

Oleochemical Manufacture and Applications



Edited by

Frank D. Gunstone and Richard J. Hamilton

Contents

1	Basic oleochemicals, oleochemical products and new industrial oils	1
	FRANK D. GUNSTONE	
1.1	Introduction	1
1.2	Basic oleochemicals	4
1.2.1	Acids	5
1.2.2	Esters	5
1.2.3	Alcohols	7
1.2.4	Fatty amines	8
1.2.5	Hydrophilisation	8
1.3	Glycerol	8
1.4	Dibasic acids	9
1.5	Dimers, isostearic acid, estolides, Guerbet alcohols and acids	10
1.6	Metathesis	12
1.7	Phospholipids, tocopherols and sterols	12
1.8	Oleochemicals from castor oil	13
1.9	Epoxides, hydroxy acids and polyurethanes	14
1.10	New industrial oils	15
1.10.1	Cuphea oils	16
1.10.2	Oils containing erucic acid	16
1.10.3	Meadowfoam oil (<i>Limnanthes alba</i>)	17
1.10.4	Calendula oil (<i>Calendula officinalis</i>)	17
1.10.5	Oils containing lesquerolic acid	17
1.10.6	<i>Dimorphotheca pluvialis</i>	18
1.10.7	Oils containing epoxy acids	18
1.10.8	Other seed oils	19
	References	19
2	Cationic and amine-based surfactants	23
	RALPH FRANKLIN, MICHAEL D. HOEY and JOSEPH ZACHWIEJA	
2.1	Introduction	23
2.2	Nitrile production	23
2.3	Primary amines	24
2.3.1	Applications of primary amines	26
2.4	Secondary amines	27
2.4.1	Applications of secondary amines	28
2.5	Tertiary amines	29
2.5.1	Methyl dialkylamines and other unsymmetrical trialkylamines	29
2.5.2	Symmetrical trialkylamines	29
2.5.3	Applications of tertiary amines	30
2.6	Etheramines	30

2.7	Amidoamines and imidazolines	31
2.7.1	Applications of amidoamines and imidazolines	32
2.8	Alkyl polyamines	32
2.8.1	Applications of diamines and polyamines	33
2.9	Alkoxyated amines	34
2.9.1	Applications of alkoxyated amines	35
2.10	Other amines	36
2.11	Amine oxides	36
2.11.1	Synthesis and reactions	37
2.11.2	Applications	39
2.12	Quaternary ammonium compounds	40
2.12.1	Production	41
2.12.2	Applications	43
	References	48
3	Manufacture of anionic surfactants	55
	DAVID W. ROBERTS	
3.1	Raw materials for surfactants	55
3.2	General features of sulfonation by sulfur trioxide	57
3.3	Sulfonation reactors	57
3.4	Manufacture of primary alcohol sulfates (PAS)	60
3.4.1	Neutralisation	63
3.5	Manufacture of alcohol ethoxy sulfates	64
3.6	Methyl ester sulfonation	66
3.6.1	Contacting of methyl ester with sulfur trioxide	68
3.6.2	Acid mix ageing	69
3.6.3	Re-esterification	71
3.6.4	Bleaching of the acid with hydrogen peroxide	71
3.6.5	Neutralisation	72
3.7	Other anionic surfactants	72
	References	72
4	Lubricants and hydraulic fluids	74
	PAOLO BONDIOLI	
4.1	Introduction	74
4.2	Nature of ester lubricants	75
4.2.1	The chemical constitution of ester lubricants	77
4.2.2	The esterification reaction	79
4.3	The evaluation of ester lubricants	88
4.3.1	Physico-chemical properties	89
4.3.2	Chemical properties	91
4.3.3	Performance properties	91
4.4	Uses of ester lubricants	97
4.4.1	Automotive applications	97
4.4.2	Aviation applications	97
4.4.3	Refrigeration lubricants	98
4.4.4	Compressor lubricants	98
4.4.5	Two stroke engine	98
4.4.6	Hydraulic fluids	98

4.4.7 Biogreases	99
4.4.8 Quenching oils	99
4.4.9 Demoulding agents	99
4.4.10 Lubricants for the food industry	101
4.5 Recycling	101
4.6 Final remarks	102
References	104
5 Biofuels derived from vegetable oils and fats	106
GERHARD KNOTHE and ROBERT O. DUNN	
5.1 History and overview	106
5.2 Sources of fuels	108
5.3 Production of fuels	108
5.4 Other uses of vegetable oil esters	109
5.5 Economics, regulatory issues and utilization	109
5.6 Diesel engines	111
5.7 Why are triacylglycerol-derived materials suitable as diesel fuel?	112
5.8 General comparisons of fuels from vegetable oils and animal fats	113
5.9 Biodiesel standards	122
5.10 Combustion and emissions: emissions of neat triacylglycerol fuels	124
5.10.1 Emissions from neat vegetable oil fuel	126
5.10.2 Engine problems with neat vegetable oil fuel	127
5.11 Transesterification and properties of ester fuels (biodiesel)	128
5.11.1 The transesterification process	128
5.11.2 Other transesterification processes	130
5.11.3 Analysis of transesterification products	132
5.11.4 Emissions from ester fuels (biodiesel)	134
5.11.5 Cetane improvers	135
5.11.6 Low-temperature properties	136
5.11.7 Storage stability	139
5.11.8 Blending of esters	141
5.11.9 Ester fuels from animal fats and waste oils	142
5.12 Dilution of vegetable oils with conventional diesel fuel	143
5.13 Vegetable oil microemulsions and co-solvent blending	144
5.14 Pyrolysis	149
5.15 Outlook	150
References	150
6 Surface coatings and inks	164
JOHN BENTLEY	
6.1 Introduction	164
6.1.1 Economics of the coatings industry	164
6.1.2 Background and introduction to coatings	165
6.2 Oils used in paint	167
6.3 Chemistry of oils in coatings	169
6.3.1 Reactions of oils and fatty acids	169
6.3.2 Autoxidative drying of oils	170
6.3.3 Other oil drying processes	175
6.3.4 Degradation and yellowing	176

