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How to Improve Rubber Compounds

1800 Experimental Ideas for Problem Solving

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Improving Degradation Resistance of Cured Rubber Compounds

■ 3.1 Improving Hot Air and/or Heat Aging Resistance

Hot air aging and heat aging resistance are becoming very important today, especially in automotive applications where “under-the-hood” operating temperatures have been increasing and there is more pressure from automotive manufacturers to have rubber parts that last longer (part of the move toward a 150,000-mile car warranty!). Anaerobic heat aging resistance can be quite different from hot air aging resistance. For example, a rubber compound might possess good reversion resistance (anaerobic), yet still be subject to oxidative attack (or vice versa). The type of aging properties that a cured rubber compound possesses is very important in determining how that compound will be classified in accordance with SAE J200/ASTM D2000 for automotive applications.

*The following **experimental** ideas might improve a rubber compound’s hot air aging resistance and/or heat aging resistance (but not always both). Also, all relevant literature sources, including the ones cited below, should be researched and read. **Caution:** these general experimental ideas may not work in all specific situations. Changes to improve hot air aging or heat aging resistance will certainly affect other properties as well, for better or for worse, and this book does not purport to show how these other properties are affected. Also, this book does not purport to address safety and health issues.*

■ Subjective Ranking of Rubber

One overall subjective ranking that can be applied to different base elastomers for heat resistance is as follows:

FKM (Best) > VMQ > Fluorosilicone > ACM > AEM > EPDM > CO/ECO
≈ CM > CSM ≈ NBR > CR > IIR ≈ NBR/PVC > SBR > NR

GEN: J. Horvath, "Selection of Polymers for Automotive Hose and Tubing Applications," *Rubber World*, December 1987, p. 21.

Another subjective ranking that can be applied to base elastomers for heat resistance is the following:

FKM (Best) \approx TFE > VMQ/PVMQ/MQ > FVMQ > AEM > EPM > EPDM \approx
ACM > CSM > CR > NR \approx NBR > AU/EU > SBR/BR

GEN: R. Mastromatteo, E. Morrisey, M. Mastromatteo, H. Day, "Matching Material Properties to Application Requirements," *Rubber World*, February, 1983, p. 28.

The so-called "continuous use" temperature rankings for specialty elastomers were reported as follows:

| Type of rubber | Continuous use temperature |
|---------------------------|----------------------------|
| HNBR | 145°C (293°F) |
| ACM | 150°C (302°F) |
| AEM | 160°C (320°F) |
| AG (DAI-EL Alloy AG-1530) | 175°C (347°F) |
| FKM | 230°C (446°F) |

GEN: M. Kishine, T. Noguchi, "New Heat-Resistance Elastomers," *Rubber World*, February, 1999, p. 40.

Perfluoroelastomers

Often perfluoroelastomers (FFKMs) are selected as the base rubber for a compound when the ultimate heat resistance is needed. FFKM polymers reportedly can impart useful service life at temperatures as high as 316°C (601°F). GEN: M. Coughlin, R. Schnell, S. Wang, "Perfluoroelastomers in Severe Environments: Properties, Chemistry, and Applications," Presented at ACS Rubber Div. Meeting, Spring, 2001, Paper No. 24.

Fluoroelastomers

Compounds based on FKM possess extremely good heat aging resistance. RT: Chapter 6, "Elastomer Selection," R. School, p. 135.

Fluoroelastomer (FKM) compounds can achieve heat resistance up to 260°C (500°F). GEN: M. Chase, "Roll Coverings Past, Present, and Future," Presented at Rubber Roller Group Meeting, New Orleans, May 15–17, 1996, p. 7.

To maximize compound high-temperature performance, the best acceptor for the chosen FKM must be selected. Common types of acceptors for FKM compounds are low-activity magnesium oxide, high-activity magnesium oxide, calcium

oxide, calcium hydroxide, zinc oxide, and lead oxide (litharge), which is toxic. RT: Chapter 6, “Elastomer Selection,” R. School, p. 136.

Fluoroelastomer-based compounds provide extremely good protection against air aging and can provide a “useful service life” at temperatures greater than 200°C (392°F). RT: Chapter 8, “Specialty Elastomers,” R. Stevens, p. 229.

