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2nd edition

# industrial toxicology

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# *Preface to the second edition*

Since the first edition of this book was published, the number of substances which potentially menace the health of the industrial worker has materially increased. These substances include some inorganic materials and many organic compounds, especially pesticides. Very likely the most important, and certainly the best publicized, have been the radioactive isotopes.

During the past few years the control of the commoner hazards has improved to such an extent that occupational illness is now rarely encountered in this country from substances such as benzene and carbon disulfide. Moreover, industrial hygiene has developed rapidly in many countries outside the U.S.A., and the findings in these countries have confirmed broadly the earlier experience of America and Western Europe with the familiar industrial poisons.

Standards of permissible concentrations of toxic substances have found increasing acceptance and become increasingly severe. Also, many new analytical methods have been developed over the past decade, with particular emphasis on the analysis of body fluids.

In the second edition an attempt has been made to include the more important of these new developments in the field of industrial toxicology.

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# *Preface to the first edition*

Although the literature of industrial toxicology contains many papers dealing adequately with the chemistry of various industrial poisons, nearly all books on the subject are written primarily from the medical point of view.

Although the vital role played by the physician in controlling occupational disease is duly recognized, it is not amiss to point out that the most important single step in the prevention of many occupational illnesses is control of fumes or dust. Measurement of the effectiveness of such control, in the long run a medical problem, can best be made initially by chemical methods. Furthermore, responsibility for the protection of workers rests primarily with industry; and those most intimately acquainted with the industrial processes and materials involved are industry's own chemists and engineers.

In this book an attempt is made to treat industrial poisons primarily from the point of view of the chemist and engineer. This means that the harmful substances themselves will be emphasized, and the industrial processes in which they are used, rather than the symptomatology and pathology of their effects on the human being. Some mention of the nature of the injuries caused is essential; but emphasis is placed on the probable seriousness of such effects, rather than on their complete physiological characterization.

It is hoped that this volume will provide a convenient source of information on the basic properties of the common industrial poisons;



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that it will stimulate the interest of the industrial chemist in problems of occupational illnesses of toxic origin; and that it will encourage employers to utilize the knowledge and training of their chemists and chemical engineers in protecting their workers from harmful substances to which they are exposed.

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its decomposition products suffer headache, nausea, and irritation of eyes, nose, and throat.[515]

### 3. Chlorinated Naphthalenes

The higher members of the chloronaphthalene series are powerful liver poisons. Mono-, tri-, and tetrachloronaphthalenes, however, are less harmful.

MONOCHLORONAPHTHALENE, $C_{10}H_7Cl$

Molecular weight: 162.5. Boiling point: 264° C.
Harmful effects: Skin irritation.
Degree: Usually transient.

Monochloronaphthalene finds considerable application as a fumigant in greenhouses, and to some extent as a solvent. No cases of systemic poisoning have been reported.

TRI- AND TETRACHLORONAPHTHALENES, $C_{10}H_5Cl_3$ and $C_{10}H_4Cl_4$

Harmful effects: Irritation of skin and respiratory tract.
Degree: Usually transient.
Maximum allowable concentration: 5 mg/m³.
Evaluation: Air analysis.

Solid waxy materials consisting mainly of tri- and tetrachloronaphthalene are used in this country under the trade name of Halowax. They are employed as dielectric media and insulation in electric condensers. The fumes of these substances may cause dermatitis and are irritating if inhaled in high concentrations but, so far as is known, have never caused systemic poisoning.

PENTA- AND HEXACHLORONAPHTHALENES, $C_{10}H_3Cl_5$ and $C_{10}H_2Cl_6$

Harmful effects: Liver damage, dermatitis.
Degree: Serious, fatal.
Maximum allowable concentration: Pentachloronaphthalene, 1.0 mg/m³. Hexachloronaphthalene, 0.5 mg/m³.
Evaluation: Air analysis.

