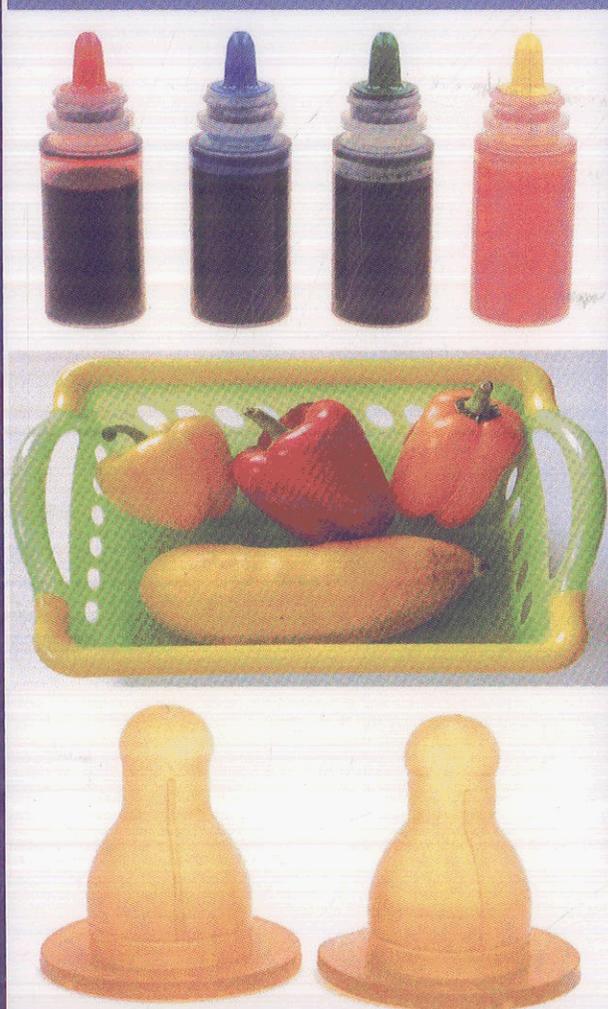


Food Contact Materials – Rubbers, Silicones, Coatings and Inks



Martin Forrest

C Contents

Preface.....	1
Introduction	3
Food Contact Rubbers – Products, Migration and Regulation	3
Silicone Products for Food Contact Applications.....	4
Coatings and Inks for Food Contact Materials.....	5

Food Contact Rubbers – Products, Migration and Regulation

1. Introduction	9
2. Rubber Materials and Products used in Contact with Food.....	10
2.1 Polymers Used in Food Contact Rubbers.....	10
2.1.1 Natural Rubber (i.e., <i>cis</i> -1,4-polyisoprene)	11
2.1.2 Nitrile Rubber.....	11
2.1.3 Ethylene-propylene Rubber.....	11
2.1.4 Fluorocarbon Rubber.....	12
2.1.5 Silicone Rubber	12
2.1.6 Thermoplastic Elastomers	12
2.1.7 Other Types of Rubbers	12
2.2 Additives Used in Food Contact Rubbers	13
2.2.1 Plasticisers/Process Oils and Fillers.....	13
2.2.2 Curatives and Antidegradants	14
2.2.3 Miscellaneous Additives	14

2.3	Rubber Products Used in the Food Industry and the Contact Conditions	15
2.3.1	Types of Rubber Product.....	15
2.3.2	Contact Areas	16
2.3.3	Contact Times.....	16
2.3.4	Contact Temperatures	16
3.	Regulations Covering the Use of Rubber as a Food Contact Material	18
3.1	European Union Legislation	18
3.2	Council of Europe (CoE) Resolution on Rubber Products	18
3.2.1	Technical Documents	18
3.2.2	Product Categories.....	19
3.2.3	R Factors	19
3.2.4	Silicone Rubbers	21
3.3	Food and Drug Administration (FDA) in the USA	21
3.4	Bundesinstitut für Risikobewertung (BfR) German Regulations	22
3.4.1	Categories of Use	22
3.4.2	Silicone Rubbers	24
3.5	Other European Legislation	24
3.5.1	Requirements in France.....	24
3.5.2	Requirements in the Netherlands	24
3.5.3	Requirements in Italy	25
3.5.4	Requirements in the United Kingdom	25
4.	Assessing the Safety of Rubber as a Food Contact Material	26
4.1	Special Considerations When Using Rubber as a Food Contact Material	26
4.2	Migration Tests.....	27
4.2.1	Overall Migration Tests	27
4.2.1.1	FDA Regulations.....	27
4.2.1.2	BfR Regulations	28

