 3 | 0.05 | Boastful, impulsive, Officially still sober. |
| 5 - 6 | 0.1 | Fumbling, staggering gait, clumsiness, slurred speech, Officially drunk. Responses and motor coordination strongly affected. |
| 8 | 0.15 | |
| 10 | 0.2 | Helpless, nausea. |
| 16 | 0.3 | Stupor. |
| 24 | 0.4 - 0.5 | Coma. |
| 30 | 0.6 - 0.7 | Paralysis of the respiratory center. — Death |

*Pfizer Spectrum, JAMA, March 27, 1954

## Skin and Body Contact

Approximately 60 per cent of all complaints received by our department are concerned with dermatitis and skin irritations resulting from contact with petroleum materials.

By far, the majority of these complaints are from customers so this is a subject that is very important in the marketing of petroleum products.

Cases among our employees or in our refineries are few when compared with those among industrial users of petroleum products, and it is believed that the reason for this is due mainly to the degree or extent of contact.

In the petroleum industry skin contact is not generally experienced to the extent that it is—for example, in the metal working industries where a daily eight hour skin contact with cutting oils often takes place.

It is definitely established that skin is not an impermeable barrier to chemical substances, and it is increasingly important as a route of absorption for many materials. Action of chemicals on skin may be local resulting in dermatitis. Examples we are familiar with are kerosene, cutting oils, and so forth, or a chemical may be absorbed through the skin and cause damage to blood or internal parts of the body.

Lead tetraethyl as an illustration does not affect the skin or cause dermatitis but can penetrate the skin and cause internal poisoning.

Regarding external or local skin effects, chemicals may be classified either as primary irritants or sensitizing agents.

A primary irritant is a chemical that may cause dermatitis in individuals frequently after only one contact. They may have a strong chemical action such as acids, alkalis, amines, and so forth or they may have a weak chemical action but require prolonged contact to cause dermatitis. Most petroleum hydrocarbons are primary irritants but are classed in the latter category in that prolonged or extensive contact is usually required to cause skin irritation.

Sensitizing agents on the other hand are chemicals that are innocuous to most skins but capable of producing dermatitis in a few susceptible individuals following repeated contacts over a long period of time. Sensitization may require weeks, months or even years of contact with the material before dermatitis develops.

The petroleum industry is now handling large quantities of chemical additives and inhibitors, many of which are strong primary irritants and very active chemical compounds. By nature, inhibitors usually have to be very potent chemicals because while they are used in very low concentrations, they exert a powerful influence on the characteristics or performance of the product, and many of the inhibitors are just as potent towards man.

One very active class of inhibitors are the amines and substituted amines, and we are particularly concerned about them because they are very damaging to the eyes, and a splash can readily result in blindness. The amines are usually strong smelling caustic liquids, insoluble in water, hence difficult to remove by washing. They can cause severe eye burns and necrosis of eye tissue. In addition, most amines are readily absorbed through the skin, and even low quantities may cause internal damage and death.

The following will show the effect on skin of one such amine-dimethyl phenylene diamine:

| Amount | Skin Area | Effect |
|---|---|---|
| 0.001cc | 1 sq. cm. | Heat — redness — rash |
| 0.005cc | 1 sq. cm. | Blister formation |
| 4.0cc | 12 sq. in. | Death |

Employees should be fully alerted as to hazards of such materials and should be educated to the use of protective goggles, gloves and aprons when handling such products, an activity within the scope of the safety engineer.

The foregoing applies to concentrated or undiluted inhibitors. Finished petroleum

products should and usually do contain such a small quantity, and the inhibitor is so diluted as to result in practically no more harm in the finished product than there would be from the straight mineral oil itself.

Industrial dermatitis cases sometimes result in bizarre and erroneous conclusions as to their cause even by those who should know better.

I recall a case of a young man who worked in a gasoline station and developed a severe dermatitis. He went to a physician who made patch tests on him and found he had a sensitivity to special gasoline but no reaction to regular gasoline. Apparently the physician had heard special gasoline contains a lot of lead because the case was diagnosed as resulting from an excess of lead tetraethyl in the special gasoline. We thought this strange because while we all know that lead tetraethyl is a violent poison and can be absorbed through the skin, it is not a primary skin irritant and has never been known to cause dermatitis. A review of records of gasoline shipments into the particular area showed the regular gasoline actually contained the same or some times more lead than the special gasoline, clearly proving that lead tetraethyl was not to blame, but that some other material was responsible.

## Inhalation

Of the three avenues by which chemicals can be taken into the body, inhalation probably has received by far the most study and investigation because it is the most important consideration in industrial health.

