SECOND EDITION

Hazardous Chemicals Handbook

P.A.CARSON • C.J.MUMFORD

危险化学品手册 第2版

Elsevier (Singapore) Pte Ltd.
世界图书出版公司

Hazardous Chemicals Handbook

Second edition

Phillip Carson
PhD MSc AMCT CChem FRSC FIOSH
Head of Science Support Services, Unilever Research Laboratory,
Port Sunlight, UK

Clive Mumford
BSc PhD DSc CEng MIChemE
Consultant Chemical Engineer

BUTTERWORTH
HEINEMANN

世界图书出版公司

书　　名：Hazardous Chemicals Handbook 2nd ed.
作　　者：P. A. Carson, C. J. Mumford
中 译 名：危险化学品手册 第 2 版
出 版 者：世界图书出版公司北京公司
印 刷 者：北京世图印刷厂
发　　行：世界图书出版公司北京公司 (北京朝内大街 137 号　100010)
联系电话：010-64015659, 64038347
电子信箱：kjsk@vip.sina.com
开　　本：16 开　　印　张：39
出版年代：2005 年 4　月
书　　号：7-5062-7254-7 / O・521
版权登记：图字:01-2005-1278
定　　价：156.00 元

Preface to the second edition

The aim of this book remains as for the first edition, namely to provide an initial point of ready reference for the identification of hazards and precautions for dangerous chemicals. It is targeted not only at those in the chemical and process industries, but also anyone likely to work with chemicals within industry and in the service sector, e.g. hospitals, universities, research laboratories, engineering, agriculture, etc. It embraces the entire life-cycle of chemicals during transport, storage, processing, marketing, use and eventual disposal and should appeal to chemists, occupational and environmental health practitioners and students, engineers, waste handlers, safety officers and representatives, and health care professionals. Clearly, more detailed texts or professional advice may need to be consulted for specific applications.

Since the first edition in 1994 there have been no significant changes in the fundamentals of chemistry, physics and toxicology upon which the safe handling of chemicals are based. There has, however, been some increase in knowledge relating to the chronic toxicological and potential environmental effects of specific chemicals, and in legislation and government guidelines. These are reflected in the second edition. In general, within the UK the predominant legislation relating to substances hazardous to health, the Control of Substances Hazardous to Health Regulations 1999 and its accompanying Approved Code of Practice, incorporate significant changes since the 1988 (and 1994) versions. There has been an increase in the controls applicable to the marketing and transportation of different classes of chemicals. Those applicable to major hazards have changed under the Control of Major Accident Hazard Regulations 1999. Other legislation has been introduced: e.g. the Confined Spaces Regulations 1997, the Reporting of Injuries, Diseases and Dangerous Occurrences Regulation 1995, the Health and Safety (Safety Signs and Signals) Regulations 1996, and the Pressure Systems Safety Regulations 2000 which is of importance to the scope of this text. Increased concern as to the possible environmental impacts of chemical discharges and disposal has been accompanied by more comprehensive legislation for control. General safety legislation was expanded by the introduction of various separate regulations in 1993, including that dealing with management of health and safety at work; workplace health, safety and welfare; workplace equipment; and personal protective equipment. These improvements are, in general, now reflected in industry.

The opportunity has been taken to improve each chapter and to update the information. The main changes include an expansion of the terminology in Chapter 2 and provision of an introduction to basic chemical principles for non-chemists in a new Chapter 3. Chapter 4 on Physicochemistry contains additional examples. Chapter 5 on Toxic chemicals has been enlarged and the table of hygiene standards updated. Chapters 6, 7 and 8 on Flammable chemicals, Reactive chemicals and Cryogens, respectively, have been updated and expanded. The scope of Chapter 9 on Compressed gases has been widened to include additional examples together with the basic techniques of preparing gases *in situ*. Chapter 10 summarizes techniques for monitoring air quality and employee exposure. It has also been expanded to provide guidance on monitoring of water and land pollution.