4.2.1.3	CoE Resolution	28
4.2.2	Specific Migration Tests	29
4.3	Fingerprinting Potential Migrants from Rubber Compounds.....	29
4.3.1	Use of Gas Chromatography-Mass Spectrometry (GC-MS) to Fingerprint Food Contact Rubber Samples	29
4.3.1.1	Rubber Formulations	30
4.3.1.2	Experimental Conditions.....	33
4.3.2	Use of Liquid Chromatography-Mass Spectrometry (LC-MS) to Fingerprint Food Contact Rubber Samples	36
4.4	Determination of Specific Species in Rubbers and Migrants in Food Simulants and Food Products	39
4.4.1	Monomers	39
4.4.2	Plasticisers and Process Oils.....	39
4.4.3	Cure System Species, Accelerators and Their Reaction Products	40
4.4.4	Antidegradants and Their Reaction Products	40
4.4.5	Oligomers	41
4.5	Research Studies Carried out at Rapra for the FSA.....	41
4.5.1	FSA Project FS2219 – Migration Data on Food Contact Rubbers	41
4.5.1.1	Introduction	41
4.5.1.2	Standard Rubber Compounds	42
4.5.1.3	Migration Experiments Carried Out on the Standard Rubber Compounds	44
4.5.1.4	Results of the Migration Experiments	45
4.5.2	FSA Project FS2248 – Further Migration Data on Food Contact Rubbers	48
4.5.2.1	Introduction	48
4.5.2.2	Standard Rubber Compounds	48
4.5.2.3	Tests Carried Out on the Seven Rubber Compounds.....	50
4.5.2.4	Results Obtained During the Course of the Project ...	51
4.5.3	Project A03038 – Rubber Breakdown Products	57

4.5.3.1	Introduction	57
4.5.3.2	Listing of the Breakdown Products for the CoE Curatives and Antidegradants	58
4.5.3.3	Factors Affecting the Formation of the Breakdown Products	61
4.5.3.4	Fingerprinting of the Breakdown Products	62
4.5.3.5	Migration Behaviour of the Breakdown Products....	69
4.5.3.6	Overall Summary of the Migration Data	86
4.5.3.7	Overall Conclusions	95
4.5.4	Project A03046 - Silicones	95
4.5.4.1	Introduction	95
4.5.4.2	Potential Migrants in Silicone Rubbers – Stage 1 of the Project.....	96
4.5.4.3	Data Obtained on Commercial Silicone Rubber Products – Stage 2 of the Project	99
4.5.4.4	Overall Summary of the Project Findings	106
4.6	Published Migration Data.....	107
4.6.1	Food Contact Products	107
4.6.1.1	Teats and Soothers	107
4.6.1.2	Meat Netting.....	108
4.6.1.3	Rubber Gloves for Handling Food	110
4.6.2	Specific Chemical Migrants from Rubber Compounds.....	110
4.6.2.1	Alkylphenol and Bisphenol A	110
4.6.2.2	Peroxide Breakdown Products.....	111
4.6.2.3	Dimethyl Siloxanes and Other Components from Silicone Rubbers	111
4.6.2.4	Accelerators and Antidegradants	112
4.6.3	General Surveys	112
4.6.4	Analytical Techniques	113
5.	Improving the Safety of Rubber as a Food Contact Material.....	114
5.1	Nitrosamines	114
5.2	Amines	116

5.3	Polyaromatic Hydrocarbons	116
5.4	Use of Alternative Compounds	117
6.	Future Trends in the Use of Rubber with Food.....	117
6.1	Increased Use of Thermoplastic Rubbers and High Performance Rubbers	117
6.2	Developments in Additives	119
6.3	Surface Coatings and Modifications	120
6.4	Developments in Analytical Techniques	121
7.	Conclusion	121
7.1	Sources of Further Information and Advice	122
7.1.1	Professional, Research, Trade and Governmental Organisations.....	122
7.1.2	Commercial Abstract Databases	123
7.1.3	Key Reference Books and Journals.....	123
7.1.4	Food Standards Agency Research Projects	124
Appendix 1		124
References.....		136

