

The Neoprenes

The Neoprenes

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PREFACE

"THE NEOPRENES", by the late N. L. Catton, was published ~~ten~~ years ago. At that time there were ten types of dry neoprene. Today, ~~there~~ are double that number. In addition to the great technical advances in neoprene manufacture which made the new types possible, equally significant progress has been made in the technology of compounding and processing both the old and new types. The purpose of this book is to set forth for the rubber technologist as much as possible of the up-to-date information of value in compounding and processing neoprene. Coincidentally, this book was written during the 30th year of Du Pont neoprene production.

Grateful thanks are due to scores of chemists and engineers throughout the rubber industry as well as to our own colleagues who have contributed to the compilation and organization of the information in these pages. We would like to acknowledge especially the assistance of G. K. Walker and the valued editorial work of J. R. A. Burton.

R. M. Murray
D. C. Thompson
Wilmington, Delaware
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We believe the information in this book to be accurate. However, with respect to the use of any formula or process described, we do not guarantee results, freedom from patent infringement, or suitability of resultant products for any suggested application. Any person proposing to use any formula or process described herein should assure himself of the patent situation and obtain any necessary licenses.

INTRODUCTION

NEOPRENE is the generic name for polymers of chloroprene (2 chloro-1,3-butadiene) manufactured by E. I. du Pont de Nemours and Company.

Neoprene is a particularly versatile elastomer because it has a combination of properties suitable for many and varied applications. Neoprene vulcanizates have high tensile strength, resilience, and abrasion resistance—and they resist deterioration by oils, solvents, weather, oxygen, ozone, heat and flame. Rubber technologists, therefore, look to neoprene when service conditions are unusually severe—especially where a product must withstand a *combination* of deteriorating conditions (e.g., oil and ozone or heat and oil).

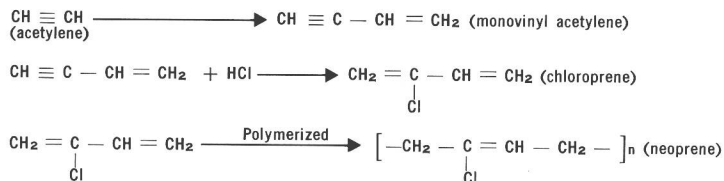
However, to develop efficiently the maximum advantages from the inherent properties of neoprene, the technologist must first choose the best type of neoprene for the job at hand and then compound, process and cure it properly. This is the key to the way "The Neoprenes" is arranged. *Chapter I* deals with the basic characteristics of, and differences among, the types most generally used. *Chapters II-IV* cover processing and basic compounding in terms of the general-purpose neoprenes described in *Chapter I*. Fundamentals related to the blending of neoprenes with each other and with other elastomers are covered in *Chapter V*. Special purpose neoprenes are covered in *Chapter VI*.

The compounding and processing principles peculiar to special end uses involving solvent systems are not treated in detail. They are largely unrelated to the balance of the book and also are well-covered in separate comprehensive reports on adhesives and maintenance coatings.

Since the technology discussed in the book covers over 30 years of experience and investigation, it was felt impractical to reproduce in detail all pertinent and still applicable data previously published. Many readers are likely to have on hand much of the existing Du Pont literature. Therefore, reference is made to many individual publications (e.g., BL-354 or Report 56-6).

Manufacture

Acetylene and hydrogen chloride are the principal raw materials used in the manufacture of neoprene. The basic chemical reactions are:



Acetylene is dimerized to monovinyl acetylene (a gas with a boiling point of 41°F.) in the presence of an aqueous catalyst solution of cuprous chloride.

