

# Contents

<b>Preface</b> .....	<b>V</b>
<b>About the Editor</b> .....	<b>VII</b>
<b>List of Contributors</b> .....	<b>IX</b>
<b>1 Rubber Compounding: Introduction, Definitions, and Available Resources</b> .....	<b>1</b>
<i>John S. Dick</i>	
1.1 Introduction .....	1
1.2 The Recipe .....	2
1.3 Classification of Rubber Compounding Ingredients .....	3
1.4 Standard Abbreviations for Compounding Ingredients .....	5
1.5 The Diversity of Rubber Recipes .....	5
1.6 Compatibility of Compounding Ingredients .....	8
1.7 Rubber Compounding Ingredients' Specifications .....	9
1.8 Raw Material Source Books .....	10
1.9 Key Source References for Formulations .....	11
1.10 Technical Organizations .....	13
1.11 Key Technical Journals and Trade Magazines .....	14
1.12 Regularly Scheduled Technical Conferences .....	15
1.12.1 Regularly Scheduled Courses .....	16
1.13 Web Sites Available .....	17

<b>2</b>	<b>Compound Processing Characteristics and Testing</b> .....	<b>19</b>
	<i>John S. Dick</i>	
2.1	Introduction .....	19
2.2	Manufacturing Process .....	19
2.2.1	Two Roll Mill .....	19
2.2.2	Internal Mixers .....	20
2.2.3	Further Downstream Processing .....	21
2.2.4	Curing Process .....	23
2.2.5	Factory Problems .....	23
2.3	Processability Characteristics and Measurements .....	25
2.3.1	Viscosity .....	25
2.3.1.1	Rotational Viscometers .....	26
2.3.1.2	Capillary Rheometer .....	27
2.3.1.3	Oscillating Rheometers .....	28
2.3.1.4	Compression Plastimeters .....	31
2.3.2	Shear Thinning .....	31
2.3.2.1	Shear Thinning by Capillary Rheometer ....	32
2.3.2.2	Shear Thinning by Oscillating Rheometer ..	33
2.3.3	Elasticity .....	34
2.3.3.1	Mooney Stress Relaxation .....	35
2.3.3.2	Elasticity by Oscillating Rheometer .....	36
2.3.3.3	Capillary Rheometer Die Swell .....	37
2.3.3.4	Compression Plastimeter Elastic Recovery ..	38
2.3.3.5	Direct Shrinkage Measurements .....	38
2.3.4	Time to Scorch .....	38
2.3.4.1	Scorch by Rotational Viscometer .....	39
2.3.4.2	Scorch by Oscillating Rheometer .....	39
2.3.4.3	Scorch by Capillary Rheometer .....	41
2.3.5	Cure Rate .....	42
2.3.5.1	Cure Rate by Rotational Viscometer .....	43
2.3.5.2	Cure Times and Cure Rate by Oscillating Rheometer .....	43
2.3.6	Ultimate State of Cure .....	45
2.3.6.1	Ring Testing .....	45
2.3.6.2	Oscillating Rheometer .....	46
2.3.7	Reversion Resistance .....	47
2.3.8	Green Strength .....	47
2.3.9	Tackiness .....	47
2.3.10	Stickiness .....	48
2.3.11	Dispersion .....	48
2.3.12	Stock Storage Stability .....	49

2.3.13	Mis-Compounding .....	49
2.3.14	Cellular Rubber Blow Reaction .....	50

**3 Vulcanizate Physical Properties, Performance Characteristics, and Testing ..... 53**

*John S. Dick*

3.1	Introduction .....	53
3.2	Density .....	54
3.3	Hardness .....	55
3.4	Tensile Stress-Strain .....	56
3.5	Stress-Strain Properties under Compression .....	57
3.6	Stress-Strain Properties under Shear .....	58
3.7	Dynamic Properties .....	58
3.8	Low Temperature Properties .....	61
3.8.1	Brittle Point .....	63
3.8.2	Gehman Test .....	63
3.9	Stress Relaxation, Creep, and Set .....	63
3.10	Permeability (Transmission) .....	66
3.11	Cured Adhesion .....	67
3.12	Tear Resistance .....	68
3.13	Degradation Properties .....	70
3.13.1	Flex Fatigue Resistance .....	70
3.13.2	Heat Resistance .....	73
3.13.3	Ozone Resistance .....	75
3.13.4	Weathering Resistance .....	76
3.13.5	Resistance to Liquids .....	77
3.13.6	Abrasion and Wear Resistance .....	77

**4 Rubber Compound Economics ..... 81**

*John M. Long*

4.1	Introduction .....	81
4.2	Compound Cost Calculations .....	81
4.2.1	Specific Gravity .....	82
4.2.2	Cost/lb .....	82
4.2.3	Lb-Volume Cost .....	82
4.2.4	Part Cost .....	82
4.2.5	Conversion Factors for Calculating Part Cost .....	83
4.2.5.1	in <sup>3</sup> and cost/lb .....	83