Coatings and Inks for Food Contact Materials

1.	Introduction	145
2.	Coating and Ink Products for Food Contact Materials.....	146
2.1	Polymers for Coatings and Inks	146
2.1.1	Acrylic	146
2.1.2	Alkyd resins	148
2.1.3	Amino Resins (Urea-formaldehyde resins).....	149
2.1.4	Epoxy Resins	151

2.1.5	Cellulosics.....	153
2.1.5.1	Nitrocellulose.....	153
2.1.5.2	Other Cellulose Esters.....	154
2.1.5.3	Cellulose Ethers.....	155
2.1.6	Polyesters – Saturated and Unsaturated.....	155
2.1.6.1	Saturated Polyesters	156
2.1.6.2	Unsaturated Polyesters	157
2.1.7	Polyurethanes.....	158
2.1.8	Rosin	160
2.1.9	Silicone Resins	160
2.1.10	Vinyl Polymers.....	162
2.1.11	Other Polymers (Hydrocarbons)	163
2.2	Constituents of Coatings	164
2.2.1	Crosslinking Agents	164
2.2.2	Other Additives.....	164
2.2.3	Solvents.....	165
2.3	Constituents of Inks.....	165
2.3.1	Solvents.....	166
2.3.2	Plasticisers.....	166
2.3.3	Driers.....	166
2.3.4	Photoinitiators	167
2.3.5	Colorants	168
2.3.5.1	Azo dyes and pigments.....	169
2.3.5.2	Phthalocyanines	169
2.3.6	Other Additives.....	170
3.	Coatings and Inks used in the Food Chain	170
3.1	Food Packaging	170
3.1.1	Packaging Types.....	170
3.1.2	Coatings Used in Metal Packaging (Tables 5 to 9).....	182
3.1.2.1	Beverage Body and End Stock External (Coatings Used in Conjunction With Inks)	182

3.1.3	Coatings and Adhesives for Flexible Packaging.....	184
3.1.4	Inks for Metal Packaging	186
3.1.4.1	Beverage Cans	186
3.1.4.2	Food Cans and Ends	186
3.1.4.3	Caps and Closures.....	187
3.1.4.4	General Line and Aerosols	187
3.1.5	Inks for Paper and Board Packaging	187
3.1.6	Inks for Flexible Packaging	187
3.2	Harvesting and Processing of Food.....	188
3.3	Storage and Transportation	190
3.4	Presentation, Dispensing and Cooking.....	191
4.	Application Techniques for Inks	191
4.1	Lithography.....	191
4.2	Flexography.....	192
4.3	Gravure	193
4.4	Inkjet	194
4.5	Influence of Substrate Type.....	194
4.5.1	Inks for Metal Packaging	194
4.5.2	Inks for Paper and Board	196
4.5.3	Inks for Flexible Plastic Packaging	196
4.5.4	Set Off	197
5.	Regulations Covering the Use of Inks and Coatings with Food	198
5.1	Regulation in the European Union.....	198
5.2	Council of Europe (CoE) Regulations.....	200
5.2.1	Coatings	200
5.2.2	Inks.....	201
5.3	National Regulations within the EU	203

5.4	FDA Regulations	204
5.5	Other Considerations for Industrial Use	205
6.	Assessing the Safety of Inks and Coatings for Food Applications	207
6.1	Global Migration Tests	208
6.2	Specific Migration Tests	209
6.3	Fingerprinting of Potential Migrants from Coatings and Inks	210
6.4	Determination of Specific Target Species in Coatings and Ink Products and in Food Simulants and Foods	211
6.4.1	Monomers, Solvents and Low Molecular Weight Additives and Breakdown Products.....	211
6.4.2	Oligomers	212
6.4.3	Plasticisers and Oil-type Additives	212
6.4.4	Polar Additives and Metal Containing Compounds	212
6.4.5	Cure System Species, Initiators, Catalysts and Their Reaction Products	212
6.4.6	Antidegradants, Stabilisers and Their Reaction Products	213
6.5	Sensory Testing	213
6.6	Toxicological Assessment of Migrants	214
7.	Potential Migrants and Published Migration Data.....	215
7.1	Acrylates.....	215
7.2	Amines	216
7.3	Aromatics from Unsaturated Polyesters	217
7.4	Aromatics from Photoinitiation Reactions and Photoinitiator Additives.....	217
7.5	BPA and BADGE and Derivatives.....	219
7.6	Epichlorohydrin.....	220
7.7	Bisphenol A	220
7.8	Solvents	221