For even better heat aging resistance of a fluoroelastomer compound, select a bisphenol AF cure system. RT: Chapter 8, “Specialty Elastomers,” R. Stevens, p. 230.

New fluoroelastomers made with vinylidene fluoride, tetrafluoroethylene, and propylene reportedly possess better aging properties for many “aggressive engine oils” at high temperatures compared to conventional FKM elastomers. This is reported to be attributable to the use of propylene in place of hexafluoropropylene in the polymerization process. GEN: W. Grootaert, R. Kolb, A. Worm, “A Novel Fluorocarbon Elastomer for High-Temperature Sealing Applications in Aggressive Motor-Oil Environments,” *Rubber Chemistry and Technology*, September–October, 1990, Vol. 63, p. 516.

The following is a general ordinal ranking of different types of fluoroelastomers in regards to the heat resistance they impart to a rubber compound:

FFKM (72% F) Best > FKM Type 2 (70% F) > FKM Type 1 (65% F)

GEN: Jim Denham (3M), “Basic Fluoroelastomer Technology,” Presented at the Energy Rubber Group, September 13, 2011, Galveston, TX.

Under severe conditions of very high pressure and very high temperature (HPHT) in “down-hole” oil drilling operations using fluoroelastomer compounds, to help avoid explosive decompression (ED) as a mode of failure, consider using the new ultra-high-viscosity (UHV) fluoroelastomers [ML (1 + 10 @ 121°C) = 150], 66% fluorine content, bisphenol AF curable. GEN: J. Denham (Dyneon 3M), “Solutions for the Oil and Gas Industry,” Presented at the Spring Meeting of the Energy Rubber Group, May 28, 2009, Arlington, TX.

HNBR

Compounds based on HNBR possess very good heat aging resistance. The higher the level of hydrogenation is, the better the heat aging will be because there are fewer unsaturated sites on the polymer backbone that can be attacked. RT: Chapter 8, “Specialty Elastomers,” M. Wood, p. 202.

Some grades of HNBR can be sulfur cured because they still possess some unsaturation. However, an HNBR compound will usually possess better heat aging resistance if it is cured with peroxide instead of sulfur. RT: Chapter 8, “Specialty Elastomers,” M. Wood, p. 202.

TOTM and TINTM plasticizers reportedly impart better heat resistance for HNBR compounds than plasticizers such as DOP and DBEEA because these trimellitate plasticizers have lower volatility and higher molecular weights. DBEEA reportedly is the “most recommended” for HNBR-based, sulfur-cured compounds because it imparts a good balance between low-temperature properties and heat resistance. GEN: S. Hayashi, H. Sakakida, M. Oyama, T. Nakagawa, “Low-Temperature Properties of Hydrogenated Nitrile Rubber (HNBR),” *Rubber Chemistry and Technology*, September–October, 1991, Vol. 64, p. 534.

NBR

High-temperature applications for NBR-based compounds often use peroxides and thiurams as curatives. RT: Chapter 6, “Elastomer Selection,” R. School, p. 131.

Using NBR grades with higher ACN content may improve compound heat aging resistance. RT: Chapter 8, “Specialty Elastomers,” M. Gozdif, p. 194.

Use an emulsion NBR that is produced from a coagulating system based on magnesium sulfate for better heat resistance. RT: Chapter 8, “Specialty Elastomers,” M. Gozdif, p. 196.

To impart better heat resistance to a nitrile formulation, consider ether thioether plasticizers, in which the sulfur functions as a secondary antioxidant. GEN: J. Dunn, “Compounding Elastomers for Tomorrow’s Automotive Market, Part II,” *Elastomerics*, February, 1989, p. 29.

To impart better heat resistance to a nitrile formulation, consider using precipitated silica, magnesium oxide, and zinc oxide in place of carbon black. GEN: J. Dunn, “Compounding Elastomers for Tomorrow’s Automotive Market, Part II,” *Elastomerics*, February, 1989, p. 29.