4.2.5.2	cm <sup>3</sup> and cost/kg	83
4.2.5.3	ft <sup>3</sup> and cost/lb	83
4.2.5.4	cm <sup>3</sup> and cost/lb	83
4.2.5.5	Relative Costs	83
4.2.5.6	Developing Conversion Factors	83
4.3	Measuring Specific Gravity (Density)	84
4.4	Cost Calculations	85
4.4.1	Base Compound	85
4.4.2	Same Ingredient Volume and Equal Cost	85
4.4.3	Low Cost/lb	87
4.4.4	High Specific Gravity	87
4.5	Compound Design and Cost	88
4.6	Reducing Compound Cost	89
4.6.1	High-Structure Carbon Blacks	89
4.6.2	White Compounds	89
4.6.3	Antioxidants/Antiozonants	89
4.6.4	Polymer Substitutions	91
4.6.4.1	High Cost/High Specific Gravity Polymers	91
4.6.4.2	Clear and Oil-Extended Polymer Replacements	92
4.6.4.3	Carbon Black/Oil Masterbatches Replacing Free Mix Compounds	94
4.6.4.4	Extrusion Productivity	96
4.6.4.5	Vulcanization Productivity	97
Appendix 4.1		98

## **5 The Technical Project Approach to Experimental Design and Compound Development** ..... 101

*Alan G. Veith*

5.1	Introduction	101
5.2	Part 1: Steps in a Technical Project	103
5.2.1	Initial Action Required	103
5.2.1.1	Planning Model	104
5.2.1.2	Work, Time, and Cost Proposal	104
5.2.2	Experimental Design	104
5.2.2.1	Selecting Variables or Factors	104
5.2.2.2	Selecting Test Instruments and Procedures	105
5.2.2.3	Developing a Response Model	105
5.2.2.4	Selecting an Experimental Design	107

5.2.3	Conduct Measurements and Obtain Data .....	112
5.2.4	Conduct Analysis and Evaluate Preliminary Model ...	112
5.2.5	Prepare Report .....	113
5.3	Part 2: Using Experimental Designs .....	113
5.3.1	Screening Designs – Simple Treatment Comparisons ..	113
5.3.1.1	Design C1 for Uniform Replication Conditions .....	114
5.3.1.2	Design C1 for Non-Uniform Replication Conditions .....	114
5.3.1.3	Design C2 for Multi-Treatment Comparisons	115
5.3.2	Screening Designs – Multifactor Experiments .....	116
5.3.2.1	Two-Level Factorial Designs .....	116
5.3.2.2	Analysis of the Designs .....	118
5.3.2.3	Calculating the Effect Coefficients .....	118
5.3.2.4	Reviewing Designs S1 to S11 .....	120
5.3.3	Exploratory Designs – Multifactor Experiments .....	121
5.3.4	Evaluating the Statistical Significance of Effect Coefficients .....	122
5.3.4.1	Evaluating Standard Errors for Effect Coefficients: Screening Designs .....	122
5.3.4.2	Four-Factor Screening Design: An Example ..	124
	Appendix 5.1 – A Catalog of Experimental Designs .....	130
<b>6</b>	<b>Elastomer Selection .....</b>	<b>147</b>
	<i>Rudy School</i>	
6.1	Overview .....	147
6.1.1	Commodity and General Purpose Elastomers .....	150
6.1.1.1	Natural Rubber (NR) .....	150
6.1.1.2	Styrene Butadiene Rubber (SBR) .....	151
6.1.1.3	Polybutadiene Rubber (BR) .....	152
6.1.2	High-Volume Specialty Elastomers .....	153
6.1.2.1	Polyisoprene (IR) .....	153
6.1.2.2	Nitrile Rubber (NBR) .....	153
6.1.2.3	Ethylene-Propylene-Diene (EPDM) .....	155
6.1.2.4	Polychloroprene (CR) .....	155
6.1.2.5	Butyl and Halogenated Butyl Elastomers ...	156
6.1.2.6	Chlorinated and Chlorosulfonated Polyethylene .....	158
6.1.3	Low-Volume Specialty Elastomers .....	158
6.1.3.1	Fluoroelastomers .....	159
6.1.3.2	Silicone and Fluorosilicone Rubber .....	160

6.1.3.3	Polyurethane Rubber .....	161
6.1.3.4	Ethylene-Acrylic Rubber .....	161
6.1.3.5	Polyacrylate Rubber .....	162
6.1.3.6	Epichlorohydrin Rubber .....	162
6.1.3.7	Polyolefin Elastomers .....	163
6.1.3.8	Polysulfide Rubber .....	163
6.1.4	Thermoplastic Elastomers .....	163
<b>7</b>	<b>General Purpose Elastomers and Blends .....</b>	<b>165</b>
	<i>Gary Day</i>	
7.1	Introduction .....	165
7.2	Natural Rubber and Polyisoprene .....	166
7.3	Polybutadiene .....	169
7.4	Copolymers and Terpolymers of Styrene, Butadiene, and Isoprene .....	173
7.5	Compounding with General Purpose Polymers .....	177
7.5.1	Polymer Characterization and Effect on Mixing .....	178
7.5.2	Polymer Effect on Cure Rate .....	180
7.5.3	Polymer Effect on Stress-Strain .....	188
7.5.4	Hysteresis .....	189
7.5.5	Compatibility with SIR 10 .....	195
7.5.6	Fatigue Properties .....	198
7.5.7	Compression Set .....	199
7.6	Conclusion .....	199
<b>8</b>	<b>Specialty Elastomers .....</b>	<b>203</b>
8.1	Introduction .....	203
8.2	Butyl Rubber .....	204
	<i>G. E. Jones, D. S. Tracey and A. L. Tisler</i>	
8.2.1	Introduction .....	204
8.2.2	Butyl Rubber Physical Properties .....	204
8.2.3	Butyl Rubber Properties, Vulcanization, and Applications .....	206
8.2.4	Gas Permeability .....	206
8.2.5	Ozone and Weathering Resistance .....	207
8.2.6	Butyl Rubber Vulcanization .....	208
8.2.6.1	Accelerated Sulfur Vulcanization .....	208
8.2.6.2	The Dioxime Cure .....	209
8.2.6.3	The Resin Cure .....	209