7.9	Plasticisers	221
7.10	Extractables from UV-Cured Coating for Cardboard.....	221
7.11	Potential Migrants	222
8.	Improving the Safety of Inks and Coatings for Food Use.....	232
8.1	New Food Approved Pigments	232
8.2	Water-Based Systems.....	232
8.3	UV/EB Curable Systems.....	232
8.4	New Initiators for UV Curable Inks.....	233
9.	Future Trends	233
9.1	Improvements in Recycling Systems.....	233
9.2	Biodegradability	234
9.3	Use of Coatings to Improve Barrier Properties of Food Packaging.....	234
9.4	Antimicrobial Systems	234
9.5	Laser Marking to Replace Conventional Inks	235
9.6	Intelligent and Active Packaging	235
9.7	Applications of Nanotechnology	236
9.8	Developments in Analytical Techniques	236
10.	Conclusion	237
	Sources of Further Information and Advice.....	238
	Reference Books.....	238
	Reports.....	239
	Professional, Research, Trade and Governmental Organisations	240
	Commercial Abstract Databases.....	241
	Acknowledgements	241
	References.....	241

Silicone Products for Food Contact Applications

1. Introduction	251
2. Silicone Products for Food Contact Applications.....	251
2.1 Silicone Polymers – Chemistry, Structure and Properties.....	251
2.1.1 Definition of a Silicone Polymer	251
2.1.1.1 Summary of Principal Food Contact Silicone Products	253
2.1.2 Chemical Bonding in Silicones	253
2.1.3 Physical Characteristics.....	254
2.1.4 Chemical Properties	255
2.2 Food Contact Silicone Products – Manufacture and Composition	256
2.2.1 Introduction.....	256
2.2.2 Manufacture of Silicone Polymers and Their Precursors	256
2.2.3 Silicone Fluids and Silicone Gums	258
2.2.4 Silicone Rubbers – from High MW Gums.....	259
2.2.5 Silicone Rubbers – From Relatively Low MW Liquids.....	260
2.2.5.1 Two-pack Liquid Silicone Systems.....	261
2.2.5.2 One-pack Liquid Silicone Systems	262
2.2.6 Silicone Resins	263
2.2.7 Silicone Greases	263
2.2.8 Copolymers.....	264
2.2.8.1 Vinyl Silicones.....	264
2.2.8.2 Phenyl Silicones.....	266
2.2.8.3 Fluorosilicones	266
2.2.9 Silicone Surfactants	267
2.3 Food Contact and Food Related Applications	267
2.3.1 Release Agents	267
2.3.2 Silicone Rubbers	268
2.3.3 Silicones as Additives for Polymers	268
2.3.4 Silicones in Food Processing.....	270

3.	Regulations Covering the Use of Silicones With Food	271
3.1	Existing EU Legislation and Guideline Documents	271
3.2	Council of Europe Resolution on Silicones (Resolution AP (2004)) ...	272
3.3	German Recommendation XV from the BfR	272
3.4	Other National Legislation in the EU	273
3.4.1	Belgium.....	273
3.4.2	Italy	273
3.4.3	Netherlands	273
3.4.4	United Kingdom.....	274
3.5	The US Food and Drug Administration (FDA)	274
4.	Assessing the Safety of Silicone Materials and Articles for Food Applications ..	275
4.1	Fingerprinting of Potential Migrants from Silicone Products	275
4.1.1	Multi-element Semi-quantitative Inductively Coupled Plasma Scan	275
4.1.2	Targeting of Specific Species	275
4.1.2.1	Specific Elements	275
4.1.2.2	Residual Peroxides in Silicone Rubbers	276
4.1.2.3	Silicone Additives	276
4.1.3	Identification of Low MW Potential Migrants	276
4.1.3.1	Dynamic Headspace GC-MS.....	277
4.1.3.2	Solvent Extraction GC-MS.....	277
4.1.3.3	Solvent Extraction LC-MS	280
4.2	Overall Migration Tests	282
4.2.1	FDA Regulations for Rubbers	283
4.2.2	Council of Europe Silicone Resolution	283
4.3	Determination of Specific Species in Food Simulants and Foods	284
4.3.1	Determination of Specific Elements	284
4.3.2	Determination of Formaldehyde	285
4.3.2.1	Silicone Rubbers.....	285
4.3.2.2	Silicone Resins.....	285

