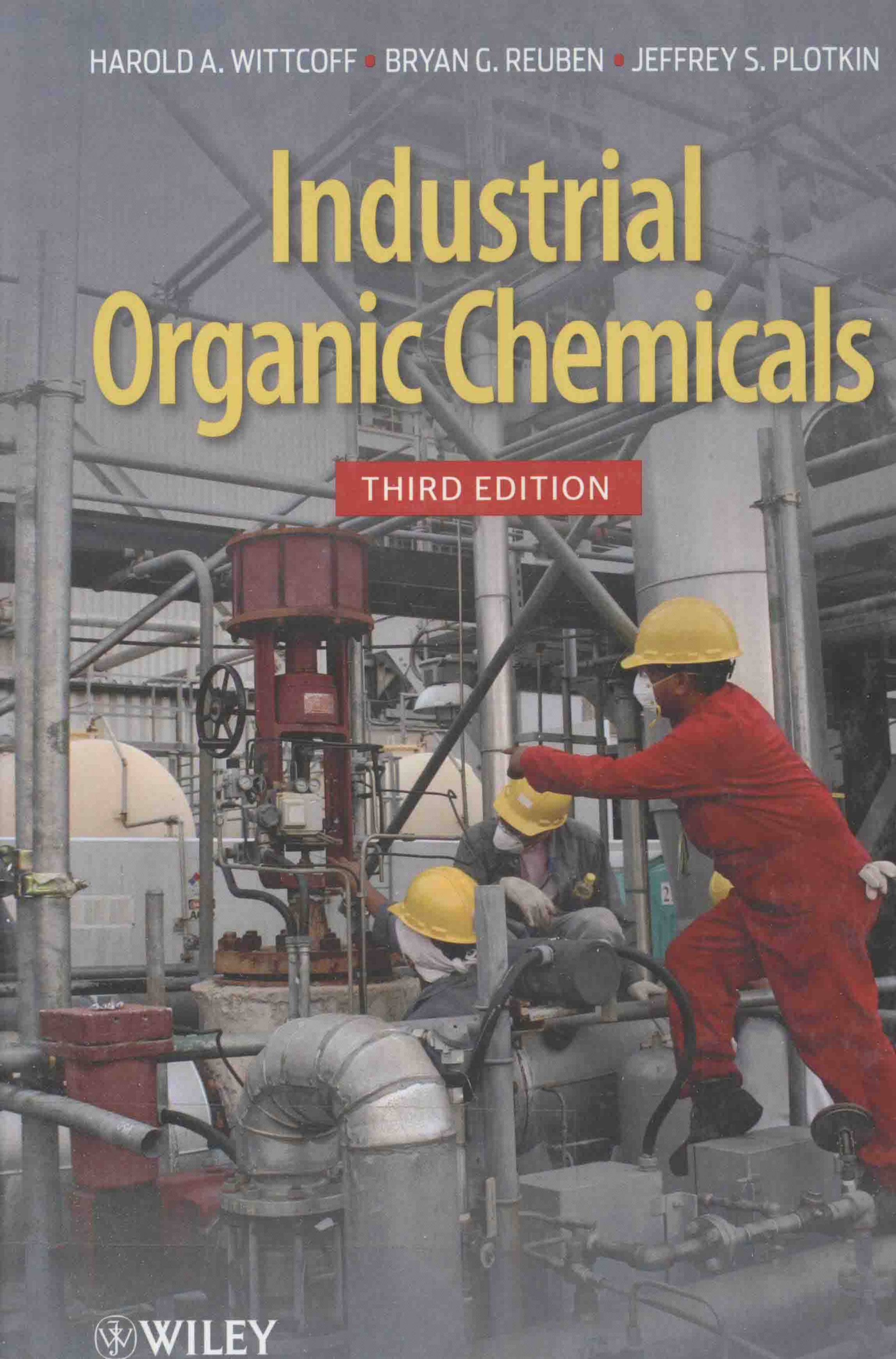
HAROLD A. WITTCOFF • BRYAN G. REUBEN • JEFFREY S. PLOTKIN

Industrial Organic Chemicals

THIRD EDITION



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INDUSTRIAL ORGANIC CHEMICALS

THIRD EDITION

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To our wives, Dorothy, Catherine, and Marisa, children, grandchildren, and great-grandchildren.

PREFACE

This third edition of *Industrial Organic Chemicals* is prompted by the impact of globalization and of threats to the environment. This is not to say that industrial chemistry has stood still – very much the reverse, and we have featured much new chemistry. All the same, our earlier books were about the exciting new world of petrochemical feedstocks and the ingenious new products that could be made from them. In this edition, the exciting new processes have become the dull traditional ones. Well-established processes of technology transfer have carried them to developing countries, especially those that produce petrochemical feedstocks. In addition, humankind's activities are seen both as depleting the resources of the planet and of polluting it to the point at which humankind will drown in its own effluvia. The extent of these threats is hotly contested; nonetheless, the chemical industry both contributes to the problems and is instrumental in trying to solve them.