8.3	Halogenated Butyl Rubber .....	210
	<i>G. E. Jones, D. S. Tracey and A. L. Tisler</i>	
8.3.1	Introduction .....	210
8.3.2	Compounding Halobutyl and Star-Branched Halobutyl Rubbers .....	211
8.3.2.1	Carbon Black .....	211
8.3.2.2	Mineral Fillers .....	211
8.3.2.3	Plasticizers .....	212
8.3.2.4	Processing Aids .....	212
8.3.3	Processing Halobutyl Rubber .....	212
8.3.3.1	Mixing .....	212
8.3.3.2	Calendering .....	213
8.3.3.3	Extrusion .....	214
8.3.3.4	Molding .....	214
8.3.4	Halobutyl Rubber Vulcanization and Applications ....	214
8.3.4.1	Straight Sulfur Cure .....	215
8.3.4.2	Zinc Oxide Cure and Modifications .....	215
8.3.4.3	Zinc-Free Cures .....	215
8.3.4.4	Peroxide Cures .....	216
8.3.4.5	Vulcanization through Bis-Alkylation .....	216
8.3.4.6	Resin Cure .....	216
8.3.4.7	Scorch Control .....	216
8.3.4.8	Stability of Halobutyl Crosslinks .....	217
8.3.5	Halobutyl Rubber General Applications .....	217
8.3.6	Cured Properties .....	218
8.3.6.1	Permeability .....	218
8.3.6.2	Heat Resistance .....	218
8.3.6.3	Resistance to Chemicals and Solvents .....	219
8.3.7	Flex Resistance/Dynamic Properties .....	219
8.3.8	Compatibility with Other Elastomers .....	219
8.3.9	Halobutyl Rubber Compound Applications .....	220
8.3.9.1	Tire Innerliners .....	220
8.3.9.2	Pharmaceutical Closures .....	220
8.3.9.3	Heat Resistant Conveyor Belt .....	221
8.4	EPM/EPDM .....	222
	<i>Rajan Vara and Janet Laird</i>	
8.4.1	Introduction .....	222
8.4.2	Ethylene/Propylene Content .....	223
8.4.3	Diene Content .....	224
8.4.4	Rheology .....	225

8.5	Acrylonitrile-Butadiene Rubber .....	226
	<i>Michael Gozdiff</i>	
8.5.1	Introduction .....	226
8.5.2	Chemical and Physical Properties - Relating to Application .....	227
8.5.2.1	Acrylonitrile Content (ACN) .....	227
8.5.2.2	Mooney Viscosity .....	228
8.5.2.3	Emulsifier .....	228
8.5.2.4	Stabilizer .....	229
8.5.2.5	Coagulation .....	229
8.5.3	Polymer (Elastomer) Microstructure .....	229
8.5.4	Polymer (Elastomer) Macrostructure .....	229
8.5.5	Gel .....	230
8.5.6	Molecular Weight .....	231
8.5.7	Hot NBR .....	231
8.5.8	Crosslinked Hot NBR .....	231
8.5.9	Cold NBR .....	232
8.5.10	Carboxylated Nitrile (XNBR) .....	233
8.5.11	Bound Antioxidant NBR .....	234
8.6	Hydrogenated Nitrile Butadiene Elastomers .....	235
	<i>Michael E. Wood</i>	
8.6.1	Introduction .....	235
8.6.2	Applications .....	236
8.6.3	Properties .....	236
8.6.4	Formulating .....	237
8.6.5	Processing .....	238
8.7	Polyacrylate Elastomers .....	238
	<i>Paul Manley and Charles Smith</i>	
8.7.1	Polymer Composition .....	238
8.7.2	Basic Compounding of Polyacrylate Polymers .....	241
8.7.3	Processing Guidelines .....	242
8.8	Polychloroprene (Neoprene) .....	243
	<i>Leonard L. Outzs</i>	
8.8.1	Introduction .....	243
8.8.2	Basic Characteristics of Polychloroprene .....	243
8.8.3	Families of Neoprene .....	243
8.8.4	Neoprene "G" Family .....	246
8.8.5	Neoprene "W" Family .....	247
8.8.6	Neoprene "T" Family .....	248



