Second Edition

Handbook of Reactive Chemical Hazards

Bretherick

Butterworths

AN INDEXED GUIDE TO PUBLISHED DATA

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Foreword

During the two years in which I chaired the Enquiry Committee on Safety and Health of people at their place of work, what was certainly borne upon us was the tremendous speed of advance of modern technology and the importance of keeping up to date with the safety factors surrounding new developments.

This handbook, the product of Mr. L. Bretherick, certainly adds a new dimension to this whole problem.

It is very clear from its exposition that every single contingency that can at present be contemplated in the whole field of laboratory safety has been covered, and there is no doubt that from time to time there will require to be reviews in the light of chemical development. Sufficient to say, however, that within these pages lies an enormous amount of research work in this whole area of laboratory work in the chemical industry, that there has been collected a tremendous amount of information on hazards in laboratories and that Mr. Bretherick has become recognised as an expert in this field.

Safety Officers who are responsible for safety in industrial laboratories will find this book absolutely essential reading if they are to do their own work to the satisfaction of themselves and of the company which they serve.

I know of no previous book containing so much information as this one, and there is no doubt at all that if the book is diligently used there will be found within its pages answers to many of the problems in relation to safety in the use of chemicals.

I can only say, having spent so much time in this whole field, that the development of the modern technologies is the area in which safety research needs to be constantly updated. In the older industries already there is sufficient information to enable us to conduct our affairs in such a manner as to provide adequate safety and a proper healthy environment for the workers in those fields. It is in the modern fields that the problems arise, because with great frequency there are new discoveries that require fresh thought in relation to safety hazards.

Mr. Bretherick has undoubtedly produced for all those in this field a handbook that will enable the greatest possible safety precautions to accompany the developing sciences. That Mr. Bretherick should have been able to produce what is a monumental contribution to safety is a matter of great credit to him and the enormous amount of research that was required in order to produce this book.

I therefore recommend most strongly a careful survey of the entries in this book relevant to the particular activities of companies in this field, and feel very strongly that Safety Officers require this constantly at their elbow in order to provide the right kind of environment in which work in laboratories can be conducted with greater safety than is possible without the research benefits that have come from this book.

It is absolutely essential in the modern world that safety factors of those employed in research must be adequately safeguarded, and this means that the maximum amount of information must be available at all times, based upon present knowledge. It is because I recognise the value of the work that this book embraces in the whole difficult field of modern research and technology that I unhesitatingly in this foreword make the strongest recommendation for its close attention and use in laboratories.

In our travels as a Committee of Enquiry, we found that many countries in the world look to the United Kingdom for a lead in these matters. This book produces further evidence of the care and attention required in this highly critical area of laboratory research and, therefore, will be welcomed both in the United Kingdom and overseas.

I am certain that as a result of this work a great many people engaged in actual research, and the companies concerned, will find this of considerable help and assistance in safeguarding all those who are engaged in breaking through the frontiers of knowledge.

Robens

LORD ROBENS OF WOLDINGHAM

November, 1974

Preface to the Second Edition

It has become apparent during the four years since preparation of the first edition that some changes in content would greatly increase the value of the Handbook, not only to practising chemists as originally envisaged, but also to those concerned with chemical safety but not so directly involved in handling chemical materials.

An introductory chapter has been added to try and give an overview of the complex subject and an understanding of the basic principles involved in minimising hazards arising from chemical reactivity.

For most of the 7000-odd entries a structural formula is now included to help to bring out the relation between structure and reactivity, both for individual compounds and for the collective group items.

A full alphabetical index to all the chemicals named in the text is also provided, and this should allow those not sufficiently familiar with the empirical formula-based arrangement of the main section to gain effective access to what they are seeking. Some synonyms of the IUPAC names, including some from the ASE-preferred selection, are given as cross-references in this index.

Some other minor changes in layout and content have been incorporated in an attempt to make this compilation more useful to a wider spectrum of users.