In turn, monovinyl acetylene is reacted with hydrogen chloride to form the chloroprene monomer, a liquid with a boiling point of 139°F. Following purification by fractionation, the chloroprene monomer is emulsified in water and then polymerized. In the case of NEOPRENE GN, the oldest neoprene type still being produced, polymerization is carried out at 104°F. under atmospheric pressure in the presence of sulfur, using potassium persulfate as a catalyst. The progress of polymerization is followed by observing the change in specific gravity of the emulsion. When polymerization has progressed to the desired conversion, a thiuram disulfide is introduced. Thiuram disulfide functions as a shortstop and, in addition, permits control of polymer viscosity by cleaving sulfur linkages during aging of the alkaline emulsion. After polymerization, additional thiuram disulfide is added to the emulsion as a stabilizer for the polymer.

The polymer is isolated from the emulsion by acidifying the latex (with acetic acid in the presence of a non-ionic stabilizer) to a point just short of coagulation. The emulsion is then fed into a large pan in which a large rotating brine-cooled drum is partially immersed. A frozen layer of coagulated emulsion deposits itself on the surface of the drum and is removed continuously by means of a doctor blade. The film then passes over a belt where it is water-washed to thaw it and remove water-soluble constituents. Following this, the wet film is squeezed through rolls and carried, festoon fashion, through hot air dryers. The dried film is cooled, gathered into rope form and cut into chips approximately 1/4" thick by 1" in diameter. The chips are coated with talc, and packaged in 50 pound polyethylene-lined bags. The bags are then stitched, passed under an electronic metal detector, palletized, and stored in 65°F. warehouses to await shipment.

Molecular Structure

Neoprene polymer is highly regular in structure, consisting primarily of a linear sequence of trans-2-chloro-2-butenylene units which result from trans-1,4 addition polymerization of chloroprene. Other structural units exist in the polymer chain resulting from cis 1,4 addition, 1,2 addition and 3,4 addition.¹ The percent of each structural unit in neoprene is shown in the chart opposite.

As a result of the 1,2 polymerization, 1.5% of the chlorine in neoprene is in an allylic form; it is labile and is believed to be the most active curing site in vulcanization.² (See page 93.)

As might be expected from the relatively high percent of trans-configuration, neoprene can become crystalline when conditions are favorable. Crystallization can occur in raw polymers, in uncured compounds, and in vulcanizates. As crystallization develops, a gradual hardening, stiffening and loss of flexibility is observed. However, crystallization is a reversible phenomenon;

¹Maynard J. T. and Mochel W. E. "The Structure of Neoprene. VII—Infrared Analysis of Configurations", *Journal of Polymer Science*, Vol. XIII page 251. (1954)

²Kovacic P. "Bisalkylation Theory of Neoprene Vulcanization", *Industrial and Engineering Chemistry*, Vol. 47 page 1090. (1955)

with warming, a crystallized specimen decrystallizes completely. The different dry neoprenes are produced with widely different crystallization rates, so that the rubber technologist can avoid crystallization if it would be a liability in his product, or he can exploit it if it would be an advantage. Crystallization is discussed more thoroughly on pages 63-65.

Structural Units in the Neoprene Polymer Chain		
Type of Addition	Formula	Approximate Percent
Trans — 1, 4	$ \begin{array}{c} \text{H}_2 \quad \text{H} \\ \quad \\ -\text{C} = \text{C}- \\ \quad \\ \text{Cl} \quad \text{H}_2 \end{array} $	85
Cis — 1, 4	$ \begin{array}{c} \text{H}_2 \quad \text{H}_2 \\ \quad \\ -\text{C} = \text{C}- \\ \quad \\ \text{Cl} \quad \text{H} \end{array} $	10
1, 2	$ \begin{array}{c} \text{H}_2 \quad \text{Cl} \\ \quad \\ -\text{C} - \text{C}- \\ \\ \text{CH} \\ \\ \text{CH}_2 \end{array} $	1.5
3, 4	$ \begin{array}{c} \text{H}_2 \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \\ \text{CCl} \\ \\ \text{CH}_2 \end{array} $	1.0

Neoprene Types

The first neoprene was sold in 1932 under the name "DuPRENE". As chloroprene polymerization technology improved, new neoprene types were developed with better processing characteristics and better vulcanizate properties. Some were improved general purpose types; others were special polymers tailored for particular applications. At this writing, 20 dry neoprenes and 13 neoprene latices are available commercially. Neoprene manufacturing plants are located in Louisville, Kentucky; Montague, Michigan; and Londonderry, Northern Ireland. Another is under construction in Japan.