8.9 Chlorinated Polyethylene (CM) .....	248
<i>Laura Weaver</i>	
8.9.1 Introduction .....	248
8.9.2 General Characteristics .....	249
8.10 Chlorosulfonated Polyethylene (CSM) .....	250
<i>Charles Baddorf</i>	
8.10.1 Introduction .....	250
8.10.2 General Purpose Types of Hypalon .....	253
8.10.3 Specialty Types of Hypalon .....	253
8.10.4 Unvulcanized Applications .....	254
8.11 Polyepichlorohydrin Elastomer .....	254
<i>Clark Cable</i>	
8.11.1 Introduction .....	254
8.11.2 Properties .....	255
8.11.3 Formulating .....	256
8.11.4 Nonlead Cure Systems .....	256
8.11.5 Adjustments .....	257
8.11.6 Processing .....	257
8.11.7 Internal Mixer - Procedure .....	258
8.11.8 Extrusion .....	258
8.11.9 Molding .....	258
Appendix 8.1 - List of Chemicals .....	259
Appendix 8.2 - List of Plasticizers .....	260
8.12 Ethylene-Acrylic Elastomers .....	261
<i>Theresa M. Dobel</i>	
8.12.1 Introduction .....	261
8.12.2 Polymer Composition and Effect on Properties .....	262
8.12.3 Polymer Selection .....	262
8.13 Polynorbornene .....	264
<i>Clark Cable</i>	
8.13.1 Introduction .....	264
8.13.2 Applications .....	264
8.13.3 Compounding .....	264
8.13.4 Fillers .....	265
8.13.5 Oils/Plasticizers .....	265
8.13.6 Cure System .....	265
8.13.7 Rebound/Resilience .....	266
8.13.8 Vibration Damping .....	266
8.13.9 Blends .....	267

8.13.10	Mixing and Processing .....	267
8.13.10.1	Mill Mixing .....	267
8.13.10.2	Internal Mixers .....	267
8.13.11	Calendering .....	268
8.13.12	Extrusion .....	268
8.13.13	Molding .....	269
8.13.14	Summary .....	269
8.14	Fluoroelastomer (FKM) .....	270
	<i>Ronald D. Stevens</i>	
8.14.1	Introduction .....	270
8.14.2	Background .....	271
8.14.3	Applications .....	271
8.14.4	Viton® Types .....	272
8.15	Silicone Elastomers .....	275
	<i>James R. Halladay and Rick A. Ziebell</i>	
8.15.1	Introduction .....	275
8.15.2	Selection .....	278
8.15.3	Fillers .....	280
8.15.4	Anti-Structuring Agents .....	281
8.15.5	Heat Stabilizers .....	282
8.15.6	Peroxide Cures .....	283
8.15.7	Platinum Cures .....	284
8.15.8	RTV Cures .....	286
<b>9</b>	<b>Polyurethane Elastomers .....</b>	<b>287</b>
	<i>Ronald W. Fuest</i>	
9.1	Introduction .....	287
9.2	Polyurethane Chemistry and Morphology .....	288
9.3	Polyurethane Products .....	291
9.4	Cast Polyurethane Processing Overview .....	292
9.5	Molding Methods .....	294
9.5.1	Open Casting .....	294
9.5.2	Centrifugal Molding .....	295
9.5.3	Vacuum Casting .....	295
9.5.4	Compression Molding .....	295
9.5.5	Transfer Molding .....	296
9.5.6	Liquid Injection Molding (LIM) .....	296
9.5.7	Spraying .....	296
9.5.8	Moldless Rotational Casting .....	296

9.6	How to Select a Polyurethane Elastomer .....	297
9.6.1	Types of Prepolymers .....	298
9.6.2	Types of Curatives .....	300
9.6.3	Processing Conditions .....	301
9.6.4	Additives .....	303
9.7	Comparison of Polyurethanes with Other Elastomers .....	304
9.7.1	Limitations of Polyurethane Elastomers .....	308
9.8	Polyurethane Selection Guidelines .....	308
9.8.1	Selecting a Polyurethane Elastomer for a New Application .....	312
9.9	Millable Gums .....	313
9.10	Thermoplastic Polyurethanes .....	314
<b>10</b>	<b>Thermoplastic Elastomers .....</b>	<b>317</b>
	<i>Charles P. Rader</i>	
10.1	Introduction .....	317
10.2	Position in Spectrum of Polymeric Materials .....	317
10.3	Classification of TPEs .....	319
10.3.1	Chemistry and Morphology .....	319
10.3.2	Styrenic Block Copolymers .....	323
10.3.3	Copolyesters .....	324
10.3.4	Thermoplastic Polyurethanes .....	325
10.3.5	Polyamides .....	326
10.3.6	Thermoplastic Elastomeric Olefins .....	327
10.3.7	Thermoplastic Vulcanizates .....	328
10.4	TPEs and Thermoset Rubbers .....	331
10.5	Fabrication of TPEs .....	333
10.5.1	Economy of Thermoplastics Processing .....	333
10.5.2	Injection Molding .....	334
10.5.3	Extrusion .....	335
10.5.4	Blow Molding .....	335
10.5.5	Other Processing Methods .....	336
<b>11</b>	<b>Recycled Rubber .....</b>	<b>339</b>
	<i>Frank P. Papp</i>	
11.1	Introduction .....	339
11.2	History .....	339
11.3	Production Methods .....	340
11.3.1	Reclaim Rubber Process .....	341