The chapter on Radioactive chemicals (Chapter 11) has been updated. Considerations of safety in design (Chapter 12) are presented separately from systems of work requirements, i.e. Operating procedures (Chapter 13). The considerations for Marketing and transportation of hazardous chemicals are now addressed in two separate chapters (Chapters 14 and 15). Chemicals and the Environment are now also covered in two chapters (Chapters 16 and 17) to reflect the requirement that the impact of chemicals on the environment should be properly assessed, monitored and controlled. Although a substantial contribution to atmospheric pollution is made by emissions from road vehicles and other means of transport, and this is now strictly legislated for, this topic is outside the scope of this text. Chapter 18 provides useful conversion factors to help with the myriad of units used internationally.

Whilst the hazards identified, and the principles and practice for the control of risks are universal, i.e. they are independent of location, in order to assist quick-reference an appendix of relevant contemporaneous UK legislation has been added as a guide together with a much-expanded Bibliography in Chapter 19. Finally, for convenience of use, the Index has been enlarged.

It is hoped that the improvements will help to achieve the objectives for which the text was originally conceived, i.e. to summarize in relatively basic terms the hazards associated with chemicals and how the ensuing risks can be controlled, and to provide sufficient detailed information to supplement that obtainable from suppliers, government publications, trade associations, and computerized data banks where recourse to specialized textbooks may be premature, difficult or unnecessary.

P.A.C.
C.J.M.

Preface to the first edition

The aim of this handbook is to provide a source of rapid ready reference to help in the often complex task of handling, using and disposing of chemicals safely and with minimum risk to people's health or damage to facilities or to the environment.

The range of chemicals and chemical mixtures in common use in industry is wide: it is obviously impossible to list them all in a concise handbook, or to refer to all their proprietary names. The approach here has been to avoid 'random listing' and to arrange by type of hazard, dealing with the most widely used substances and those properties and characteristics of behaviour that are directly relevant to common use and to compliance with safety legislation. Numerous sources not restricted to those in the Bibliography were searched for information and although not listed, to achieve conciseness, these are acknowledged. The multiplicity of data sources also means that minor variations occur due to differences in the procedures and methods for their determination; however they provide general guidance. Whilst the data quoted in this text has been carefully collated, its accuracy cannot be warranted. For this reason, and to avoid overlooking consideration of other chemical-specific hazards or location-dependent legislation, it is advisable to refer to a Chemical Safety Data Sheet before using any chemical. These are readily available from suppliers (e.g. in the UK under S.6 of the Health & Safety at Work etc. Act 1974). For exhaustive treatment of physical, toxicological, flammable/explosive and reactive properties, and the background to – and limitations of – their determination or prediction, the reader is referred to standard textbooks (see Bibliography) such as:

The Safe Handling of Chemicals in Industry (Carson and Mumford)
Dangerous Properties of Industrial Materials (Sax and Lewis)
Handbook of Reactive Chemical Hazards (Bretherick)
Handbook of Toxic and Hazardous Materials (Sittig)
Patty's Industrial Hygiene and Toxicology (Clayton and Clayton)

The identification, assessment, control and monitoring of chemical-related hazards and environmental pollution control are, of course, required under a wide range of statutory legislation, dependent upon the country concerned. For example, in the UK the Health and Safety at Work etc. Act 1974, the Control of Substances Hazardous to Health Regulations 1988, the Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972, the Control of Pollution Act 1974 and the Environmental Protection Act 1990 are supplemented by a wide variety of other measures. Legislative controls tend to change frequently and it is important to ensure that a check is made on current requirements and constraints in any specific situation involving chemicals.

It is hoped that this book will prove valuable to safety advisers, environmental health officers, emergency services personnel, safety representatives and those engaged in the transport or disposal of wastes – in fact, to anyone involved with chemicals 'in the field', i.e. away from ready access

to chemical safety data sheets, detailed texts, library facilities or computerized databanks. It also provides a useful summary for those who may need to make only passing reference to the hazardous properties and potential effects of chemicals, such as general engineering students and occupational health nurses.

