# CHEMISTRY & TECHNOLOGY of
# LUBRICANTS

Edited by
R. M. Mortier & S.T. Orszulik

B L A C K I E
USA and Canada: VCH Publishers, Inc., New York

# Chemistry and Technology of Lubricants

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**Blackie**
Glasgow and London

**VCH Publishers, Inc.**
New York

Blackie and Son Ltd
Bishopbriggs, Glasgow G64 2NZ
and
7 Leicester Place, London WC2H 7BP

Published in the USA and Canada by
VCH Publishers, Inc.
220 East 23rd Street, Suite 909
New York, NY 10010–4606

10 9 8 7 6 5 4 3 2 1


First published 1992



**British Library Cataloguing in Publication Data**

Chemistry and technology of lubricants.
I. Mortier, R.M. II. Orszulik, S.T.
665

ISBN 0-216-92921-0

**Library of Congress Cataloging-in-Publication Data**

Chemistry and technology of lubricants / edited by R.M. Mortier and S.T. Orszulik.
p. cm.
Includes bibliographical references and index.
ISBN 0-216-92921-0 (Blackie). ISBN 1-56081-594-9 (VCH)
1. Lubrication and lubricants. I. Mortier, R.M. II. Orszulik, S.T.
TJ1077.C418 1992
665.5'385—dc20 91-44485
CIP

Photosetting by Advanced Filmsetters (Glasgow) Ltd
Printed in Great Britain by St Edmundsbury Press Ltd, Bury St Edmunds, Suffolk

# Chemistry and Technology of Lubricants

# Preface

The use of lubricants began in ancient times and has developed into a major international business through the need to lubricate machines of increasing complexity. The impetus for lubricant development has arisen from need, so lubricating practice has preceded an understanding of the scientific principles. This is not surprising as the scientific basis of the technology is, by nature, highly complex and interdisciplinary. However, we believe that the understanding of lubricant phenomena will continue to be developed at a molecular level to meet future challenges. These challenges will include the control of emissions from internal combustion engines, the reduction of friction and wear in machinery, and continuing improvements to lubricant performance and life-time.

More recently, there has been an increased understanding of the chemical aspects of lubrication, which has complemented the knowledge and understanding gained through studies dealing with physics and engineering. This book aims to bring together this chemical information and present it in a practical way. It is written by chemists who are authorities in the various specialisations within the lubricating industry, and is intended to be of interest to chemists who may already be working in the lubricating industry or in academia, and who are seeking a chemist's view of lubrication. It will also be of benefit to engineers and technologists familiar with the industry who require a more fundamental understanding of lubricants.

Throughout the book the range of uses of liquid lubricants, the base fluid types, and the various classes of additives available are covered. In the chapters on lubricant technology, the authors have been given the opportunity to draw on their extensive industrial experience. Although it has not been possible to cover all aspects of such a broad subject, the aim is to provide an insight into the more important aspects of the chemistry of lubricants, together with an indication of how lubricants are formulated to meet the needs of lubrication technology.

We would like to express our thanks to the authors for their contributions and for their patience during the editing process. The additional contribution by Tony Lansdown after the very late withdrawal of one of our authors is particularly appreciated. Thanks are also due to the publishers for the layout of the book and for guiding us through the editing. Finally, we would welcome comments, criticisms and suggestions.

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# Introduction

D. DOWSON

The recorded use of lubricants dates back almost to the birth of civilisation (Dowson, 1979), with early historical developments being concerned with the use of lubricants of animal or vegetable origin in transportation or machinery. During the Middle Ages (AD 450–1450) there was a steady development in the use of lubricants, but it was not until AD 1600–1850 (particularly the industrial revolution in AD 1750–1850) that the value of lubricants in decreasing friction and wear was recognised.

The classical studies of friction (Amontons, 1699; Coulomb, 1785) suggested that surface roughness played a major role in determining the resistance to sliding between two surfaces. It was therefore thought that lubricants were effective because they filled up the hollows in surfaces and reduced the roughness. This view was widespread and long sustained, but the classical experimental investigations by Tower (1883) and Petrov (1883) clearly indicated that in successful bearings the rotating journal was completely separated from the bearing by a coherent film of lubricant. The principle of fluid-film lubrication was fully recognised when Reynolds (1886) analysed the slow, viscous flow of lubricants in plain bearings and derived the differential equation for pressure that underpins bearing design procedures to the present day.

When the principle of fluid-film lubrication had been established for almost 40 years, Hardy (1922) drew attention to another form of protection now known as boundary lubrication. In this condition—normally associated with high loads, low speeds and low viscosities—the surfaces cannot be separated by coherent fluid films that exceed in considerable measure the composite surface roughness. The friction and wear characteristics in this regime are thus determined by the properties of surface films, often of molecular proportions formed on the solids, or generated by adsorption or by chemical reaction between constituents of the lubricant and the solids. The recognition of this major mode of lubrication provided a sound basis for the spectacular development of certain forms of additives later in the 20th century.