11.3.2	Rubber Powder via Ambient and Cryogenic Processes . .	342
11.3.3	Rubber Powder via Ultra-High Pressure Water Jet Milling . . . . .	343
11.3.4	Treated or Functionalized Rubber Powder . . . . .	345
11.4	Classification, Characterization, and Testing of Recycled Rubber Powders . . . . .	346
11.4.1	Classification System . . . . .	346
11.4.2	Testing Methods for Particle Size Determination . . . . .	349
11.4.2.1	ASTM D5644 Method A - The Ro-Tap Procedure . . . . .	349
11.4.2.2	ASTM D5644 Method B - Ultrasonic and Light Microscopy Technique . . . . .	351
11.4.2.3	Laser Particle Size Analysis . . . . .	351
11.4.2.4	Surface Area Determination . . . . .	352
11.4.2.5	Surface Characterization . . . . .	352
11.5	Comparison of Ambient and Cryogenically Prepared Recycled Rubber Powder . . . . .	353
11.6	Physical and Rheological Properties of Rubber Compounds Mixed with Recycled Rubber Powder . . . . .	359
11.6.1	RRP Baseline Study . . . . .	359
11.6.2	Addition Point of Recycled Rubber Powder . . . . .	367
11.6.3	Sulfur-Accelerator Optimization with Recycled Rubber Powder . . . . .	369
11.6.4	Weathering Resistance with Recycled Rubber Powder . .	377
11.6.5	Heat Aging Resistance of Recycled Rubber Powder Containing Optimized Recipe . . . . .	380
11.6.6	Selecting the Appropriate Recycled Rubber Powder Particle Size/Surface Area . . . . .	385
11.6.7	Use of Recycled Rubber Powder in Solution SBR/Silica-Silane Tire Tread . . . . .	389
11.7	New Technology for Recycled Rubber . . . . .	400
11.7.1	EkoDyne™ Test Results in a Carbon Black Model Compound . . . . .	401
11.7.2	EkoDyne™ Test Results in a Silica-Silane Model Compound . . . . .	407
11.8	Executive Summary . . . . .	416
<b>12</b>	<b>Compounding with Carbon Black and Oil . . . . .</b>	<b>419</b>
	<i>Steve Laube, Steve Monthey, and Meng-Jiao Wang</i>	
12.1	Introduction: Carbon Black Affects Everything . . . . .	419

12.2	Characterization of Carbon Black .....	420
12.2.1	The Particle, the Aggregate, and the Agglomerate ....	420
12.2.2	Surface Area, Structure, and Surface Activity .....	421
12.2.3	Constituents Other than Carbon (Impurities) .....	423
12.2.4	Pellets .....	424
12.2.5	ASTM Nomenclature .....	424
12.3	Handling Carbon Black .....	426
12.4	Mixing Carbon Black .....	426
12.4.1	Pellet Properties and Analyticals (Also Called Colloidal Properties) .....	426
12.4.2	Effect of Analyticals on Dispersion .....	427
12.4.3	The Mixing Process .....	428
12.5	Subsequent Processability of the Compound .....	429
12.6	Compounding Carbon Black .....	429
12.6.1	Optimum Loading .....	432
12.6.2	Importance of Dispersion .....	433
12.6.3	Carbon Black Compounding Tips .....	434
12.6.3.1	Hardness .....	434
12.6.3.2	Processing Oil .....	435
12.6.3.3	Other Vulcanizate Properties .....	437
12.6.3.4	Vulcanizate Hysteresis .....	437
12.6.4	The Tire Industry's Tradeoffs .....	440
12.7	Hysteresis Reducing Tips .....	441
12.7.1	"Radical Compounding" .....	441
12.7.2	Lower Loadings of High Structure Carbon Blacks .....	442
12.7.3	Carbon-Silica Dual Phase Fillers .....	443
12.8	Practical Applications: Tire Examples .....	444
12.8.1	OE Passenger-Tire Treads .....	444
12.8.2	Replacement Passenger-Tire Treads .....	444
12.8.3	HP Passenger-Tire Treads .....	444
12.8.4	Medium Radial Truck Treads .....	445
12.8.5	Wire Coat or Skim Stocks .....	445
12.8.6	Innerliner Compounding .....	445
12.9	Major Tradeoffs for Industrial Rubber Products .....	445
12.9.1	Loading/Reinforcement/Cost .....	446
12.10	Compounding Tips: Industrial Rubber Products .....	446
12.10.1	Extrusion Profiles and Products .....	446
12.10.2	Molded Products .....	447
12.10.3	Hose Applications .....	447