A considerable amount of new and revised information has become available or has been located in the 4 year period since completion of the manuscript of the first edition. The main new sources have been the major inorganic textbooks edited by Bailar and Pascal, the laboratory handbook by Sorbe, the continuing compilations of Leleu and the Institution of Chemical Engineers, and, above all, the one keyword 'Safety' used in *Chemical Abstracts* indexes since January 1974. A further source of much relevant information is the *Manual of Hazardous Chemical Reactions*.

The new material available up to September 1977 has been treated in the same general way as previously, and has been added into the revised text format. Of the 150-odd new alphabetical group entries, those bringing together information on the hazards of industrial unit process operations (nitration, polymerisation, etc.) and all the preparative hazards noted may prove to be the most useful.

I am again indebted to my employers, The British Petroleum Company, Ltd, for their continued generous support of my activities in this area, and to my colleagues, both at Sunbury and elsewhere in the Company, for assistance with information sources.

Other professional colleagues, both in the UK and overseas, have usually responded generously to my written requests for particular information. On the other hand, it is slightly disappointing to have to record that of the many thousands who have by now consulted the first edition, only two persons have been inspired to send information for inclusion in this second edition. However, the appearance of the new *Journal of Hazardous Materials* may be expected to give further stimulus to the dissemination of information vital to those making, handling and using chemicals.

I again record my thanks to the editorial staff of Butterworths, and to Dr R.S. Cahn and Dr E.R. Smith of the Chemical Society for assistance with matters of IUPAC nomenclature.

I am again greatly indebted to my wife and family for their continuing cheerful acceptance of my time-consuming occupation.

L.B.

Preface to the First Edition

Although I had been aware during most of my career as a preparative chemist of a general lack of information relevant to the reactive hazards associated with the use of chemicals, the realisation that this book needed to be compiled came soon after my reading *Chemistry & Industry* for June 6th, 1964. This issue contained an account of an unexpected violent laboratory explosion involving chromium trioxide and acetic anhydride, a combination which I knew to be extremely hazardous from close personal experience 16 years previously.

This hazard had received wide publicity in the same journal in 1948, but during the intervening years had apparently lapsed into relative obscurity. It was then clear that currently existing arrangements for communicating 'well-known' reactive chemical hazards to practising chemists and students were largely inadequate. I resolved to try to meet this obvious need for a single source of information with a logically arranged compilation of available material. After a preliminary assessment of the over-all problems involved, work began in late 1964.

By late 1971, so much information had been uncovered but remained to be processed that it was apparent that the compilation would never be finished on the spare-time basis then being used. Fortunately I then gained the support of my employers, the British Petroleum Company, Ltd., and have now been able to complete this compilation as a supporting research objective since January, 1972.

The detailed form of presentation adopted has evolved steadily since 1964 to meet the dual needs for information on reactive chemical hazards in both specific and general terms, and the conflicting practical requirements of completeness and brevity. A comprehensive explanation of how this has been attempted, with suggestions on using this Handbook to best advantage, is given in the Introduction.

In an attempt to widen the scope of this work, unpublished information has been sought from many sources, both by published appeals and by correspondence. In this latter area, the contribution made by a friend, the late Mr. A. Kruk-Schuster, of Laboratory

Chemicals Disposal Company, Ltd., Billericay, has been outstanding. During 1965–1968 his literature work and global letter campaign to 2000 University chemistry departments and industrial institutions yielded some 300 contributions.

The coverage attempted in this Handbook is wide, but is certainly incomplete because of the difficulties in retrieving relevant information from original literature when it does not appear in the indices of either primary or abstract journals. Details of such new material known to users of this Handbook and within the scope given in the Introduction will be welcomed for inclusion in supplementary or revised editions of this work.

L.B.

Acknowledgments

It is a pleasure to acknowledge the contributions of unpublished information on hazardous chemical reactions which have been made by both close colleagues and distant correspondents during the course of several years. Many of the earlier contributors must have despaired of ever seeing their help acknowledged in print (as private communications) in the text, but I hope that they will feel the long delay has been worthwhile. Thanks are also due to those whose contributions could not be incorporated.