Mineral oil was first produced commercially in the 18th and early 19th centuries, but this ubiquitous lubricant really established itself towards the end of the 19th century, following the drilling of Drake's Well at Titusville, Pennsylvania, USA in 1859. Production started at a similar time in Russia and Roumania, but it was the involvement of the Nobel brothers after 1873 that established the Baku field as a major producer. An account of lubricants and lubrication in the 19th century has been presented by Dowson (1974).

Mineral oil rapidly overtook oils of animal and vegetable origin as the essential lubricant of the 20th century. The disparate nature of the mineral oils derived from different sources of crude oil is outlined in chapter 1. Mineral oils readily oxidise at temperatures above about 100°C and are reluctant to flow at temperatures lower than about −20°C. As the aerospace industry developed in the 20th century it became necessary to introduce alternative, synthetic base oils. Synthetics still represent a small volume proportion of the base oils used today, but their range of applications is extending steadily and they have enabled machinery to operate under conditions that could not have been accommodated by mineral oils. An account of synthetic base oils is given in chapter 2.

Fluid-film lubrication is associated with the physical rather than the chemical nature of lubricants, and modern bearings rely substantially on this exceptional mechanism for separating sliding solids. However, all bearings start and stop, and the surfaces of the sliding solids come into contact with each interruption of movement. Furthermore, the major economic pressure for improved efficiency in most forms of machinery in the latter years of the 20th century has caused designers to adopt higher mean bearing pressures and lower viscosity fluids, thus reducing the effective minimum film thickness in bearings. In many dynamically loaded bearings and most severely-taxed, lubricated machine elements such as gears, cams and piston rings, the friction and life of the machine is greatly influenced by the protection afforded by films of molecular proportions formed on the solids by additives. Such substances, added to mineral oil, have contributed in a major way to the spectacular development of lubricants in the second half of the 20th century. Additives are also added to oils to restrict oxidation of the lubricant, to act as rust inhibitors, and to perform a role as detergents. Furthermore, they can be used to modify the viscosity–temperature characteristics of lubricants and to depress the pour point. Detailed accounts of the roles of additives are given in chapters 3, 4, 5, 6 and 12.

The greatly improved ability to analyse and design lubricated machine elements in the latter stages of the 20th century has progressed alongside the formulation of additive-containing mineral oils and the introduction of synthetic lubricants. It is therefore particularly helpful to have chapters of the present book devoted to the nature of lubricants developed specifically for the internal combustion engine (chapter 7), general industrial machinery (chapter 8) and aviation and marine applications (chapters 9 and 10). Finally, chapters 11 and 13 deal with greases and environmental aspects of lubricants, both topics of major significance. The response to ever more demanding pressures for improved efficiency and reliability of equipment, for machinery to operate in severe environments has been quite remarkable. If the engineer or tribologist can draw some satisfaction from the fact that improved analysis, design and manufacture have permitted most lubricated components to function well with effective fluid films of thickness 0.1–1 μm, the chemist or lubricant technologist can certainly claim that none of this would have been possible if additive packages had not produced thin protective layers of molecular proportions on the surfaces of the bearing solids.

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# Contents

# 1 Base oils from petroleum

R.J. PRINCE

## 1.1 Introduction

Modern lubricants are formulated from a range of base fluids and chemical additives. The base fluid has several functions but primarily it is the lubricant, providing a fluid layer separating moving surfaces or removing heat and wear particles while keeping friction at a minimum. Many of the properties of the lubricant are enhanced or created by the addition of special chemical additives to the base fluid. For example, stability to oxidation and degradation in an engine oil can be improved by the addition of antioxidants while extreme pressure (EP) anti-wear properties needed in gear lubrication are created by the addition of special EP additives. The base fluid also functions as the carrier for these additives and must therefore be able to keep the additives in solution under all normal working conditions.

The majority of lubricant base fluids are produced by the refining of crude oil. Bromilow (1990) has estimated that 24.1 million tonnes of petroleum base oils were used in the world in 1989 (excluding the USSR, China and Eastern Europe which are thought to use some 15 million tonnes of lubricant). The reasons for the predominance of refined petroleum base oils are simple and obvious—performance, availability and price. Large scale oil refining operations can produce base oils which have excellent performance in modern lubricant formulations at economic prices. Non-petroleum base fluids find application where special properties are necessary, where petroleum base oils are in short supply or where substitution by natural products is practicable or desirable.

This chapter concerns base oils made from crude oil petroleum. Crude oil is an extremely complex mixture of organic chemicals ranging in size from simple gaseous molecules, such as methane, to very high molecular weight asphaltic components. Obviously only some of these crude oil constituents are desirable in a lubricant base fluid and so a series of physical refining steps are needed to separate the good from the bad. Other process steps involving chemical reactions may also be used to enhance properties of the oil. Different types of base oils are produced at refineries; oils which have different viscosities or chemical properties are needed for different applications.