12.11 Basics of Carbon Black Manufacture .....	448
12.11.1 History .....	448
12.11.2 The Oil-Furnace Process .....	448

### **3 Precipitated Silica and Non-Black Fillers .....** **451**

*Chenchy Jeffrey Lin and W. Michael York*

13.1 Introduction .....	451
13.1.1 General Properties and Costs of Non-Black Fillers ....	452
13.1.2 Use and Selection of Non-Black Fillers for Rubber Compounds .....	453
13.1.3 Factors Considered for Reinforcing Rubber with Fillers	456
13.1.3.1 Filler Particle Size and Surface Area .....	457
13.1.3.2 Filler Anisometry - Shape and Morphology ..	458
13.1.3.3 Surface Activity and Surface Energy .....	459
13.2 Mineral Fillers .....	460
13.2.1 An Overview of the Most Commonly Used Non-Black Fillers .....	460
13.2.1.1 Calcium Carbonate .....	460
13.2.1.2 Clay .....	463
13.2.2 Other Mineral Fillers .....	470
13.2.2.1 Talc .....	470
13.2.2.2 Barite .....	471
13.2.2.3 Mica .....	472
13.2.2.4 Alumina Trihydrate (ATH) .....	472
13.3 Synthetic Silica .....	476
13.3.1 Precipitated Silica .....	479
13.3.2 Precipitated Silica Characterization .....	481
13.3.2.1 Structure and Surface Chemistry .....	481
13.3.2.2 Surface Area .....	483
13.3.2.3 Pore Volume and Void Volume .....	485
13.3.2.4 Void Volume .....	485
13.3.2.5 Silica Dispersion and Silanization .....	486
13.3.3 Highly Dispersible Silica (HDS) .....	487
13.3.4 Rice Husk Silica .....	491
13.3.5 Silica Surface Treatment .....	492
13.3.6 Pre-treated Silica .....	498
13.3.7 Masterbatching .....	498
13.4 Non-Black Nanoparticles and Polymeric Nanocomposites .....	505
13.4.1 Nano-Precipitated CaCO <sub>3</sub> (Ultrafine Precipitated CaCO <sub>3</sub> ) .....	505

13.4.1.1	Nano-CaCO <sub>3</sub> Surface Modification and Their Use for Nano-Composites .....	507
13.4.1.2	Application Examples of Nano-CaCO <sub>3</sub> in Various Rubbers .....	507
13.4.2	Layered Silicates and Their Nanocomposites .....	508
13.4.2.1	Organoclay (Organic Layer Silicate) - Montmorillonite .....	509
13.4.2.2	Cationic Clays - Hectorite and Their Applications in Rubber Nanocomposites ...	511
13.4.2.3	Anionic Clays - Layered Double Hydroxide (LDH) and Their Applications in Rubber Composites .....	512
13.4.3	Polymeric Core-Shell Nanoparticles .....	514
13.4.3.1	Synthesis of Core-Shell Polymeric Nanoparticles .....	515
13.4.3.2	Reinforcement and Performance of Rubber Compounds by Adding Tailored Polymeric Core-Shell Nanoparticles .....	515
13.5	Applications of Non-Black Fillers in Selected Segments of the Rubber Industry .....	521
13.5.1	Tires .....	521
13.5.1.1	Tread Compounds .....	522
13.5.1.2	Innerliner Compound .....	523
13.5.1.3	White Sidewall Compounds .....	524
13.5.2	Wires and Cables .....	526
13.5.2.1	Rubbers for High Voltage Insulation .....	527
13.5.3	Automotive Hose .....	528
13.5.4	Shoe and Footwear Products .....	529
13.5.5	Silicone-Rubber Compounding .....	530
<b>14</b>	<b>Ester Plasticizers and Processing Additives .....</b>	<b>533</b>
14.1	Ester Plasticizers for Elastomers .....	533
	<i>Wesley H. Whittington</i>	
14.1.1	Derivation .....	533
14.1.2	Philosophical .....	538
14.1.3	Applications .....	539
14.1.3.1	Low-ACN Content NBR .....	539
14.1.3.2	Neoprene Blend GN 88/WHV 12 .....	541
14.1.3.3	Different Elastomers with the Same Plasticizer .....	542
14.1.3.4	Medium Acrylonitrile-Content NBR .....	542

14.1.3.5	Medium ACN NBR .....	544
14.1.3.6	Medium-High ACN-Content NBR .....	547
14.1.3.7	NBR/PVC Polyblends .....	549
14.1.3.8	Ethylene Acrylic and Polyacrylate Elastomers .....	549
14.1.3.9	Chlorosulfonated Polyethylene (CSM) .....	551
14.1.3.10	Chlorinated Polyethylene (CPE) .....	552
14.1.4	Application Trends .....	554
14.2	Process Additives .....	556
<i>Christopher R. Stone</i>		
14.2.1	Control of Viscosity .....	557
14.2.1.1	Viscosity Control of Natural Rubber .....	557
14.2.1.2	Viscosity Control of Synthetic Rubber .....	562
14.2.2	Mode of Action of Process Additives .....	562
14.2.2.1	Surface Lubricants .....	565
14.2.2.2	Process Additives for Homogenizing and Improving Filler Dispersion .....	566
14.2.3	Application of Process Additives .....	567
Appendix 14.1 - Common Esters for Rubber .....		572
Appendix 14.2 - Abbreviations and Definitions .....		574
<b>15</b>	<b>Sulfur Cure Systems .....</b>	<b>575</b>
<i>Byron H. To</i>		
15.1	Introduction and Historical Background .....	575
15.2	Vulcanizing Agents .....	577
15.3	Activators .....	577
15.4	Accelerators .....	579
15.5	Conventional, Semi-Efficient, and Efficient Cures .....	583
15.6	Retarders and Inhibitors .....	583
15.7	Recent Developments .....	585
<b>16</b>	<b>Cures for Specialty Elastomers .....</b>	<b>593</b>
<i>Byron H. To</i>		
16.1	Introduction .....	593
16.2	Cure Systems for EPDM .....	593
16.3	Cure Systems for Nitrile .....	600
16.4	Cure Systems for Polychloroprene .....	603
16.5	Cure Systems for Butyl and Halobutyl Rubber .....	605