The higher chlorides of naphthalene, also known as Halowax, are used largely in impregnating the insulation of electric wires, especially when resistance to both fire and water is essential. The fumes of these compounds are highly toxic and have caused several deaths from yellow atrophy of the liver.[150] The author made the first industrial air analyses for the fumes of these compounds in a plant where two such deaths had occurred and found from 1 to 2 mg of

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chloronaphthalene per cubic meter of air. Drinker and others showed that concentrations of this order damaged the livers of rats, on long exposure.[150, 160]

When hot, these compounds should be handled in closed systems or with very effective ventilation. In addition to serious systemic effects, these waxes are bad dermatitis producers, causing a skin condition known as chloracne. Occasionally such dermatitis results from handling wires whose insulation is impregnated with this wax, but it is more prevalent where the wax is handled in a molten state.

The concentrations of chloronaphthalene fumes found in various processes in Massachusetts are listed in Table 31.

TABLE 31

HALOWAX FUME CONCENTRATIONS

| *Operation* | *Type of Wax* | *Number of Studies* | *Concentration (mg/m³)* Max | Avg |
|---|---|---|---|---|
| Condenser impregnating | Trichloronaphthalene | 7 | 20 | 7.6 |
| Condenser sealing | Hexachloronaphthalene | 2 | 2 | 1.4 |
| Condenser soldering | Trichloronaphthalene | 3 | 2 | 1.0 |
| Wire impregnating | Hexachloronaphthalene | 2 | 11.1 | 5.6 |

Other fatal cases of liver atrophy attributed to chlorinated naphthalene fumes arising from condenser-sealing processes and coating of electric cables have been reported in this country.[161] One death and several cases of dermatitis were caused in England by chlorinated naphthalene used for protecting metals in chromium plating, according to Collier.[162] An outbreak of dermatitis occurred in Missouri from the employment of marking crayon, containing chlorinated naphthalene binder, on hot metal castings.[163]

### 4. Chlorinated Diphenyls, $C_{12}H_xCl_{(12-x)}$

Harmful effects: Irritation; liver damage.
Degree: Can be serious.
Maximum allowable concentration: 0.5–1.0 mg/m³.
Evaluation: Air analysis.

The chlorodiphenyls, known as Aroclor or Dykanol, are used as heat-transfer media and for the impregnation of dielectrics, wire insulation, etc. Animal experiments have indicated that some of these

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compounds are relatively non-toxic, whereas others apparently cause liver damage.[169] According to Treon and co-workers, Aroclor 1254, consisting chiefly of pentachlorodiphenyl, is several times as toxic as the trichlorodiphenyl, Aroclor 1242.[210] Some of the references in the literature regarding the toxicity of chlorinated diphenyl refer to Drinker's original experiments with chlorinated triphenyl.

Atmospheric concentrations of various chlorodiphenyl fumes found in Massachusetts plants are given in Table 32.

TABLE 32

AROCLOR FUME CONCENTRATIONS

| Process | Chlorodiphenyl Fume Concentration (mg/m³) Max | Avg |
|---|---|---|
| Condenser impregnating | 10.5 | 5.8 |
| | 5.5 | 4.3 |
| Condenser impregnating | 0.3 | 0.2 |
| Condenser soldering | 0.9 | 0.8 |
| Oil mixing | 1.1 | 0.6 |
| Regulator filling | 0.2 | 0.1 |

In none of these plants was there any evidence of toxic effects from the chlorodiphenyl; but the highest concentrations found, of the order of 10 mg per cubic meter, were unbearably irritating.

### 5. Chlorinated Triphenyl

In the manufacture of chlorinated diphenyl, certain by-products, consisting mainly of a mixture of chlorotriphenyls, are produced. Some of these mixtures are even more powerful liver poisons than hexachloronaphthalene, according to the animal studies by Drinker and others. They have been used for similar purposes and are known by the same trade name, Aroclor, as certain of the true chlorodiphenyls.

### 6. Dichlorodiphenyltrichloroethane, $(C_6H_4Cl)_2—CH—CCl_3$ (DDT)

Melting point: 108° C.
Harmful effects: Damage to nervous system, liver.
Degree: Can be serious.
Maximum allowable concentration: (2 mg/m³).
Evaluation: 1. Air analysis.
2. Urine analysis.