The dry types of neoprene may be conveniently divided into two broad classifications—the more widely used general purpose types and the specialty types. The general purpose types, NEOPRENES GN, GNA, GRT, W, W-M1, WHV, WHV-100, WX, WRT, WD and WB, are all used in a wide variety of elastomer products. No single general purpose neoprene is especially associated with any one class of finished product. The special-purpose types are NEOPRENES AC, AD, CG, FB, FC, HC, ILA, KNR and S. Each special-purpose neoprene is designed primarily for a particular application (e.g., adhesives, coatings, crepe soles).

INDEX

A

Abrasion resistance, 62
 AC Polyethylene 617A, 10, 41
 Accelerators, 23-28
 for the G types, 23
 for the W types, 24
 masterbatching of, 9
 with red lead, 28
 Acetone,
 as a solvent, 96
 resistance to, 72
 Acetylene (in the manufacture of neoprene), xi
 Acids, resistance to, 71
 Activity number of magnesia, 22
 Adhesion,
 to fabrics, 74
 to metals, 73
 Adhesives, neoprenes for, 83
 Aging, 60
 Air marking, 14
 Air, permeability to, 66
 AKROFLEX CD, 29
 Ammonia, permeability to, 66
 Aniline, resistance to, 72
 Aniline point,
 effect on compatibility, 39
 effect on swelling, 73
 Antimony trioxide, 62
 Antioxidant 2246, 29, 60, 67
 Antioxidants, 29
 Antiozonants, 29
 Aranox, 29, 60
 Aromatic oils, 39
 Asarco 281, 19
 SQUAREX NS, 42
 Aqueous solutions, resistance to, 70

B

Backrinding, 15
 Balata, comparison with NEOPRENE HC, 86
 Banbury mixing, 7-9

Basic compounding, 21-53
 Batch size, 6
 Benzaldehyde, resistance to, 72
 Benzoic acid, 42, 56
 Bisalkylation theory of vulcanization, 93
 Blanc fixe, 31
 Blends, 77-82
 NEOPRENE HC with phenolic resin, 88
 NEOPRENE ILA and W, 89
 neoprene with butyl rubber, 82
 neoprene with natural rubber, 78
 neoprene with NBR, 80
 neoprene with neoprene, 77
 neoprene with polysulfide rubber, 82
 neoprene with SBR, 79
 Blisters, 14
 Bloom, 39, 59, 63
 Blow-holes, 14
 Blowing agents, 42
 Bonding agents, 73
 Brass, adhesion to, 74
 BRC 22, 40
 Brittleness temperature, 40, 64
 of ILA/W blends, 89
 Building tack, compounding for, 56
 Butane, permeability to, 66
 Butter, resistance to, 72
 Butyl acetyl ricinoleate, 70
 Butyl laurate, 70
 Butyl oleate, 40, 59, 65, 70
 Butyl rubber, blends with neoprene, 82
 Butyric acid, resistance to, 72

C

Cable jackets, 69
 lead press curing, 18
 Cadmium stearate, 67
 Calcined clay, 34
 Calcium silicate, 31, 35
 Calendering, 10-13
 Carbon black, 31-39, 43-53
 loading table, 32-33