<b>17</b>	<b>Peroxide Cure Systems</b> .....	<b>611</b>
	<i>Leonard H. Palys</i>	
17.1	Introduction .....	611
17.1.1	What is an Organic Peroxide? .....	611
17.1.2	Classes of Organic Peroxides .....	611
17.1.3	General Peroxide Selection Guidelines .....	613
17.1.3.1	Half-Life .....	613
17.1.3.2	Minimum Cure Time .....	614
17.1.3.3	SADT (Self Accelerating Decomposition Temperature) .....	614
17.1.3.4	Maximum Storage Temperature (MST) .....	615
17.1.3.5	Energy of Peroxide Free Radicals .....	615
17.1.3.6	Peroxide Polymer Masterbatches .....	617
17.1.3.7	High Performance (HP) Peroxide Formulations for Improved Productivity .....	619
17.2	Peroxides Used in Crosslinking .....	622
17.2.1	Diacyl Peroxides .....	622
17.2.2	Peroxyester and Monoperoxy carbonate Peroxides .....	623
17.2.3	Peroxyketal and Dialkyl Type Peroxides .....	624
17.2.4	Performance Characteristics of Dialkyl Type Peroxides .....	630
17.2.5	t-Amyl and t-Butyl Type Peroxides .....	631
17.2.6	Effect of Additives When Crosslinking with Peroxides ..	632
17.3	Role of Monomeric Coagents in Peroxide Crosslinking .....	634
17.3.1	Crosslinking PE with Coagents and Peroxides .....	634
17.3.2	Crosslinking EPDM with Coagents and Peroxides .....	635
17.3.3	Crosslinking HNBR with Coagents and Peroxides .....	636
17.4	Advantages and Disadvantages of Peroxide Crosslinking versus Sulfur Vulcanization .....	637
<b>18</b>	<b>Tackifying, Curing, and Reinforcing Resins</b> .....	<b>641</b>
	<i>Bonnie Stuck</i>	
18.1	Introduction .....	641
18.2	Phenol-Formaldehyde Resins .....	642
18.2.1	Types of Phenol-Formaldehyde Resins .....	643
18.2.1.1	Reinforcing Resins .....	643
18.2.1.2	Tackifying Resins .....	647
18.2.1.3	Curing Resins .....	648
18.3	Methylene Donor Resins .....	649
18.4	Resorcinol-Based Resins .....	650

18.5	High Styrene Resins	650
18.6	Petroleum-Derived Resins	650
18.7	Wood-Derived Resins	650
<b>19</b>	<b>Antidegradants</b>	<b>653</b>
	<i>Fred Ignatz-Hoover</i>	
19.1	Introduction	653
19.2	Properties of Antidegradants	654
19.2.1	Discoloration and Staining	654
19.2.2	Volatility	655
19.2.3	Solubility and Migration	655
19.2.4	Chemical Stability	656
19.2.5	Physical Form	656
19.2.6	Antidegradant Concentration	657
19.3	Antidegradant Types	657
19.3.1	Non-Staining, Non-Discoloring Antioxidants	658
19.3.1.1	Hindered Phenols	658
19.3.1.2	Hindered "Bis" Phenols	658
19.3.1.3	Substituted Hydroquinones	659
19.3.1.4	Phosphites	659
19.3.1.5	Organic Sulfur Compounds	659
19.3.1.6	Hindered Amine and Nitroxyl Compounds	659
19.3.2	Staining/Discoloring Antioxidants	660
19.3.2.1	Phenylnaphthylamines	660
19.3.2.2	Dihydroquinolines	660
19.3.2.3	Diphenylamine Derivatives	661
19.3.2.4	Substituted Paraphenylenediamines (PPDs)	661
19.3.2.5	Amine-based, "Bound-in" or "Polymer Bound" Antioxidants	661
19.3.3	Antiozonants	662
19.3.3.1	Petroleum Waxes	663
19.3.3.2	Nickel Dibutyldithiocarbamate (NBC)	663
19.3.3.3	6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETMQ)	663
19.3.3.4	Substituted Paraphenylenediamines (PPDs)	664
19.4	Examples of Antidegradant Activity	665
19.4.1	Oxidation Resistance	665
19.4.2	Effect of Antidegradants on Fatigue Life	666
19.4.3	Combinations of Antiozonants and Antioxidants	668
19.4.4	Resistance to Metal Poisoning	668