6.3.5	Isomerised oils and fatty acids	177
6.3.6	Oil based unsaturated monomers	177
6.4	Oils and oil based resins systems in coatings	178
6.4.1	Simpler systems	178
6.4.2	Alkyds—an introduction	178
6.4.3	Alkyd formulating	179
6.4.4	Use of alkyds in paint	180
6.4.5	Other resin systems	181
6.4.6	Legislation and compliant coatings	181
6.4.7	High solids alkyds	182
6.4.8	Waterborne alkyds	185
6.4.9	Emulsion polymers and the use of surfactants	188
6.4.10	Emulsion polymers and emulsion polymerisation	188
6.4.11	Surfactants in emulsion polymerisation	189
6.4.12	Surfactant developments for emulsion polymerisation	189
6.4.13	Other surfactants in paints and resins	190
6.4.14	Hybrid polymers including dispersions	191
6.4.15	Epoxidised oils and fatty acids	192
6.5	Inks	192
6.6	Summary of status and developments	193
	References	193
7	Agricultural uses of oleochemicals	199
	REIDAR LIE, JARL M. PETTERSEN and RICHARD J. HAMILTON	
7.1	Introduction	199
7.1.1	Extraction of oils and fats	199
7.1.2	Refining of oils and fats	199
7.1.3	Methylated oils	200
7.1.4	Winterisation	200
7.2	Pesticide adjuvants	201
7.2.1	Introduction	201
7.2.2	Cuticular surfaces	202
7.2.3	Types of adjuvants	205
7.2.4	Mineral oil, triacylglycerol oils and their derivatives	206
7.2.5	Examples of adjuvant application	210
7.3	Applications of molten wax on plants	214
7.3.1	Introduction	214
7.3.2	Grafting and wax	214
7.3.3	Bark feeding insects and wax	218
7.3.4	Wax treatment of young leaves	219
7.4	Insect:insect and insect:plant interactions	220
7.4.1	Introduction	220
7.4.2	Controlled release matrix for semiochemicals	221
7.4.3	Conclusion	224
	References	224

8	Analysis of oleochemicals	227
	THIN SUE TANG	
8.1	Introduction	227
8.1.1	General	227
8.1.2	Reference methods	228
8.2	Sampling	228
8.3	Classical analyses	229
8.3.1	Physical characteristics	229
8.3.2	Basic chemical characteristics	237
8.3.3	Minor constituents	243
8.4	Instrumental analysis	245
8.4.1	Gas chromatography	246
8.4.2	High performance liquid chromatography	254
8.4.3	Supercritical fluid chromatography	257
8.4.4	Spectroscopy	258
8.4.5	Nuclear magnetic resonance	259
8.4.6	Mass spectrometry	260
8.5	Future development	260
	References	261
9	New chemistry of oils and fats	266
	URSULA BIERMANN, SANDRA FÜRMEIER and JÜRGEN O. METZGER	
9.1	Introduction	266
9.2	Reactions of unsaturated fatty compounds	266
9.2.1	Olefin metathesis	268
9.2.2	Radical additions	268
9.2.3	Lewis acid induced cationic additions	274
9.2.4	Nucleophilic additions to reversed-polarity unsaturated fatty acids	281
9.3	Reactions of saturated fatty compounds	285
9.3.1	Radical C—C coupling	285
9.3.2	Functionalizations of C—H bonds	287
9.3.3	Lack of flexibility	288
9.4	Heterocyclic fatty compounds	288
9.4.1	O- and S- Heterocyclic fatty acids	288
9.4.2	Nitrogen-containing fatty acid derivatives	290
	References	293
10	Oleochemicals and the environment	300
	FRANK HIRSHINGER	
10.1	History	300
10.2	LCI of surfactants	302
10.3	LCI concept and methodology	302
10.3.1	Consumption of raw materials	305
10.3.2	Energy consumption	305
10.3.3	Atmospheric emissions	308
10.3.4	Waterborne emissions	308

10.3.5 Solid wastes	308
10.4 Results	308
10.4.1 Raw materials	308
10.4.2 Energy consumption	309
10.4.3 Emissions	310
10.4.4 Waterborne emissions	312
10.4.5 Solid waste	313
10.5 Lifecycle impact assessment	314
References	315
Abbreviations	317
Index	320