- Carbon dioxide, permeability to, 66
- Carbon tetrachloride, resistance to, 72
- Catechol, effect on modulus, 94
- Caulking compounds, 85
- Cellular rubber, 42
- Celogen AZ, 42
- Cements, 83-85, 96
- Chalking, 58
- Chemical peptizers, 30
- Chemical resistance, 72
- Chlorinated paraffins, 62
- Chloroprene, *xi*, 93-95
- Chromium oxide green, 58
- Clash-Berg stiffness, 65
- Clay, 31-40, 43-53
 - loading table, 34-35
- Coal tar oil, 57
- Coated fabrics, 74
 - calendering, 11
- Coefficient of thermal expansion, 102
- Compatibility of plasticizers, 39, 63
- Compounding,
 - basic, 21-53
 - for abrasion resistance, 62
 - for adhesion to fabrics, 74
 - for adhesion to metals, 73
 - for building tack, 56
 - for calender release, 56
 - for chemical resistance, 72
 - for compression set resistance, 60
 - for crystallization resistance, 64
 - for discoloration resistance, 67
 - for economy, 75
 - for electrical properties, 69
 - for extrusion, 56
 - for fast cure rate, 58
 - for flame resistance, 62
 - for flex-cracking resistance, 61
 - for freedom from bloom, 63
 - for frictioning, 57
 - for heat resistance, 60
 - for high resilience, 61
 - for high viscosity, 55
 - for low cost, 75
 - for low hysteresis, 61
 - for low nerve, 55
 - for low permeability, 65
 - for low temperature flexibility, 63
 - for low viscosity, 55
 - for mill release, 56
 - for minimum lead press discoloration, 67
 - for oil resistance, 72
 - for ozone resistance, 59
 - for processing safety, 58
 - for solvent resistance, 72
 - for staining resistance, 67
 - for tear strength, 68
 - for water resistance, 70
 - for weather resistance, 58
- Compression set resistance,
 - compounding for, 60
 - effect of cure time on, 61
 - effect of fillers on, 37
 - effect of plasticizer concentration and filler loading on, 48-49
- Conoco H-35, 67
- Continuous curing, 18
- Cost, compounding for low, 75
- Cotton seed oil, resistance to, 72
- Coumarone-indene resins,
 - blends with NEOPRENE HC, 88
 - to provide tack in frictioning compounds, 57
- Cover cements, 74
- Crepe soles, NEOPRENE S in, 86
- Crosslinking in vulcanization, 93
- Crystallization, 63-65
 - in adhesives, 83
 - in NEOPRENE HC, 86
- Cure, theory of, 93-95
- Curing, 16-20
 - acceleration systems, 23-28
 - continuous, 18
 - equivalent cures, 17
 - fast cures, 58
 - lead press curing, 18
 - liquid curing media, 19
 - theory, 93-95
- Curing bags, effect of neoprene in, 82
- Cyclohexane,
 - as a solvent, 96
 - resistance to, 72

D

- DACRON, adhesion to, 74
- DC Resistivity, 69
- Dibutyl phthalate, resistance to, 72
- Dibutyl sebacate, 70
- Dielectric properties of process oils and plasticizers, 70
- Dielectric strength, 69
- Diethylthiourea, 24, 58
- Diisooctyl adipate, 70
- Diocetyl sebacate, 40, 70
- Diocetyl phthalate, 70
- Discoloration (lead press),
 - compounding for minimum, 67
- Dispersion, 6
- Distilled water, resistance to, 70
- Distortion, 14
- Dodecyl mercaptan, 60
- DOTG, 26, 30
- DPG, 30
- DuPrene, *xii*
- Dynamic ozone testing, 59

E

- ELA, 7
- Elastic phase, 6
- Electrolytic concentration, effect on water absorption, 71
- Elongation, effect of plasticizer concentration and filler loading on, 46
- Equilibrium swell, 73
- Equivalent cures, 17
- Ester plasticizers, 40, 61, 64-65, 69-70
- Ethyl acetate, as a solvent, 96 resistance to, 72
- Ethyl alcohol, resistance to, 72
- Ethylene glycol, resistance to, 72
- Extended compounds, 75
- Extenders, 41
- Extrusion, 9-10 compounding for, 56-57