There have been many developments since the second edition, and the following topics have gained especially in significance:

- The world chemical industry has migrated from the United States, Western Europe, and Japan to the Middle East and to Asia-Pacific, especially China. Will shale oil and gas bring it back? (See Appendix D).
- There is increased emphasis on environmental issues, with pressure on companies to clean up polluting processes or replace them with environmentally friendly ones.
- Globalization has changed patterns of transportation of chemicals with, for example, solid polymers rather than petrochemical feedstocks being shipped from the Middle East.
- The discovery of vast reserves of shale gas has altered the long-term predictions of resource depletion in the United States and other countries.
- Considerations of sustainability and the threat of climate change have prompted research into processes (including electricity generation) that produce less or no carbon dioxide, or come from renewable resources.

We have retained some material that is now largely of historical interest, partly for sentimental reasons, but partly because the three authors have watched the meteoric rise of the chemical industry from its early days to its present-day maturity. We think there is a value in our readers observing how technology has developed, and the social, technological, and economic changes that have brought it to its present position.

HAROLD A. WITTCOFF

PREFACE TO THE FIRST EDITION

In the early 1970s, one of us (BGR) wrote a book celebrating the rapid growth of the adolescent chemical industry. The organic chemicals industry at the time was growing at four times the rate of the economy. It was indicated nonetheless that "trees do not grow to the sky." In 1980, in another book, we both declared the industry to be middle-aged with slow or zero growth. In this totally revised and expanded version of our earlier book, we reflect that the industry, at any rate in the developed world, is showing many of the illnesses of late middle-age.

The problems have arisen first from the undisciplined building of excess capacity with consequent fierce competition and low prices. Second, the entry of numerous developing countries into the industry has exacerbated the situation (Section 1.3.6), and third, there has been much stricter government legislation (Section 1.3.7). There is massive worldwide restructuring and continual shifting of commodity chemical manufacturing to areas other than the United States, Western Europe, and Japan. The Middle East and Southeast Asia are the principal new players in the game. Perhaps this trend will continue and the present developed world will in the future confine itself to the manufacture of specialties, but the economic and political forces at work are more complex than that. We hope to be able to discuss their resolution in another edition in about 10 years' time.

Meanwhile, some things have not changed. The organic chemicals industry is still based on seven basic raw materials all deriving from petroleum and natural gas. The wisdom of teaching about the chemical industry on the basis of these seven building blocks has been confirmed by the fact that, since the publication of our first book, one of us (HAW) has delivered by invitation 300 courses in 28 countries on the fundamentals of the industry based on this pattern. Most of these courses are for industrial personnel but academia has not been neglected.

Furthermore, some changes have been positive. For example, there have been exciting new processes such as the development of metallocene catalysts (Section 15.3.12). Section 4.6.1 describes new methyl methacrylate processes that give a potentially cheaper product, that do not produce ecologically undesirable ammonium hydrogen sulfate by-product or (in another process) that eliminate the use of dangerous hydrogen cyanide.

In this book, our main objective is still to present the technology of the organic chemicals industry as an organized body of knowledge, so that both the neophyte and the experienced practitioner can see the broad picture. Nonetheless, we have expanded its scope to include not only new processes but many apparently less important reactions that are significant because they give rise to the more profitable specialty chemicals. The lesser volume chemicals have been clearly delineated as such and the reader who wishes to see the industry on the basis of its large tonnage products can omit these sections.

We hope this book will be useful both to college students who have studied organic chemistry and to graduates and industrial chemists who work in or are interested in the chemical industry. Even though much of the chemistry has remained the same, the change in the way the industry looks at its problems provides ample justification for our offering this edition as a fresh perspective on industrial organic chemicals.

PREFACE TO THE SECOND EDITION

In the preface to the first edition, we expressed the hope that we could comment on the chemical industry's evolution in 10 years' time. Dramatic changes have motivated us to compress this time frame. There have been unprecedented restructuring, severe and complicated feedstock problems, and massive shifts of capacity to developing countries, whose economic and political stability is in doubt. Possible terrorist activity dictates elaborate safety and security procedures and the design of plants with small inventories is a priority.

To increase our cover, particularly of the patent literature, we have invited Dr. Jeffrey S. Plotkin, Director of the Process Evaluation and Research Planning program at Nexant ChemSystems to join us as co-author.

ACKNOWLEDGMENTS

We are grateful to the many friends and colleagues with whom we spoke often during the revision of this book. Much knowledge and clarification evolved in this way. Nexant ChemSystems Inc.'s numerous multiclient reports provided detailed information on both reaction conditions and production economics.