P.A.C.
C.J.M.

Contents

1

Introduction

Industrial hazards cover a wide spectrum including fire and explosion, mechanical hazards (e.g. from moving machinery), electrical hazards, occupational exposures to ionizing and non-ionizing radiation, biological hazards (e.g. acute or chronic infections, parasitism, and toxic or allergic reactions to plant and animal matter), physical hazards (e.g. tripping, falling, impact from vehicles or falling objects) and ergonomical hazards (e.g. lifting or carrying heavy or awkward loads or from repetitive operations). Work-related stress can also lead to mental and physical ill-health. Different hazards may be associated with the manufacture, storage, transport, use, and disposal of chemicals. Environmental hazards, through persistent or accidental losses of chemicals, may also be related to these operations.

Working with pathogenic micro-organisms bears passing similarity to chemicals. Hence, in the UK micro-organisms are classified as *hazardous substances* under the Control of Substances Hazardous to Health Regulations and there is an accompanying Code of Practice. However, biological hazards arising from the working environment or from more specialized activities, e.g. working with pathogenic organisms in laboratories, are beyond the scope of this book. This text deals solely with occupational, industrial and environmental hazards associated only with chemicals. It includes fires and explosions since they inevitably involve chemical compounds.

Chemicals are ubiquitous as air, carbohydrates, enzymes, lipids, minerals, proteins, vitamins, water, and wood. Naturally occurring chemicals are supplemented by man-made substances. There are about 70 000 chemicals in use with another 500–1000 added each year. Their properties have been harnessed to enhance the quality of life, e.g. cosmetics, detergents, energy fuels, explosives, fertilizers, foods and drinks, glass, metals, paints, paper, pesticides, pharmaceuticals, plastics, rubber, solvents, textiles; thus chemicals are found in virtually all workplaces. Besides the benefits, chemicals also pose dangers to man and the environment. For example:

- Of the many industrial fires in the UK in 1997 each of some 411 cost more than £50 000 with total losses amounting to £186m. These spanned a wide range of industrial and related premises as shown in Table 1.1. The most common sources of ignition (see Chapter 6) that year are shown in Table 1.2.
- In the UK alone occupational health risks due to chemicals are illustrated by:
  - 152 incidents in 1998 involving supply and use of flammable gas with around 70% causing carbon monoxide poisoning and 30 fires/explosions;
  - 554 new cases of pneumoconiosis (excluding asbestosis) and 3423 assessed cases of bronchitis or emphysema (in coal miners) during the same period;
  - annually there are 4500 cases of work-related skin disease (80% contact dermatitis), ca 1500 cases of occupational asthma (mainly from solder flux, isocyanates, wood dust, spray painting, metal treatment, plastics), ca 200 cases of allergic rhinitis;
  - between 2% and 8% of all cancer deaths are of occupational origin;

Table 1.1 Breakdown of U.K. fires causing more than £50 000 damage in 1997

Occupancy	*No. of fires*	*Loss £000*	*% of total cost of all fires*
Agriculture, forestry and fishing	27	3282	2
Paper, printing and publishing	14	6480	3
Food, drink and tobacco	13	7235	4
Rubber and plastic	7	5371	3
Textiles, footwear and clothing	7	1894	1
Timber and wood products excluding furniture	6	1042	1
Chemicals and allied products	5	4543	2
Construction	5	515	–
Metal manufacture	4	871	–
Engineering	4	545	–
Other manufacturing industries	25	20249	11
Retail distribution	27	15021	8
Transport and communications	18	13390	7
Wholesale distribution	8	26250	14
Education	39	23407	13
Recreational/cultural	30	6946	4
Clubs and public houses	19	4668	3
Cafes/restaurants	14	2431	1
Insurance, banking and business services	10	1730	1
Hotels/boarding houses	6	2516	1
Hospitals	4	925	–
Public admin./defence/law enforcement	3	430	–
Hostels/holiday camps	1	99	–
Homes for disabled	1	100	–
Domestic dwellings	63	9970	5
Other	26 434	518	14