F

- Fabric frictioning, 11 compounding for, 57
- Fabrics, adhesion to, 74
- Factice, 41
- Fast cure rate, compounding for, 58
- Filler loading, effect on compression set, 48-49 effect on elongation, 46 effect on hardness, 43 effect on modulus, 44 effect on oil resistance, 53 effect on permanent set, 47 effect on resilience, 52 effect on tear strength, 50-51 effect on tensile strength, 45
- Fillers, 31-41 carbon black loading table, 32-33 effect on abrasion resistance, 62 effect on adhesion to metals, 73 effect on building tack, 56 effect on compression set resistance, 37, 60 effect on electrical properties, 69 effect on extrusion characteristics, 56 effect on flame resistance, 62 effect on flex-cracking resistance, 61 effect on heat resistance, 60 effect on nerve, 56 effect on oil resistance, 38, 72 effect on ozone resistance, 59 effect on permeability, 66 effect on tear strength, 36, 67 effect on tensile strength, 36, 68 effect on water resistance, 71 effect on weather resistance, 58 highly extended compounds, 75 mineral filler loading table, 34-35 weight-volume relationship, 97

- Flame resistance, compounding for, 62
- Flash, 16
- Flex-cracking resistance, 61
- Flexalyn 80M, 30
- Flexibility at low temperatures, 63
- Flow cracks, 14
- FREON, permeability to, 66
- Frictioning, 11 compounding for, 57
- Fungus resistance, 41 effect of linseed oil on, 30
- Fura-Tone NC 1012, 30
- Furfural, resistance to, 72

G

- G types [All the G types are mentioned frequently in the book. A summary of the main characteristics of each is given on page 2.]
- Gas permeability, 65
- Gel content, 83
- General purpose neoprenes, 1
- Glass temperature, 40, 63-64
- Gilsonites, 41
- Granular phase, 6

H

- Hard clay, 31, 34-38, 43-53
- Hardness, effect of plasticizer concentration and filler loading on, 43
- Heat aging, 60 in the absence of air, 60
- Heat history, 5
- Heat resistance, compounding for, 60
- HELIOZONE, as an antiozonant, 29 as a release agent, 41
- Helium, permeability to, 66
- Heptane, as a solvent, 96
- Hexane, as a solvent, 96
- High viscosity, compounding for, 55
- Highly extended compounds, 75
- Hi-Sil 233, 62, 68, 71
- HITEC heat transfer salt (in LCM process), 19
- Hose, lead press curing, 18, 67
- Hot air cures, 18
- Hydrated alumina (Hydral 710), 62
- Hydrogen, permeability to, 66
- Hydrous magnesium silicate, 35
- HYLENE, as a bonding agent, 74
- Hysteresis, compounding for control of, 61

I

Insulation, electrical, 69
 Internal mixing, 7
 Inventories, 5
 Iron oxide, 23, 58
 Isopropyl ether, resistance to, 72

J

Jet fuel, resistance to, 72

K

Kempore 125, 42
 Kenflex A, 40, 69
 Kerosene,
 as a solvent, 96
 resistance to, 72
 Knitting, 14

L

Laminations, 14
 Lard, resistance to, 72
 Lauric acid, 41
 LCM process, 19
 compounding for, 57
 Lead oxides, 23, 28, 70
 Lead press curing, 18, 67
 Linseed oil
 as a plasticizer/antiozonant, 30, 41, 59
 resistance to, 72
 Liquid curing media, 19
 Litharge, 28
 Loading factor in internal mixers, 7
 Loading tables,
 carbon black, 32-33
 mineral fillers, 34-35
 Low cost, compounding for, 75
 Low gas permeability, compounding for, 65
 Low molecular weight polyethylene, 10, 41
 Low nerve, compounding for, 55-56
 Low temperature flexibility, 63-65
 Low temperature plasticizers, 40
 Low viscosity, compounding for, 35
 Low viscosity neoprenes, 84-86
 Lubricants, 41