DDT achieved sudden prominence by reason of its remarkable properties as an insecticide and its wide use in World War II as a

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delousing agent and in large-area mosquito control. *p,p'*-Dichlorodiphenyltrichloroethane is the active ingredient of DDT, but the less active *ortho-para* isomer occurs as a major impurity in the technical product.

At present, DDT is probably the most widely used insecticide. In spite of the fact that it is toxic to warm-blooded animals, there have been relatively few proven cases of serious human poisoning. In the majority of deaths following ingestion of DDT solutions, the clinical picture has been characteristic of solvent poisoning.[818] Unless grossly misused, the hazard from DDT application is not great. Similarly the mixing of DDT dusts produces only a moderate hazard, provided a reasonable degree of dust control is maintained.

DDT is excreted in the urine as DDA (bis-*p*-chlorophenyl acetic acid). Analysis of fat for stored DDT has also been used as a measure of absorption.

### 7. Chlordane, $C_{10}H_6Cl_8$

(1,2,4,5,6,7,8,8-Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane)

Harmful effects: Damage to nervous system, liver.
Degree: Can be serious.
Maximum allowable concentration: (2 mg/m³).
Evaluation: 1. Urine analysis.
2. Air analysis.

Although the toxicity of chlordane, as measured by ingestion experiments with animals, is less than that of DDT and similar chlorinated insecticides, several human poisonings have followed its use or ingestion. Of 15 such cases reported by Conley, 5 were fatal. Ingestion was responsible for 6 of these cases, skin absorption and inhalation for the rest.[817] Chlordane appears to be absorbed through the skin more readily than DDT.

### 8. Dieldrin, $C_{12}H_8Cl_6O$

(1,2,3,4,10,10-Hexachloro-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-indo-oxo-5,8-dimethanonaphthalene)

Harmful effects: Damage to central nervous system.
Degree: Can be serious.
Maximum allowable concentration: (0.25 mg/m³).

Although dieldrin is known as one of the most toxic of the chlorinated insecticides, its use in this country has not produced any notable

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incidence of intoxication. Numerous cases have been reported in South America, however. Hayes, in discussing 63 clinical cases among spraymen in Venezuela, Ecuador, and Nigeria, lists the following symptoms: headache, blurred vision, twitching, sweating, insomnia, nausea, and general malaise.[168] In severe poisoning involuntary jerking of muscle groups, sometimes causing falling, momentary loss of consciousness, and epileptic convulsions occurred. One such case terminated fatally.

These effects were apparently due to chronic intoxication and recovery, following removal from exposure, was frequently slow. Some abnormality in electroencephalograms was noted in dieldrin spraymen who were considered well clinically.

It is clear that dieldrin, and the closely related endrin and aldrin, require greater precaution in handling than is customarily used with insecticides.

Other chlorinated compounds used as insecticides are discussed in Chapter 11.

## HALOGENATED ALCOHOLS, ETHERS, AND ESTERS

### 1. Ethylene Chlorohydrin, $CH_2OHCH_2Cl$

Molecular weight: 80.5. Boiling point: 132° C.
Harmful effects: Liver, kidney, and brain damage.
Degree: Serious, fatal.
Maximum allowable concentration: (5 ppm).
Evaluation: Air analysis.

This water-soluble liquid, chloroethyl alcohol, is among the most toxic solvents commercially available. Several poisonings, some of them fatal, have been reported. Some were attributed to skin absorption, others to inhalation. Dierker and Brown report a fatal case resulting from a 2-hour exposure to a concentration estimated at 300 ppm.[169] Goldblatt and Chrisman report chronic effects, nausea, and allied symptoms, in a plant where the average concentration of ethylene chlorohydrin vapor was found to be 18 ppm.[169] Ethylene dichloride was also present, in concentrations of the order of 60 ppm. There were two fatal cases, one acute and one chronic, following 2 months' exposure. Fatal poisoning has also resulted from the employment of ethylene chlorohydrin vapor to stimulate the sprouting of potatoes.

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