I should like to record my special indebtedness to the following, who all provided substantial quantities of information from their own files or experience:

Mr R. N. Beer, BP Chemicals International Limited, Grangemouth
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Thanks are also due to the British Chemical Industries Safety Council, London, and the Manufacturing Chemists Association Inc., Washington, whose secretaries gave free use of their regularly published safety material.

I am indebted to colleagues, library and clerical staff at the BP Research Centre for much general encouragement and assistance, and to my employers, the British Petroleum Company Limited, without whose close support since 1971 this work would not have been completed. My former colleagues at May and Baker Limited, Dagenham, were largely responsible for the original development of my personal interest in laboratory safety matters.

The assistance rendered during preparation of this book by the Publisher's staff and their IUPAC nomenclature consultant, Dr R. S. Cahn, is also gratefully acknowledged.

Finally, I would record my heartfelt gratitude to my wife, who has cheerfully during several years converted miles of illegibility into a coherent typescript. To her I dedicate this work.

Introduction

THIS SHOULD BE READ THROUGH CAREFULLY TO GAIN FULL BENEFIT FROM THE FOLLOWING SECTIONS.

Aims of the Handbook

This compilation has been prepared mainly to give the research student, practising chemist or safety officer access to a wide selection of documented information to allow him or her readily to assess the likely reaction hazard-potential associated with an existing or proposed chemical compound or reaction system.

A secondary, longer-term purpose is to present the information in a way which will, as far as possible, bring out the causes of, and interrelationships between, apparently disconnected facts and incidents. This should encourage an increased awareness of potential chemical reactivity hazards in school, college and university teaching laboratories and help to dispel the considerable ignorance of such matters which appears to be widespread in this important area of safety training during formative years.

Others involved in a more general way with the storage, handling, packing and transport of chemicals are likely to find information of relevance to their activities.

Scope and Source Coverage

This Handbook includes all information which had become available to the author by September 1977 on the reactivity hazards of individual elements or compounds, either alone or in combination. Appropriate source references are included to give access to more expansive information than that compressed into the text entries.

A wide variety of possible sources of published information has been scanned to ensure maximum coverage. Primary sources have largely been restricted to journals known to favour or specialise in publication of safety matters, and the textbook series specialising in synthetic procedures.

Secondary sources have been a fairly wide variety of both specialised and general textbooks (notably those of Bailar, Pascal, Mellor and Sidgwick in the inorganic area), part of *Chemical Abstracts*, and various safety manuals, compilations, summaries, data sheets and case histories which cover the industrial area. Details of all the secondary sources and the primary textbooks will be found in Appendix 1. Textbook references are characterised by the absence of an author's initials.

Information on toxic hazards has been specifically excluded because this is collectively available elsewhere and its attempted inclusion would have delayed publication by several more years. For similar reasons, no attempt has been made to include details of all flammable materials capable of burning explosively when mixed with air and ignited, or any incidents related to this frequent cause of accidents.

However, to focus attention on the potential hazards always associated with the use of flammable substances, some 530 gases and liquids with flash points below 25°C and/or autoignition temperatures below 225°C have been included, their names prefixed with a dagger. The numerical values of the fire-related properties of flash point, autoignition temperature and explosive limits in air where known are given in the tabular Appendix 2. Those elements or compounds which ignite on exposure to air are also included in the text.

General Arrangement

The information herein on reactive hazards is of two main types, specific or general, and these have been arranged differently in their respective separate sections. Specific information on instability of individual chemical compounds and on hazardous interactions of elements and/or compounds is contained in the main formula-based second section of the Handbook.