M

Magnesia, 21-22
 addition of in mixing, 6
 Magnesium silicate, 35

Manufacture of neoprene, *xi*
 Masterbatching of accelerators, 9
 Mastication, 5
 MBTS, 24, 26
 Mechanism of vulcanization, 93-95
 Mercaptobenzoic acid, 31
 Metallic oxides, 21-23
 Metals, adhesion to, 73
 Methane, permeability to, 66
 Methyl acetate, 96
 Methyl ethyl ketone,
 as a solvent, 96
 resistance to, 72
 Methyl isobutyl ketone, 96
 Methylene chloride, resistance to, 72
 Mica, 66
 Milk coating on calender rolls, 11
 Mill release, compounding for satisfactory, 56
 Milling, 5-7
 Mineral fillers, 31
 loading table, 34-35
 Mineral rubber, 41
 Mixing, 6-9
 Modulus, effect of plasticizer concentration and
 filler loading on, 44
 Mold design, 15
 Mold shrinkage, 13
 Molding, 13-16
 Molecular structure of neoprene, *xii*
 Molecular weight of neoprene, 1
 Monovinylacetylene (in the manufacture of
 neoprene), *xi*

N

NA-22, 23-28
 in NEOPRENE GN, 23
 in NEOPRENE W, 24-28
 Naphthenic oils, 39
 Natural rubber,
 blends with neoprene, 78
 in neoprene to improve tear strength, 68
 resilience, 61
 thermal properties, 102
 NBC, 30
 NBR,
 blends with neoprene, 80
 permeability, 66
 NEOPRENE
 [Most of the general purpose neoprenes
 (GN, GNA, GRT, W, WB, WD, WHV,
 WRT, WX) are mentioned frequently
 throughout the book. The following
 references are places where particular
 note is made of the properties or ap-
 plication of an individual neoprene.]

- NEOPRENE AC and AD, 83
 - in adhesives, 83
 - in blends to speed crystallization, 77
 - NEOPRENE CG, 83
 - NEOPRENE FB and FC, 85
 - as plasticizer in flame resistant compounds, 62
 - in blends to lower viscosity, 55, 77
 - in blends to increase building tack, 56
 - NEOPRENE GN and GNA, 2
 - acceleration of, 23-24
 - blends with NBR, 81
 - blends with NEOPRENE W, 77
 - carbon black in, 32-33
 - effect of fillers in, 36-38
 - effect of plasticizer concentration and filler loading, 43-53
 - flex-resistance, 61
 - mineral fillers in, 34-35
 - NA-22 in, 23-24
 - resilience, 62
 - NEOPRENE GRT, 2
 - building tack, 56
 - friction compound, 57
 - NEOPRENE HC, 86
 - NEOPRENE ILA, 88
 - NEOPRENE KNR, 84
 - NEOPRENE S, 86
 - NEOPRENE W, 3
 - acceleration of, 24-28
 - blends with butyl rubber, 82
 - blends with natural rubber, 78
 - blends with NEOPRENE GN, 77
 - blends with NEOPRENE ILA, 89
 - blends with SBR, 79
 - carbon black in, 32-33
 - compression set resistance, 61
 - cure rate, 27
 - effect of fillers in, 36-38
 - effect of plasticizer concentration and filler loading, 43-53
 - heat resistance, 60
 - mineral fillers in, 34-35
 - NA-22 in, 24-28
 - permeability, 66
 - NEOPRENE W-MI, 3
 - NEOPRENE WB, 3
 - for extrusion compounds, 56
 - in blends to reduce nerve, 56
 - NEOPRENE WD, 3
 - low temperature properties, 64
 - in blends to increase viscosity, 55, 57
 - NEOPRENE WHV,
 - highly extended compounds, 75
 - in blends to increase viscosity, 55, 57
 - NEOPRENE WRT, 3
 - cure rate, 27
 - low temperature properties, 64
 - in blends to reduce viscosity, 57
 - NEOPRENE WX, 3
 - cure rate, 27
 - NEOZONE A, 29
 - NEOZONE D, 29
 - Nerve, compounding for low, 55
 - Nitro benzene, resistance to, 72
 - Nitrogen, permeability to, 66
 - Nitrogen releasing type blowing agents, 42
 - Non-staining antioxidants, 29
 - Nylon, adhesion to, 74
- O
- Octamine, 29, 60
 - Oil resistance, 72
 - effect of plasticizer concentration and filler loading on, 53
 - effect of filler on, 38
 - of NEOPRENE ILA, 89
 - Oleic acid, resistance to, 72
 - Olive oil, resistance to, 72
 - Open steam cures, 18
 - ORLON, adhesion to, 74
 - Orthodichlorobenzene, resistance to, 72
 - Ottacide P, 41
 - Oxygen, permeability to, 66
 - Ozone resistance,
 - antiozonants, 29
 - compounding for, 59
- P
- Palm oil, 41
 - Paraffin, 41
 - Paraffinic oils, 39
 - Para-Flux, 40
 - Pebbling, 15
 - Pendulum type feed, 10
 - Peptizers, 30
 - PERMALUX, 24
 - Permeability, 65
 - Petrolatum, 41
 - Petroleum oil plasticizers, 39
 - Phenolic resins, blends with NEOPRENE HC, 88
 - Phenolic type antioxidants, 29
 - Plastic phase, 6
 - Plasticity, as a test for identification, 98
 - Plasticizer SC, 70
 - Plasticizers, 39-41
 - compatibility, 63
 - dielectric properties, 69-70
 - effect on electrical properties, 69
 - effect on flame resistance, 62
 - effect on flex cracking, 62
 - effect on flexibility, 64
 - effect on heat resistance, 60
 - effect on oil resistance, 72
 - effect on ozone resistance, 59