4.3.3	Determination of Low MW Species Using GC-MS and LC-MS	286
4.3.3.1	Two Dimensional Gas Chromatography Time-of-Flight Mass Spectroscopy (GCxGC-ToFMS)	286
4.3.3.2	Liquid Chromatography - Mass Spectrometry (LC-MS)	290
5.	Foods Standards Agency Silicone Project – Contract Number A03046	292
5.1	Silicone Products Studied in the Project	292
5.1.1	Silicone Rubbers	292
5.1.2	Silicone Fluids	293
5.1.3	Silicone Resins – Uncured Products	293
5.1.4	Silicon Resin Coated Bakeware from Supermarkets	294
5.1.5	Compositional Fingerprinting Work	294
5.2	Migration Experiments with Food Simulants	294
5.2.1	Overall Migration Work	294
5.2.1.1	Silicone Rubbers	295
5.2.1.2	Silicone Fluids	296
5.2.1.3	Silicone Resins	298
5.2.2	Specific Migration Work	299
5.2.2.1	Determination of Specific Elements	299
5.2.2.2	Determination of Formaldehyde	299
5.2.2.3	Analysis of Food Simulants by GCxGC-ToFMS	300
5.3	Migration Experiments with Food Products	302
5.3.1	Contact Tests Performed on the Silicone Products	302
5.3.1.1	Silicone Rubbers	302
5.3.1.2	Silicone Fluids	303
5.3.1.3	Silicone Resins	303
5.3.2	Determination of Specific Migrants in Food Products	304
5.3.2.1	Determination of Silicon	304
5.3.2.2	Determination of Specific Migrants by GCxGC-ToFMS	304

5.4	Summary of Project Results	306
5.4.1	Summary of the Data Obtained on the Silicone Rubber Samples.....	306
5.4.1.1	Determination of Potential Migrants – Fingerprinting Data	306
5.4.1.2	Migration Work Using Food Simulants	308
5.4.2	Summary of the Data Obtained on the Silicone Fluids	312
5.4.2.1	Potential Migrants – from Fingerprint Data	312
5.4.2.2	Migration Work Using Food Simulants	312
5.4.2.3	Migration Work Using Food Products.....	314
5.4.3	Summary of the Data Obtained on the Silicone Resin Samples..	318
5.4.3.1	Potential Migrants – from Fingerprinting Data	318
5.4.3.2	Migration Work Using Food Simulants	319
5.4.3.3	Migration Work Using Food Products.....	321
5.4.4	Overall Summary of the Project and the Results Obtained ...	324
5.4.4.1	Overview.....	324
5.4.4.2	Data Obtained for Silicone Rubbers	324
5.4.4.3	Data Obtained for Silicone Resins.....	325
5.4.4.4	Data Obtained for Silicone Fluids	326
6.	Migration Mechanisms, Potential Migrants and Published Migration Data...	327
6.1	Possible Migration Mechanisms for Chemical Species from Silicone Products	327
6.1.1	Migration to Air (Volatilisation)	327
6.1.1.1	Potential for Chemical Change Upon Thermal Volatilisation	328
6.1.1.2	Potential for Change on Ionisation	329
6.1.2	Migration into Fluids.....	331
6.1.3	Migration into Foodstuffs	333
6.2	Potential Migrants from Silicone Products.....	333
6.2.1	Summary of Potential Migrants	333
6.2.2	Specific Potential Migrants.....	334

6.2.2.1	Silicone Oligomers	334
6.2.2.2	Cure System Species in Silicone Rubbers	336
6.2.2.3	Low MW Products Formed Due to Oxidation Reactions	339
6.3	Published Migration Data.....	339
6.3.1	Silicone Rubber Study	339
6.3.2	Silicone Rubber Teats and Soothers.....	339
6.3.3	Peroxide Breakdown Products	340
6.3.4	Polydimethylsiloxane Oligomers.....	340
6.3.5	General Assessment of Silicone Rubbers	340
7	Improving the Safety of Silicones for Food Use and Future Trends.....	341
7.1	Silicone Foams.....	341
7.2	Antibacterial Additives and Coatings.....	341
7.3	Intelligent Packaging.....	342
7.4	Barrier Coatings	342
7.5	Non-stick Additives	342
7.6	Nanoparticulate Silicones	343
7.7	Inks and Varnishes.....	343
7.8	Radiation-cured Release Coatings	343
8.	Conclusion	343
	Acknowledgements	344
	Structural Assignments for Silicone Polymers and Oligomers.....	345
	References.....	345
	Abbreviations and Acronyms.....	351
	Index.....	357