See ETHYL PERCHLORATE, $C_2H_5ClO_4$
NITRIC ACID, HNO_3 : Acetone

General information relating to types or groups of elements or compounds possessing similar structural or hazardous characteristics is contained in the smaller alphabetically based first section:

See ACYL NITRATES
PYROPHORIC METALS

Individual materials of variable composition and materials which cannot conveniently be formulated are also included in this section:

See BLEACHING POWDER
CELLULOSE NITRATE

Both theoretical and practical hazard topics, some indirectly related to the main theme of this book, are also included:

See DISPOSAL
EXPLOSIBILITY
GAS CYLINDERS
OXYGEN ENRICHMENT

Specific Formula Entries

1. A single unstable compound of known composition is placed in the main (formula) section on the basis of its molecular formula expressed in the Hill system used by *Chemical Abstracts* (C and H if present, then all other elements alphabetically). The use of this indexing basis permits a compound to be located if its structure can be drawn, irrespective of whether it can be named or not. A representation of the structure of each compound, usually in abbreviated linear form, is given except where the empirical formula coincides exactly with the structural formula. The IUPAC name (and occasionally a synonym) corresponding to the indexing formulation appears in capitals to the left of the formula. References to the information source are given, followed by a statement of the observed hazard, with any relevant explanation. Cross-reference to similar compounds, preferably as a group entry, completes the item:

See TRIFLUOROACETYL NITRITE, $C_2F_3NO_3$

2a. Where two or more elements or compounds are involved in a reactive hazard, and an intermediate or product of reaction is identifiable as being responsible for the hazard, both reacting substances are normally cross-referred to the identified product. The well-known reaction of ammonia and iodine to give explosive nitrogen triiodide–ammonia is of this type. The entries

AMMONIA, H_3N: Halogens
IODINE, I_2: Ammonia

are referred back to the main entry under the identified material

NITROGEN TRIIODIDE–AMMONIA, $I_3N{\cdot}H_3N$

No attempt has been made, however, to list all combinations of reactants which can lead to the formation of a particular unstable main entry compound.

2b. In a multi-reactant system where no identification of an unstable product was possible, one of the reactants had to be selected as primary reactant to prepare and index the main entry, with the other material(s) as secondary reactant(s). No strictly logical basis of choice for this is obvious.

However, it emerged during the compilation phase that most two-component reaction hazard systems of this type involve a fairly obvious oxidant material as one of the reactants. Where this situation was recognised, the oxidant has normally been selected as primary (indexing) reactant with its name in capitals, secondary reactant(s) following in lower case type:

See POTASSIUM PERMANGANATE, $KMnO_4$: Acetic acid, etc.

In the markedly fewer cases where an obvious reducant has been involved as one reactant, this has normally been selected as primary reactant:

See LITHIUM TETRAHYDROALUMINATE, AlH_4Li: 3,5-Dibromocyclopentene

In the relatively few cases where neither (or none) of the reactants can be recognised as oxidant or reducant, the choice was made which appeared to give the more informative main entry text:

See CHLOROFORM, $CHCl_3$: Acetone, etc.

Where some hazard has been noted during the preparation of a specific compound, but without it being possible to identify a specific cause, an entry for that compound states 'preparative hazard', and back-refers to the reactants involved in the preparation:

See SULPHUR DIOXIDE, O_2S

Occasionally, departures from these considerations have been made where such action appeared advantageous in bringing out a relationship between formally unrelated compounds or hazards. In all multicomponent cases, however, the secondary reactants (except air and water) appear as formula entries back-referred to the main entry text, so the latter is accessible from either primary or secondary reactants:

See DIMETHYL SULPHOXIDE, C_2H_6OS: Acyl halides (main entry)
ACETYL CHLORIDE, C_2H_3ClO: Dimethyl sulphoxide (back reference)

Grouping of Reactants

There are advantages to be gained in grouping together elements or compounds showing similar reactivities, because this tends to bring out the relationships between structure and reactivity more clearly than separate treatment. This course has been adopted widely for primary reactants (see next section), and for secondary reactants where one primary reactant has been separately involved in hazardous reactions with a large number of secondary materials. Where possible, the latter have been collected together under a suitable general group title indicative of the composition or characteristics of the collected materials, with a general formula where possible.

See CHLORINE, Cl_2 : Hydrocarbons
HYDROGEN PEROXIDE, H_2O_2 : Metals, Metal oxides, Metal salts
HYDROGEN SULPHIDE, H_2S: Oxidants

This arrangement means, however, that some practice will be necessary on the user's part in deciding into what group an individual secondary reactant falls before the longer-term advantages of the system become apparent. The group titles listed in Appendix 2 will be of use in this connection.