Table 1.2 Accidental fires (UK) in 1997: sources of ignition

Ignition source	*No. of fires*	*% of all fires*	*Loss £000*	*% of total cost of all fires*
Electrical appliances	110	26.8	55 491	29.8
Smokers' materials	17	4.1	2138	1.1
Gas appliances (excluding blowlamps and welding)	10	2.4	2595	1.4
Blowlamps: all fuels	7	1.7	2176	1.2
Welding and cutting appliances	7	1.7	1340	0.7
Oil and petroleum appliances (excluding blowlamps and welding)	6	1.5	714	0.4
Unspecified appliances	5	1.2	578	0.3
Rubbish burning	4	1	417	0.2
Chimney, stovepipe and flue	2	0.5	303	0.2
Natural occurrence	2	0.5	215	0.3
Ashes/soot	1	0.2	50	0.1
Other	22	5.4	3789	2
Total	193	47	69 806	37.7

  - ca 1760 cases per year of acute poisonings and injuries from chemicals, the most common being from acids, caustic, and gases, with process operatives and tradesmen being at greatest risk;
  - an estimated 9000 cases of sick building syndrome per year.
- The UK Environment Agency deals with over 6000 oil pollution incidents each year. One estimate suggests that the chemical industry contributes to 50% of all air pollution with proportions approximating to sulphur dioxide (36%), carbon dioxide (28%), nitrogen oxides (18%), carbon monoxide (14%) and black smoke (10%). Motor spirit refining is responsible for ca 26% of emissions of volatile organic compounds to the atmosphere. In 1996 there were over 20 000 reports of water pollution incidents with 155 successful prosecutions.
- The EC produces in excess of 2 billion tonnes of waste each year. 414 million tonnes arise in the UK and a further 68 million tonnes of hazardous waste are imported. All wastes must be disposed of safely.

Society must strike a balance between the benefits and risks of chemicals. In the workplace it is a management responsibility to ensure practices control the dangers, and it is for employees to collaborate in implementing the agreed procedures. Management must also prevent uncontrolled environmental releases and ensure all wastes are disposed of safely and with proper regard for their environmental impact. The aims of this book are to raise awareness and to help users identify, assess and control the hazards of chemicals to permit optimum exploitation whilst minimizing the dangers.

The hazards of 'chemicals' stem from their inherent flammable, explosive, toxic, carcinogenic, corrosive, radioactive or chemical-reactive properties. The effect of exposure on personnel may be acute, e.g. in a flash-fire or due to inhalation of a high concentration of an irritant vapour. Alternatively, prolonged or intermittent exposure may result in an occupational disease or systemic poisoning. Generally acute effects are readily attributable; chronic effects, especially if they follow a long latency period or involve some type of allergic reaction to a chemical, may be less easy to assign to particular occupational exposures. The possible permutations of effects can be very wide and exposure may be to a combination of hazards. For example, personnel exposed to a fire may be subject to flames, radiant heat, spilled liquid chemicals and vapours from them, leaking gases, and the pyrolytic and combustion products generated from chemical mixtures together with oxygen deficient atmospheres. However, whether a hazardous condition develops in any particular situation also depends upon the physical properties of the chemical (or mixture of chemicals), the scale involved, the circumstances of handling or use, e.g. the processes involved and degree of containment, and upon the control measures prevailing, e.g. provision of control and safety devices, local exhaust ventilation, general ventilation, personal protection, atmospheric monitoring and systems of work generally.

Hazard recognition and assessment always start from a knowledge of the individual properties of a chemical. What this may include is exemplified by Table 1.3. Additional properties, including those in Table 1.4, are relevant to environmental hazards, e.g. relating to behaviour on spillage or emission, and determination of permissible levels for disposal to air, land or water systems. Other properties may be relevant, e.g. odour which can serve as an, albeit often unreliable, means of detection. (Refer to Table 5.12.)