We thank Prof. Maurice Kreevoy for his review of the catalyst chapter and his many helpful suggestions. We also thank librarians Mrs. Denise Phillips and Ms Lorraine Moneypenny who searched the literature diligently for us. Ms Pat Cairns cheerfully did many things to make the revision easier, and we thank her sincerely. We also thank Mr. Ted Wittcoff who good naturedly compensated for his father's computer shortcomings.

BRYAN GODEL REUBEN 1934–2012

Bryan was one of the UK's first mass-spectometrists and a pioneering teacher in industrial chemistry. His early love of chemistry was developed with experiments—many of them explosive—in his father's pharmacy. Bryan won a scholarship to the Queen's College, Oxford, to study chemistry. With his PhD he went onto a post-doctoral fellowship at Brookhaven National Laboratory in New York, where he worked with Lewis Friedman on the kinetics of gas-phase ion-molecule reactions. Bryan found living in the U.S. both exciting and stimulating and was always pleased to return there for work and for holidays.

Bryan returned to the UK to work for Distillers as a physical chemist but after only a year moved to sales development. This led to a career determining lifelong interest in the relationship between chemistry and economics. In 1963 he moved from commerce to academia at Battersea College of Advanced Technology (soon to become the University of Surrey) where he first met his great friend Michael L. Burstall. Together they developed a ground breaking industrial chemistry course and wrote one of the standard works in the field, *The Chemical Economy* (1973). In 1977 Bryan moved to the chemical engineering department of Borough Polytechnic (later London South Bank University) as principal lecturer responsible for organizing and developing research. He was appointed Professor of Chemical Technology in 1990.

Bryan was a teacher with a gift for explaining complex problems with clarity and wit, which is probably why he had many invitations to work abroad. In 1972 he spent a sabbatical year at the Hebrew University, Jerusalem, where he helped to set up the Master's program in applied chemistry and lectured on industrial processes and catalysis. He later taught at the Weizmann Institute and at the universities of Bar Ilan and Ben Gurion and acted as a consultant for the Israel Ministry of Development. In 1979 he taught at the Universities of Texas, Oregon, Michigan, and Missouri and in 1981 was visiting professor and consultant at the University of Campinas, Brazil.

Apart from his scientific work, Bryan had a life long interest in the arts. At Oxford he wrote comedy revues and sketches and at Brookhaven he directed the local amateur dramatic society in several revues and plays and also took to the stage as an actor, a hobby which he continued on his return to England. His journalism continued until 2012. He delighted in writing satirical articles and book reviews on a wide variety of subjects. However it was always his wish to write a book for the popular market ("such as people might buy at airports" as he used to say) and in 2008 he wrote *Bread–a Slice of History*, together with John Marchant and Joan Alcock, colleagues from South

Bank University. He enjoyed appearing as an authority on bread on the BBC4 program "In Search of the Perfect Loaf."

Since his early twenties, Bryan had been an enthusiastic and expert skier. He delighted in taking his family and later also his grandchildren, on skiing holidays. He continued to do this until 2011, despite a catastrophic ski accident in 1987 in which he broke many bones and tore his aortic valve. In the preface to *Pharmaceutical Chemicals in Perspective*, which he wrote with Harold Wittcoff in 1988, Bryan thanked the doctors in Grenoble who had saved his life. He was also grateful to the pharmaceutical industry, whose drugs allowed him to survive for many more years and two further open heart operations.

Professionally, Bryan published more than 140 papers on the chemical, pharmaceutical and process industries, as well as 13 books, many of which became standard works, including *Industrial Organic Chemicals in Perspective* (1980) with Harold Wittcoff. Harold met Bryan after the publication of *The Chemical Economy* (1973). In the years to come, Bryan and Harold worked together on many projects and they became close friends as well as colleagues. Their collaboration was a source of great joy not only to Bryan but to his entire family. Bryan was planning to work on the proofs of this third edition *of Industrial Organic Chemicals* the week before he died. He would be delighted and proud to know that all their hard work has come to fruition.