Plasticizer concentration,
 effect on compression set, 48-49
 effect on elongation, 46
 effect on hardness, 43
 effect on modulus, 44
 effect on oil resistance, 53
 effect on permanent set, 47
 effect on resilience, 52
 effect on tear strength, 50-51
 effect on tensile strength, 45

Plying-up, 11

Polyether, 40

Polyethylene, low molecular weight, 10, 41

Polymeric plasticizers, 40

Polymerization of chloroprene, *xi*

Polysulfide rubber, blends with neoprene, 82

Porosity, 14

Potassium persulfate (catalyst in the
 manufacture of neoprene), *xii*

Power factor, 69

Precipitated silicon dioxide, 31, 35, 62, 68, 71

Processing, 5-19
 calendering, 10
 extruding, 9
 mixing, 6
 molding, 13

Processing requirements, compounding for, 55-58

Propane, permeability to, 66

Q

Quick grab, in adhesives, 83

R

Rapeseed oil, 41, 60

Raw neoprene, identification of, 98-101

Raw polymer stability, 1

Rayon, adhesion to, 74

Red iron oxide, 58

Red lead, 23, 28, 70

Reinforcing agents (see "Fillers"), 31-41

Release agents, 7, 41

Resilience,
 compounding for high, 61
 effect of plasticizer concentration and
 filler loading on, 52

Resinous plasticizers, 40

RETARDER W, 24, 26

Retarders, 28
 for NA-22 accelerated NEOPRENE W, 26

Rosin Oil No. 5, 30

RPA No. 3, 31

RR-10, 58

Rubber substitute, 41

S

Safety, compounding for maximum, 58

Safflower oil, 41

Salicylic acid (RETARDER W), 24, 26

Santowhite crystals, 60

SBR,
 blends with neoprene, 79
 permeability, 66

Screws, extrusion, 9

Sealant compounds, 85

Second order transition temperature, 40, 63

Shrinkage, 13

Silicone dioxide, 31, 35, 62, 68, 71

Skim-coating, 12

Sodium acetate, 28, 58

Sodium chloride, resistance to, 72

Soft clay, 31

Sol content, 83

Solvent resistance, 72

Solvents for neoprene, 96

Special purpose neoprenes, 83-90

Specific heat, 95

Specific inductive capacity, 69

Sponge, blowing agents for, 42

Sponging, 14

Staining, compounding for minimum, 67

Staining antioxidants, 29

Static ozone testing, 59

Stearic acid, 7, 41

Sticking, prevention of, 41

Stock lubricants, 41

Storage, 5

Structure of neoprene, *xii*

Sulfur, 24, 28
 for adhesion to brass, 74

Sulfur dioxide, permeability to, 66

Swelling by oils, chemicals and solvents, 72

T

Talc, 31

Tear strength, 67
 effect of fillers on, 36
 effect of plasticizer concentration and
 filler loading on, 50-51
 of neoprene/natural rubber blends, 78

