Oleochemical Manufacture and Applications

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Oleochemical Manufacture and Applications

Chemistry and Technology of Oils and Fats

Series Editor: R.J. Hamilton

A series which presents the current state of the art in chosen areas of oils and fats chemistry, including its relevance to the food and pharmaceutical industries. Written at professional and reference level, it is directed at chemists and technologists working in oils and fats processing, the food industry, the oleochemicals industry and the pharmaceutical industry, at analytical chemists and quality assurance personnel, and at lipid chemists in academic research laboratories. Each volume in the series provides an accessible source of information on the science and technology of a particular area.

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Oleochemical Manufacture and Applications
Edited by F.D. Gunstone and R.J. Hamilton

Preface

World production of oils and fats is expected to be around 117 million tonnes in the harvest year 2000/01. This will come from vegetable (80%) and animal (20%) sources, and will be used as food (80%), feed (6%), and for oleochemical purposes (14%). This book is therefore concerned with the use of over 16 million tonnes of oils and fats by the oleochemical industry. It is not possible to cover all the products of this industry, and the editors have together selected those topics that they consider to be important.

The first chapter presents an overview and provides some key references to oleochemical procedures and products that are not detailed in subsequent chapters.

The major oleochemicals are surface-active molecules (~90%), which depend on a very important property of many fatty acids and their derivatives, *viz*. their amphiphilic nature. Such molecules contain a long alkyl chain which is lipophilic and a charged and/or polar head group which is hydrophilic. As a consequence of their 'schizophrenic' nature, the compounds are stable at and have great influence on air-lipid and water-lipid interfaces. The latter are particularly important in emulsions, foods and biological systems. Life as we know it would be impossible without such molecules. Soap is a traditional surface-active molecule which has been known and used for centuries, but this is only one of a growing number of improved molecules which are gentler to the skin, have superior cleansing properties and are easier on the environment. Some of the other uses of oleochemicals described in this book also depend on the amphiphilic properties of the materials. This applies to their use as lubricants and in agriculture.

The preparation of cationic and amine-based surfactants from new feedstocks such as meadowfoam and crambe is detailed. Applications of primary amines for mineral flotation and metal coating and as a feedstock for the production of ethoxylated amines and quaternary ammonium salts are highlighted. The preparation and use of secondary amines, tertiary amines, amidoamines, and imidazolines are covered in detail. Alkoxylated amines have good emulsification properties, which enable them to be used in oil field chemicals, in metal-working fluids and in textile applications. Amine oxides and quaternary amines with their wide spectrum of applications are also described.

Techniques for sulfation and sulfonation, important in the production of the major anionic surfactants, are reported. The processes and kinetics of the reactions are fully described. The recently introduced methyl ester sulfonates, adopted in both Japan and North America, require hydrogenation of the feedstock methyl esters before sulfonation, because unsaturation has an adverse effect on the colour of the methyl ester sulfonate.

The need to use biodegradable materials for the protection of air, water and soil should enable vegetable oil-based lubricants and hydraulic fluids to take 10-40% of the total market over the next five years. The chapter on lubricants explains how mono- and poly-alcohols can be combined with both monocarboxylic acids and dicarboxylic acids (the latter being produced from oleic acid and ricinoleic acid). The physical and chemical properties used to evaluate the effectiveness of the synthetic esters are described.

The dominance of petroleum-based compounds for use in agriculture is being challenged by the availability of vegetable oil-based products. Methyl esters of several commodity vegetable oils provide good spray adjuvants, which are much more environmentally friendly than petrochemicals. Methods of preparing methyl esters from crude vegetable oils are described. The use of oleochemicals as controlled release matrices for volatiles is outlined, as well as the use of hot-melt application of waxes.

A thorough outline is provided of the analytical techniques required if oleochemicals are to be produced and traded. Explanations of weaknesses in some of the tests are considered. This topic has been overlooked in many accounts of oleochemical compounds.

The natural oils are easily converted to methyl esters. These are intermediates in the production of other basic oleochemicals and are used both as solvents and as automotive and heating fuel. There are many reasons for wanting to reduce the consumption of mineral oils. One way of doing this is to use biodiesel (fatty acid methyl esters) as an alternative fuel. The problems and opportunities associated with this development are described.

If the oleochemical industry is to have a future as well as a past, then new and improved procedures and products must be developed. In one chapter we examine some fascinating recent chemistry based on double bonds. Not all the molecules described are likely to have a commercial future but, among the many reported here, there may be some which have. We present this information as a way of provoking further discussion on their potential.

It is often assumed that, because oleochemicals are based on renewable resources, they are easily biodegradable and more environmentally friendly than similar petrochemical products. This is often too simple a view, as full recognition has to be given to the environmental costs of producing, processing, and transporting the raw materials and the products. Because of the importance of this issue, we felt obliged to include a chapter on this topic.

We thank all the contributors who accepted our invitations to write, and their readiness to be bullied by editors and publishers alike to produce their manuscripts on time – more or less! We thank Dr Graeme MacKintosh of Sheffield Academic Press for his wise advice and generous encouragement

and we hope that our readers will appreciate the efforts made by many people to produce this book.

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Contents

1 Basic oleochemicals, oleochemical products and new industrial oils

Frank D. Gunstone

1.1 Introduction

Before the general availability of mineral oil and its fractions, oils and fats of vegetable and animal origin were widely used as illuminants and as lubricants. In biblical times, lamps were based on wicks burning, presumably, in olive oil and there is evidence that the same oil was used as a lubricant when manhandling large stones for the building of the pyramids. It has also been reported that the axles of ancient chariots were greased with a mixture of animal fat and lime, no doubt producing calcium soaps.

Eventually the oils and fats used for this purpose were replaced by products derived from mineral oil and its fractions. Lamps used kerosene before the arrival of first gas and then electricity. Lubricants are now based on mineral oils enhanced with a range of additives. Today, there is a limited return to oils and fats as alternatives to mineral oil-based products. The driving forces for this change are mainly environmental. Oils and fats are a renewable resource, when degraded they liberate carbon dioxide trapped from the atmosphere only months earlier, and they are easily biodegraded, so that these compounds remain in the environment for a short time only. These are important issues but, since the annual production of mineral oil and gas is about 30 times greater than that of oils and fats and the latter must necessarily be consumed as food and feed, the impact of environment-friendly products based on oils and fats can only have a marginal effect on the total use and consumption of mineral oil products. For example, biodiesel cannot fully replace the demand for conventional diesel fuel and is likely to diminish it by 5–10% at the most.

In the five year period 1996–2000, 17 commodity oils, charted by *Oil World* for over 40 years, reached an average annual production level of 104 million tonnes. This is expected to rise to an average of 121 million tonnes per year in the next five years (2001–2006). Figures for each commodity oil/fat are listed in table 1.1 along with the major producing areas in each case. These figures relate to where the *oil is produced by crushing and/or solvent extraction*, and not necessarily to the country where the seed or fruit is grown. For example, Japan grows virtually no rapeseed, yet produces 7% of the world supply of rapeseed/canola oil by indigenous extraction of imported seed.