LIST OF ACRONYMS AND ABBREVIATIONS

ABS	Acrylonitrile–butadiene–styrene
ACS	American Chemical Society
AFC	Alkali fuel cell
AMOCO	Formerly American Oil/Standard Oil of Indiana, now owned by BP
AO	Acid optimization
APPE	Association of Petrochemicals Producers in Europe
ARCO	Formerly Atlantic Richfield Oil Company, now owned by Lyondell
BASF	German chemical company: formerly Badische Anilin und Soda Fabrik
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BP	British Petroleum
BPA	Bisphenol A
Btu	British thermal units (see Appendix B)
BTX	Benzene–toluene–xylene
CAA	Clean Air Act
CEFIC	Centre Européen des Fédérations de L'Industrie Chimique
CFCs	Chlorofluorocarbons having no hydrogen atoms
CHP	Combined heat and power
CIA	UK Chemical Industries Association
CIS	Commonwealth of Independent States (formerly USSR)
CMA	Chemical Manufacturers' Association
CMC	Carboxymethylcellulose
CMRs	Carcinogens, mutagens, and reprotoxins
CNI	Chemical News Intelligence
COCs	Cyclic olefin copolymers
CRG	Catalytic rich gas
DCC	Deep catalytic cracking
DDT	Bis(chlorophenyl)trichloromethylmethane
DEA	Diethanolamine
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSM	Dutch chemical company; formerly Dutch State Mines
EDTA	Ethylenediaminetetraacetic acid
ENI	Italian chemical company: Ente Nazionale Idrocarburi (Enichemi is a subsidiary)

EP	Ethylene–propylene (rubber)
EPA	Environmental Protection Agency
EPDM	Ethylene–propylene–diene monomer
EVA	Ethylene-vinyl acetate
EVC	European Vinyls Corporation
FCC	Fluid catalytic cracking
FDA	Food and Drug Administration
GATT	General Agreement on Trade and Tariffs
GLA	Gamma-linolenic acid
GMP	Good Manufacturing Practice
GTL	Gas to liquid
HTE	High throughput experimentation
HCFCs	Hydrochlorofluorocarbons
HCN	Hydrocyanic acid and hydrogen cyanide
HDPE	High density polyethylene
HIPS	High-impact polystyrene
HMDA	Hexamethylenediamine
HMDI	Hexamethylene diisocyanate
HMSO	Her Majesty's Stationery Office
ICI	UK Chemical Company; formerly Imperial Chemical Industries
IFP	Institut Français de Pétrole
IPDI	Isophorone diisocyanate
IR	Infrared
ISP	International Specialty Products
IUPAC	International Union of Pure and Applied Chemistry
KA	Ketone/alcohol
LAB	Linear alkylbenzene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LPG	Liquid petroleum gas
LVN	Light virgin naphtha
M/F	Melamine–formaldehyde
MBS	Methyl acrylate–butadiene–styrene
MCFC	Molten carbonate fuel cell
MDI	4,4′-Diphenylmethane diisocyanate
MEK	Methyl ethyl ketone; 2-butanone
MOI	Mobil olefin interconversion
MON	Motor octane number
MTBE	Methyl *tert*-butyl ether
MTG	Methanol to gasoline
MTO	Methanol to olefins
MTP	Methanol to propylene
NAICS	North American Industry Classification System
NPRA	National Petroleum Refiners Association
OSHA	Occupational Safety and Health Act

P/F	Phenol-formaldehyde
PAFC	Phosphoric acid fuel cell
PAMAM	Poly(amidoamine)
PAN	Peroxyacetyl nitrate
PBBs	Polybrominated biphenyls
PBDEs	Polybrominated diphenyl ethers
PBT	Persistent bioaccumulative toxic
PDJ	Patents and Design Journal
PEEK	Poly(ether ether ketone)
PEMFC	Polymer electrolyte–proton exchange membrane fuel cell
PEN	Poly(ethylene naphthalate)
PERP	Process evaluation and research planning
PET	Poly(ethylene terephthalate)
PIMM	Process integrated management methods
PMDA	Pyromellitic dianhydride
PO	Propylene oxide
POX	Noncatalytic partial oxidation
PTA	Pure terephthalic acid
PTFE	Polytetrafluoroethylene
PVC	Poly(vinyl chloride)
REACH	Registration, authorization, and evaluation of chemicals
RIM	Reaction injection molding
RIPP	Chinese Research Institute of Petroleum Processing
RON	Research octane number
SABIC	Saudi Arabia Basic Industries Corporation
SAN	Styrene–acrylonitrile
SAPO	Silicaaluminophosphate
SBR	Styrene–butadiene rubber
S-B-S	Styrene–butadiene–styrene
S-E-B-S	Styrene–ethylene–butylene–styrene
S-E-P-S	Styrene–ethylene–propylene–styrene
SHOP	Shell Higher Olefins Process
SI	Systeme International
S-I-S	Styrene–isoprene–styrene
SMDS	Shell Middle Distillate Synthesis
SNG	Substitute natural gas
SOFC	Solid oxide fuel cell
SOHIO	Was Standard Oil of Ohio; now part of BP
TAME	*tert*-Amyl methyl ether
TBA	*tert*-Butylbenzaldehyde
TDI	Toluene diisocyanate
THF	Tetrahydrofuran
TMA	Trimellitic anhydride
TNT	Trinitrotoluene
TPA	Terephthalic acid