An elementary introduction to chemistry is given in Chapter 3; this serves only to provide background and for more advanced consideration reference will be necessary to specific text books, e.g. as listed in the Bibliography. A brief discussion of the relevance of physicochemical principles to hazard identification is given in Chapter 4. Relevant toxic and flammable properties, and summaries of appropriate precautions to cater for them during handling, use and disposal, are provided in Chapters 5 and 6, respectively. Reactive hazards are discussed in Chapter 7. The special problems with cryogenic materials and chemicals under pressure, typified by compressed

Table 1.3 Comprehensive information possibly required for a hazardous chemical

Name of chemical; other names
Uses
General description of hazards
General description of precautions
  Fire-fighting methods
  Regulations
  Sources of advice on precautions

Characteristics: evaluate as appropriate under all process conditions
Formula (chemical structure)
Purity (identity of any contaminants), physical state, appearance, other relevant information
Concentration, odour, detectable concentration, taste

Physical characteristics
  Molecular weight
  Vapour density
  Specific gravity
  Melting point
  Boiling point
  Solubility/miscibility with water
  Viscosity
  Particle size; size distribution
  Foaming/emulsification characteristics
  Critical temperature/pressure
  Expansion coefficient
  Surface tension
  Joule–Thompson effect
  Caking properties

Corrosivity
Contamination factors (incompatibility), oxidizing or reducing agent, dangerous reactions

Flammability information
  Flash point
  Fire point
  Flammable limits (LEL, UEL)
  Ignition temperature
  Spontaneous heating
  Toxic thermal degradation products
  Vapour pressure
  Dielectric constant
  Electrical resistivity
  Electrical group
  Explosion properties of dust in a fire

Reactivity (instability) information
  Acceleration rate calorimetry
  Differential thermal analysis (DTA)
  Impact test
  Thermal stability
  Lead block test
  Explosion propagation with detonation
  Drop weight test
  Thermal decomposition test
  Influence test
  Self-acceleration temperature
  Card gap test (under confinement)
  JANAF
  Critical diameter
  Pyrophoricity

Toxicity information
  Toxic hazard rating
  Hygiene standard (e.g. OEL, TLV)
  Maximum allowable concentration (MAC)
  Lethal concentration (LC_{50})
  Lethal dose (LD_{50})

Biological properties

Exposure effects
  Inhalation (general)
  Respiratory irritation
  Ingestion
  Skin/eye irritation
  Skin and respiratory sensitization
  Mutagenicity
  Teratogenicity
  Carcinogenicity

Radiation information
  Radiation survey
  Alpha/beta/gamma/neutron exposure and contamination

gases, are dealt with in Chapters 8 and 9. The unique problems associated with radioactive chemicals are described in Chapter 11.

The foregoing relates mainly to normal laboratory or commercial quantities of chemicals. Additional considerations arise with those quantities of flammable, explosive, reactive, bulk toxic, or hypertoxic chemicals which constitute *major hazards*, i.e. which may pose a hazard to neighbouring factories, residents, services etc. or a more substantial potential risk to the environment. Within the UK the Control of Major Accident Hazards Regulations 1999 requires that the operator of any establishment where a dangerous substance listed in column 1 of Parts 2 or 3 of Schedule 1 (reproduced here as Tables 1.5 and 1.6) is present in a quantity equal to or greater than that listed in column 2 of those Parts shall notify the competent authority. Detailed procedures and precautions are then applicable to such sites depending partly upon whether they are 'lower tier' or 'upper tier', i.e. sites at which the quantity present is equal to or exceeds that listed in column 3. The special considerations with such installations are detailed in specialist texts noted in the Bibliography. In the UK the Planning (Hazardous Substances) Regulations 1992 also require the holder to obtain a 'hazardous substances consent' for any site on which it is intended to hold a bulk quantity of any of 71 substances above a 'controlled quantity' (Table 1.7).