General Group Entries

In some cases literature references relevant to well-defined hazard topics or groups of hazardous compounds have been found, and these are given, with a condensed version of appropriate information, at the beginning of the topic or group entry.

Cross-references to related group or sub-group entries are also included, with a group list of individually indexed main-section entries which lie within the structural or functional scope of the group entry, these lists being arranged in order of formulae. Compounds which are closely similar to, but not in strict conformity with, the group definition are indicated by an initial asterisk.

The group entries thus serve as sub-indexes for each structurally based group of hazardous compounds. Conversely, each individual compound entry is back-referred to the group entry, and thence to all its strict structural analogues and related congeners included in this Handbook.

These features should be useful in attempts to estimate the stability or reactivity of a compound or reaction system which does not appear in this Handbook. The effects on stability or reactivity of changes in the molecular structure to which the destabilising group(s) is attached are in some cases discussed in the group entry. Otherwise such information may be gained from comparison of the information available from the individual compound entries collectively listed in the group entry.

Care is, however, necessary in extrapolating from described hazardous compounds or systems to others in which the user of this Handbook may be interested. Due allowance must be made for changes in elemental reactivity up or down the columns of the Periodic Table, and for the effects of variation in chain length, branching and point of group-attachment in organic systems. Purity of materials, possible catalytic effects (positive or negative) of impurities, and scale of operations may all have a direct bearing upon a particular reaction rate. These and other related matters are dealt with in more detail in the following Introductory Chapter.

Nomenclature

With the direct encouragement and assistance of the Publishers, an attempt has been made in this Handbook to use chemical names which conform to the most recent recommendations of IUPAC. While this has not been an essential part of the compilation, because each name has a corresponding molecular formula adjacent, it seems nonetheless desirable to minimise possible confusion by adopting the unambiguous system of nomenclature presented in the IUPAC publications.

Where the IUPAC name for a compound is very different from the previously used trivial name, the latter is included in parentheses (and in quotes where no longer an acceptable name). Generally, retained trivial names have not been used as main entry titles, but they have been used in the entry texts. Rarely, on the grounds of brevity, names not strictly conforming to IUPAC principles but recommended for chemicals used in industry in BS 2474: 1965 (amended 1970) have been used. The prefix *mixo-*, to represent the mixtures of isomers sometimes used as industrial materials, is a case in point.

No attempt has been made to use only one of the nomenclature systems acceptable to IUPAC, but no non-preferred or deprecated names are believed still to lurk in the text.

Some of the rigidly systematic names selected by the Association for Science Education in 1972 from the IUPAC possibilities are given as synonyms in the Index of Chemical Names (Appendix 5). This should assist those who will be coming into industry and research with a command of ASE nomenclature but who may be unfamiliar with the current variety of names used for chemicals.

In connection with the group titles adopted for the alphabetical section, it has been necessary in some cases to devise group names (particularly in the inorganic field) to indicate in a very general way the chemical structures involved in various classes, groups or subgroups of compounds.

For this purpose, all elements have been considered either as METALS or NON-METALS, and, of the latter, HALOGENS, HYDROGEN, NITROGEN, OXYGEN and SULPHUR were selected as specially important. Group names have then been coined from suitable combinations of these, such as the simple

METAL OXIDES, NON-METAL SULPHIDES
N-HALOGEN COMPOUNDS, NON-METAL HALIDES
METAL NON-METALLIDES, COMPLEX HYDRIDES

or the more complex

METAL OXOHALOGENATES
AMMINECHROMIUM PEROXOCOMPLEXES
OXOSALTS OF NITROGENOUS BASES
METAL OXONON-METALLATES

Organic group entries are fairly conventional, such as

HALOALKENES
NITROSO COMPOUNDS

Where necessary, such group names are explained in the appropriate group entry, of which a full listing is given in Appendix 4.