Tearing (on removal from mold), 15

Tendering of fabrics, 74

Tensile strength, 68
 effect of fillers on, 36
 effect of plasticizer concentration and
 filler loading on, 45

Terpene resins, blends with NEOPRENE HC, 88

Tests for identifying raw neoprenes, 98

Tetraethyl lead, resistance to, 72
Tetraethylene glycol di-2-ethylhexoate, 70
TETRONE A, 29
Theory of cure, 93-95
Thermal conductivity, 97
Thermal expansion, coefficient of, 97
THERMOFLEX A, 29
Thiokol, blends with neoprene, 82
THIONEX, 24
Thiourea, theory of vulcanization by, 94
THIURAM E, 30
THIURAM M, 24, 26
Tie cements, 74
Titanium dioxide, 23, 35
Toluene,
 as a solvent, 96
 resistance to, 72
Torsional stiffness, 64
TP-90B, 70
Tributoxyethyl phosphate, 70
Trichloroethylene, resistance to, 72
Triethanolamine, 42, 56
Triethylene caprylate-caprate, 40
Trioctyl phosphate, 40, 70
Tubing (extruding), 9
Turpentine, resistance to, 72

U

Ucon 50-HB-280X, 19
UNICEL ND and S, 42
Unsupported sheets, calendering of, 10
Urea, 42
U. S. Patents,
 2,427,192, 80
 2,519,231, 82
 2,617,755, 22
 2,617,782, 22

V

Vegetable oil plasticizers, 30, 41
Viscosity,
 as a means of identification, 100
 compounding for different, 55
 effect of on milling, 5
 of NEOPRENE FB and FC, 85
 of NEOPRENE HC, 88
 of NEOPRENE KNR, 84
 of the G types, 2
Volume-weight relationship of fillers, 100
Vulcanization, 16-19
 continuous, 18
 in a lead press, 18
 theory of, 93-95
Vulcanized vegetable oil, 30, 41

W

W types
 [All the W types are mentioned frequently
 in the book. A summary of the main char-
 acteristics of each one is given on page 3.]
Warehousing, 5
Water resistance, 70-71
Wax,
 as an antiozonant, 29
 as a release agent, 41
Weather resistance, 58
Weight-volume relationship of fillers, 100
Whiting, 31, 35
Wing-stay 100, 30
Wire jackets, 18, 69
Wool grease, 41

Z

Z type four roll calender, 11
Zinc oxide, 21-22
 addition of in mixing, 18
Zinc stearate, 7

CONTENTS

INTRODUCTION	xi
<i>Chapter I</i> GENERAL PURPOSE NEOPRENES	
The G types	2
The W types	3
<i>Chapter II</i> PROCESSING	
Storage and heat history	5
Mastication	5
Mixing	6
Extruding	9
Calendering	10
Molding	13
Curing	16
<i>Chapter III</i> BASIC COMPOUNDING	
Metallic oxides	21
Accelerators	23
Retarders	28
Sulfur	28
Antioxidants	29
Antiozonants	29
Peptizers	30
Reinforcing agents and fillers	31
Plasticizers	39
Extenders	41
Release agents, lubricants and extrusion aids	41
Blowing agents	42
<i>Chapter IV</i> COMPOUNDING FOR SPECIFIC PROPERTIES	
Special processing requirements	55
Weather resistance	58
Ozone resistance	59
Heat resistance	60
Compression set resistance	60
Resistance to flex-cracking	61
High resilience, low hysteresis	61