Table 1.4 Typical data on hazards to the environment

Aquatic toxicity (e.g. to fish, algae, daphnia)
Terrestrial toxicity (to plants, earthworms, bees, birds)
Biotic degradation
Abiotic degradation
Photodegradation
Biochemical oxygen demand
Chemical oxygen demand
Hydrolysis as a function of pH
Bioaccumulation
Oil/water partition coefficient

To proceed to assess, and recommend control strategies for, any operation involving a mixture of chemicals – e.g. a chemical process, welding fume, mixed effluents – can be a complex exercise. It can rarely be solved by rigidly following a checklist, although checklists, examples of which are given in the various chapters, can provide useful guidelines. And although associated hazards are not covered here, the control of chemical hazards in the workplace cannot be achieved in isolation from a consideration of electrical, mechanical, ergonomic, biological and non-ionizing radiation hazards. Hence these must be included in any hazard analysis and control system.

To ensure that an operation is under control may necessitate environmental monitoring; this is summarized in Chapter 10. Principles of safe design are given in Chapter 12. General safety considerations, administration and systems of work requirements, including elementary first aid, are summarized in Chapter 13. For example, the recommended strategy is to include provision for appropriate first aid procedures within the system of work before specific chemicals are brought into use; to so order work practices that the risk of exposure is minimized; and in the event of an accident involving any but the most trivial injuries – with no foreseeable likelihood of complications or deterioration – to seek immediate medical assistance.

Additional considerations, e.g. relating to labelling, information supply and emergency procedures, arise when marketing and transporting chemicals. While – as with Chapter 13 and with control measures generally – what is required will vary with specific legislation and basic requirements are summarized in Chapters 14 and 15.

Table 1.5 Schedule 1 Part 2 of the COMAH Regulations Named Substances (Explanatory notes omitted)

Column 1 *Dangerous substances*	*Column 2* *Quantity in tonnes*	*Column 3* *Quantity in tonnes*
Ammonium nitrate (as described in Note 1 of this Part)	350	2500
Ammonium nitrate (as described in Note 2 of this Part)	1250	5000
Arsenic pentoxide, arsenic (V) acid and/or salts	1	2
Arsenic trioxide, arsenious (III) acid and/or salts	0.1	0.1
Bromine	20	100
Chlorine	10	25
Nickel compounds in inhalable powder form (nickel monoxide, nickel dioxide, nickel sulphide, trinickel disulphide, dinickel trioxide)	1	1
Ethylenimine	10	20
Fluorine	10	20
Formaldehyde (concentration ≥ 90%)	5	50
Hydrogen	5	50
Hydrogen chloride (liquefied gas)	25	250
Lead alkyls	5	50
Liquefied extremely flammable gases (including LPG) and natural gas (whether liquefied or not)	50	200
Acetylene	5	50
Ethylene oxide	5	50
Propylene oxide	5	50
Methanol	500	5000
4,4-Methylenebis (2-chloroaniline) and/or salts, in powder form	0.01	0.01
Methylisocyanate	0.15	0.15
Oxygen	200	2000
Toluene diisocyanate	10	100
Carbonyl dichloride (phosgene)	0.3	0.75
Arsenic trihydride (arsine)	0.2	1
Phosphorus trihydride (phosphine)	0.2	1
Sulphur dichloride	1	1
Sulphur dioxide	15	75
Polychlorodibenzofurans and polychlorodibenzodioxins (including TCDD), calculated in TCDD equivalent	0.001	0.001
The following CARCINOGENS:		
4-Aminobiphenyl and/or its salts, Benzidene and/or its salts, Bis(chloromethyl) ether, Chloromethyl ether, Dimethylcarbamoyl chloride, Dimethylnitrosoamine, Hexamethylphosphoric triamide, 2-Naphthylamine and/or its salts, 1.3-Propane sultone, 4-Nitrodiphenyl	0.001	0.001
Automotive petrol and other petroleum spirits	5000	50 000