The vast amount of research on the inhalation of materials has resulted in publication of very useful data on safe human exposure levels known as Threshold Limit Values or Maximum Allowable Concentrations.

This is a list of several hundred commonly encountered chemicals, solvents, dusts, and so forth, the toxicology of which has been carefully studied by medical research and industrial experience.

The list is compiled annually by the American Conference of Governmental Industrial Hygienists and is published by the American Medical Association. It tabulates the maximum amount of the various materials workers can safely be exposed to for an eight hour working day without injury to health.

A few of the materials commonly encountered in the petroleum industry are listed below:

*Gases and Vapors*

| Substance | PPM |
|---|---|
| Benzene (benzol) | 35 |
| Carbon dioxide | 5000 |
| Carbon monoxide | 100 |
| Carbon tetrachloride | 225 |
| Gasoline | 500 |
| Hydrogen sulfide | 20 |
| Naphtha (petroleum) | 500 |
| Octane | 500 |
| Sulfur dioxide | 10 |

*Toxic Dusts, Fumes, and Mists*

| Substance | Mg. Pe Cu. M |
|---|---|
| Iron oxide fume | 15 |
| Lead | 0.15 |
| Sulfuric acid | 2 |

*Mineral Dusts*

| Substance | MPPCF |
|---|---|
| Asbestos | 5 |
| Dust (nuisance, no free silica) | 50 |
| Silica | |
| high (above 50% free $SiO_2$) | 5 |
| medium (5 to 50% free $SiO_2$) | 20 |
| low (below 5% free $SiO_2$) | 50 |

These values are based on the best available information from industrial experience, from experimental studies, and when possible, from a combination of the two. They are not fixed values but are reviewed annually by the Committee on Threshold Limits for changes, revisions, or additions as further information becomes available.

Threshold Limits should be used as guides in control of health hazards and should not be regarded as fine lines between safe and dangerous concentrations. They represent conditions only within which it is felt that workers may be repeatedly exposed, day after day, without their health being adversely affected. It is felt, at the present time, that workers should not be exposed to a working environment containing any of these substances in excess of the value indicated.

I cannot over emphasize the importance of the Threshold Limit Values and believe that every safety man should be familiar with them and have copies of the complete table, because they have been incorporated in states' codes and have the force of law in many states, and therefore, must be complied with. So far some nineteen states have written Threshold Limit Values into their laws and often management is not aware of such requirements but would be in a vulnerable position if trouble resulted from excessive exposure to any of the materials. Usually it is up to safety people and indus-

trial hygienists to alert management to the existence of these codes and to institute measures for measurement of air contaminants so as to insure compliance.

Even a common material like gasoline has a maximum safe level which is 500 parts per million. The results of exposure to concentrations greater than 500 ppm is shown by the following:

### Gasoline Exposure

*Symptoms:* Headache, irritation of eyes and throat, dizziness, nausea, loss of consciousness, death.

| | Parts Per Million | % |
|---|---|---|
| Maximum Allowable concentration for prolonged exposure | 500 | 0.05 |
| Slight symptoms after several hours | 1000 | 0.1 |
| Maximum concentration tolerable for 1 hr. | 5000 | 0.5 |
| Dangerous for short exposure | 15000 | 1.5 |
| Fatal for short exposure | 25000 | 2.5 |
| Low explosive limit | 14000 | 1.4 |

### Product Labeling

One very important function of the industrial hygienist in the petroleum industry is precautionary labeling of product. This is receiving more and more emphasis as state after state passes labeling regulations. The most recent is the state of New York where the Council on Public Health passed on February 26, 1954 labeling regulations which became effective August 24, 1954 as Chapter IX-A of the New York State Sanitary Code. These labeling regulations have the force and effect of law and require precautionary labeling on any product which entails a hazard in a reasonably anticipated use.

A hazard is defined as—the risk of injury or illness which may be encountered during or as a result of any reasonably anticipated type of handling or use of a substance or during its specified use, or any by reason of the toxicity of the substance through ingestion, inhalation or absorption through the skin, or due to its corrosiveness or irritating properties, or because of its flammability or explosiveness.

Similar labeling regulations already exist in California, Illinois, Oregon, and the Territory of Hawaii and are in the making in New Jersey, New Hampshire, Ohio and Rhode Island. More can be expected. Fortunately most state regulations are guided by recommendations of the Manufacturing Chemists Association, Inc. and with some few exceptions, conformity in one state results in conformity in other states.

It is recognized that as a rule labeling regulations of many products are advisable and result in safer handling of the material by customers, but it requires extensive work, knowledge of product and toxicological information to determine what products must be labeled and how they should be labeled. In our company's operations we use somewhat over 2,000 basic chemicals or raw materials and manufacture some 3,500 finished products which must be reviewed individually in regard to the above.