<b>20</b>	<b>Compounding for Brass Wire Adhesion</b> .....	<b>671</b>
	<i>Alex Peterson</i>	
20.1	Introduction .....	671
20.2	Wire Bonding Systems .....	672
20.2.1	Cobalt .....	672
20.2.2	RF Resin-Cobalt .....	673
20.3	The Adhesion Mechanism .....	674
20.4	Compound Ingredient Effects .....	674
20.4.1	Mixing .....	675
20.4.2	Testing .....	675
20.4.3	Regression Plots .....	676
20.4.3.1	Carbon Black .....	676
20.4.3.2	Zinc Oxide/Stearic Acid .....	677
20.4.3.3	Sulfur/DCBS .....	678
20.4.3.4	Cobalt .....	678
20.4.3.5	RF Resin/HMMM .....	679
20.4.3.6	Carbon Black/Silica .....	680
20.4.3.7	Summary of Test Results .....	681
20.5	Model NR Ply Compounds .....	681
20.5.1	Black Control Compound .....	682
20.5.2	Black/Cobalt Compound .....	682
20.5.3	Black/Cobalt/RF Resin .....	682
20.5.4	Black/Silica/Cobalt/RF Resin .....	682
20.6	Summary .....	683
<b>21</b>	<b>Chemical Blowing Agents</b> .....	<b>685</b>
	<i>Ralph A. Annicelli</i>	
21.1	Introduction .....	685
21.2	Terminology .....	685
21.2.1	Open Cell Structure .....	686
21.2.2	Closed Cell Structure .....	686
21.3	Inorganic Blowing Agents .....	687
21.4	Organic Blowing Agents .....	688
21.4.1	Azodicarbonamide (ADC) .....	689
21.4.1.1	Properties .....	690
21.4.1.2	Activation .....	690
21.4.1.3	Factors Affecting Performance .....	690
21.4.1.4	Effect of Particle Size .....	692
21.4.1.5	Effect of Temperature .....	693
21.4.1.6	ADC Activation and Cell Size .....	693

21.4.2	Sulfonyl Hydrazides .....	694
21.4.2.1	Properties .....	694
21.4.2.2	Activation .....	694
21.4.2.3	Applications .....	694
21.4.3	Dinitrosopentamethylenetetramine (DNPT) .....	695
21.4.3.1	Properties .....	695
21.4.3.2	Activation .....	695
21.5	Methods of Expansion .....	696
21.5.1	Low Pressure Molding Process .....	696
21.5.2	High Pressure Molding Process .....	696
21.5.2.1	Precure Stage .....	696
21.5.2.2	Final Cure Stage .....	697
21.5.3	Continuous Vulcanization (CV) .....	697

## **22 Flame Retardants ..... 699**

*Kelvin K. Shen and David R. Schultz*

22.1	Introduction .....	699
22.2	Fire Standards, Testing, and Applications .....	700
22.3	Commonly Used Flame Retardants in Elastomers .....	701
22.3.1	Aliphatic and Alicyclic Halogen Sources .....	701
22.3.2	Aromatic Halogen Sources .....	702
22.3.3	Synergists of Halogen Sources .....	702
22.3.3.1	Antimony Oxide .....	702
22.3.3.2	Zinc Borate .....	702
22.3.3.3	Phosphorus Compounds .....	703
22.3.4	Flame Retardant Fillers .....	703
22.3.4.1	Alumina Trihydrate (ATH) .....	703
22.3.4.2	Magnesium Hydroxide .....	703
22.3.4.3	Calcium Carbonate .....	703
22.3.4.4	Clay, Talc, and Silica .....	704
22.3.4.5	Carbon Black .....	704
22.4	Compounding and Dispersion Considerations .....	704
22.4.1	Polychloroprene (CR) .....	705
22.4.2	Chlorinated Polyethylene (CM) .....	706
22.4.3	Chlorosulfonated Polyethylene (CSM) .....	707
22.4.4	Ethylene-Propylene-Diene-Monomer (EPDM) .....	708
22.4.5	Styrene-Butadiene (SBR) .....	711
22.4.6	Nitrile-Butadiene Rubber (NBR) and Hydrogenated- Nitrile-Butadiene Rubber (HNBR) .....	711
22.4.7	Silicone Elastomer .....	713
22.4.8	Ethylene-Vinyl Acetate (EVM) .....	713

22.4.9	Ethylene-Propylene Elastomer (EPR) .....	714
22.4.10	Thermoplastic Elastomers (TPE) .....	714
<b>23</b>	<b>Rubber Mixing</b> .....	<b>717</b>
	<i>W.J. Hacker</i>	
23.1	Introduction .....	717
23.2	History .....	717
23.3	Equipment .....	718
23.3.1	Mills .....	718
23.3.2	Internal Mixers .....	719
23.3.2.1	Tangential Rotor Type .....	720
23.3.2.2	Intermeshing Rotor Type .....	720
23.3.2.3	Variable Internal Clearance Mixer .....	720
23.3.2.4	Continuous Mixers .....	721
23.3.2.5	Extruders .....	722
23.4	Mixing .....	723
23.4.1	Mill Mixing .....	723
23.4.2	Internal Mixer .....	725
23.4.2.1	Batch Size .....	725
23.4.2.2	Batch Conversion Factor .....	727
23.4.2.3	Density and Cost Calculations .....	727
23.4.2.4	Mixing Procedures .....	727
23.4.2.5	Mixing Temperatures .....	728
23.5	Mixing Methods .....	729
23.5.1	Natural Rubber Mastication .....	729
23.5.2	Masterbatch Mixing .....	730
23.5.3	Phase Mixing .....	730
23.5.4	Single-Stage Mix .....	732
23.5.5	Single-Cycle Mix .....	732
23.5.6	Two-Stage Mix .....	732
23.5.7	Tandem Mixing .....	733
23.5.8	Three-Stage Mix .....	733
23.5.9	Upside Down Mix .....	734
23.5.10	Variable Speed Mixing .....	734
23.5.11	Final Mix .....	735
23.5.12	Continuous Mixing .....	735
23.5.13	E-SBR Carbon Black Masterbatch .....	736
23.5.14	Energy Mixing .....	737
<b>Index</b>	.....	<b>739</b>