To illustrate the following are just a few of the hazardous materials that are encountered in petroleum refinery operations or that might be compounded into finished products:

*Materials Encountered in Petroleum Refinery Operations*

| Respiratory Irritants | Toxic Materials | Skin Irritants |
|---|---|---|
| Acrolein | Aniline, liquid | Acids — all kinds |
| Acetaldehyde | Aniline, dyes | Ammes |
| Aluminum Chloride | Benzol (Benzene) | Benzol (Benzene) |
| Ammonia | Cadmium | Caustics |
| Asbestos | Carbon Monoxide | Chromium Salts |
| Ditertiary butyl para cresol | Chlorinated hydrocarbons | Coal-tar Compounds |
| Dusts, physiologically inert, general | Chrome compounds | Cobalt, metal and compounds |
| Dusts, attapulgus clay | Cobalt, metal | Dyes |
| Dusts, bauxite | Hydrogen sulfide | Inhibitors |
| Dusts, catalyst | Inhibitors | Nickel salts |
| Formaldehyde | Lead, metal & fumes | Oils, general |
| Fluorides | Lead, oxide, litharge | Oils, high boiling fine = Cat. & Steam Cracking |
| Furfural | Lead, tetraethyl | Oils, insoluble cutting |
| Inhibitors | Lead, soaps | Phenol |
| Lime | Manganese | Pitch |
| Nitrogen oxides | Mercury | Solvents |
| Ozone | Methanol | Ultra Violet Radiation |
| Silica | Radioactive materials, general | Wax, untreated |
| Smoke | Toluol (Toluene) | |
| Sulfur dioxide | Xylol (Xylene) | |
| Pine Oil | Zinc | |
| Welding fumes | | |

The petroleum industry has made remarkable progress in development of new and better products and in improving processing operations. Accompanying this progress has been new problems of toxicology and health engineering which must be studied and investigated with the same zeal as other types of research.

The advent of catalytic cracking resulted in production and handling of aromatic hydrocarbons, and of importance to us, health problems long associated with the coal-tar industry.

The use of new chemical catalysts, inhibitors, and other chemical compounds involve health problems that chemical industries have faced for years.

To illustrate this trend we need only look at the modern gasolines, fuel oils and motor oils. Years ago motor oils were practically 100 per cent petroleum in nature with little if any additives; today they contain up to 15 to 20 per cent of chemicals, additives and inhibitors, and this trend will continue because there is no question that additives are necessary and contribute much to improve performance characteristics.

Every step in this direction, however, does pose new problems of health and safety among our plant personnel and our customers. Because the petroleum industry is becoming more and more involved in the handling of all kinds of chemicals having various degrees of physiological effects upon man, I would like to quote the following concerning chemicals from a publication issued by Du Pont's *Haskell Laboratory of Toxicology*:

"It Takes All Sorts"

*"Chemicals, like people, can be mild, vicious and often exasperating."* Like people, chemicals are of many types and dispositions. Most are uncomplaining, law-abiding citizens who present no special problems. Some are unstable and unpredictable. Some are out-and-out neurotics, requiring a sharp and observant discipline. Others, harmless by themselves, may be influenced by bad company. Still others are troublemakers in solitary, but docile and helpful in tandem. Some are just plain bad actors."

It is my firm opinion that good industrial hygiene in the petroleum industry is dependent upon combined skills of many and requires earnest cooperation of industrial physicians, industrial nurses, toxicologists, chemists, safety men and industrial hygienists working together as a team. We all have a very important part in the picture.

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# Safe Handling of Insecticides

By F. R. WILLSEY

Farm Safety Specialist, Purdue University, Lafayette, Ind.

Insecticides are *supposed* to kill! Of course, they are supposed to kill only insects but the fact that they are intended to kill anything at all should be enough to cause us to be alert.

In one sense this problem of "Safe Handling of Insecticides" isn't a new problem at all. For years, we've had insecticides that could and occasionally did kill humans. We have also had some that were less dangerous. On the other hand, in a few short years we've changed from a few old standbys to over 5,000 products involving about 70 chemicals.

Why all this change?

1. Apparently people don't like to eat worms as well as they did. At least public opinion seems to demand higher quality products now that people realize such products can be produced.

2. And the government doesn't think people should eat so many insects. That's indicated by the fact that we have more laws and regulations governing quality of products, labeling of insecticides, spray residue, and so forth.

3. Insects travel more. They hitch-hike rides on the very latest transportation facilities. As a result they get more places and get there quicker than they could a few years ago.

4. New chemicals, plus research, makes new insecticides possible. In fact with each