Natural Rubber

For NR compounds, cure at a lower temperature for a longer period of time to increase the preponderance of monosulfide crosslinks for better aging properties. GEN: M. Studebaker, J. Beatty, “Vulcanization,” *Elastomerics*, February, 1977, p. 41.

For NR formulations, selecting diphenylguanidine (DPG) as the secondary accelerator (“kicker”) instead of a dithiocarbamate or a thiuram “kicker” for a primary accelerator may improve the compound’s heat aging characteristics. GEN: B. Ashworth, K. Crawford, “Effect of Secondary Accelerator Selection on the Aging Characteristics of Natural Rubber Vulcanizates,” *Rubber World*, December, 1982, p. 20.

Never use nickel dibutyldithiocarbamate (NBC) in a natural rubber compound because NBC is a strong pro-oxidant and degradant to NR. RT: Chapter 19, "Antidegradants," F. Ignatz-Hoover, p. 453.

Cardanol-formaldehyde (CF) novolak curing resin can be used with HMTA to cure a natural rubber compound so as to impart good aging properties. CF novolak curing resins are more compatible with NR than phenol-formaldehyde novolak curing resins. In addition, the CF resins have some antioxidant properties. The CF resins are manufactured using cardanol as a raw material. Cardanol is usually extracted from CNSL or "cashew nut shell liquid," which is relatively inexpensive and a natural product. GEN: Y. Vu, J. Mark, L. Pham, "Blends of Natural Rubber with Cardanol-Formaldehyde Resins," Presented at ACS Rubber Div. Meeting, Spring, 1998, Paper No. 58.

Consider using a diurethane cure (Novor[®] crosslinking agents from Hughson Chemical Co.), which reportedly impart better heat aging resistance to a NR vulcanizate. GEN: T. Kempermann, "Sulfur-Free Vulcanization Systems for Diene Rubber," *Rubber Chemistry and Technology*, July–August, 1988, Vol. 61, p. 422.

For an all-natural rubber motor mount, consider applying a curable formulated chloroprene/polyoctenamer undercoat (drying the solvent) followed by the application of a formulated curable halobutyl/polyoctenamer top coating followed by drying. When properly applied and cured on the surface of the NR motor mount, this two-layer coating serves as an effective barrier against ozone attack as well as thermooxidative attack of the natural rubber. It significantly slows down the diffusion of ozone and oxygen into the NR and prevents the cleavage of the backbone of the NR molecules. Reportedly, fatigue cycling testing of NR motor mounts showed that the two-layer coating improved the cycles-to-failure results significantly. GEN: H. Graf, E. Sayej, "Reversion Resistance of Engine Mounts," *Rubber World*, February, 2000, p. 55.

Consider coating products of natural rubber with a thin layer of HXNBR to help prolong high-temperature service life. GEN: Rani Joseph (Cochin University, India), "HXNBR for Improving Ageing Resistance of Natural Rubber Products," Paper No. 1 presented at the Fall Meeting of the Rubber Division, ACS, November 1–3, 2005, Pittsburgh, PA.

■ Polychloroprene

W-type neoprenes generally impart better heat aging properties to a vulcanizate than G-type neoprene. RT: Chapter 6, "Elastomer Selection," R. School, p. 133; Chapter 8, "Specialty Elastomers," L. L. Outz, p. 208.

Octylated diphenylamine is reported to be one of the better antioxidants for polychloroprene-based compounds. GEN: R. Tabar, P. Killgoar, R. Pett, "A Fatigue

Resistant Polychloroprene Compound for High Temperature Dynamic Applications,” *Rubber Chemistry and Technology*, September–October, 1979, Vol. 52, p. 781.

Reportedly, for better AO protection for a CR compound, try Stalite S (octylated diphenylamine) at 4 phr, Aranox (*N*-phenyl-*N'*-Cp-toluenesulfonyl) at 1 phr, zinc oxide at up to 10 phr, and magnesium oxide up to 6 phr. GEN: L. Outzs, “Neoprene,” Presented at the DuPont Compounders Course, May, 2006, Fairlawn, OH.

EVM

Ethylene vinyl acetate (EVM), sometimes called the “forgotten rubber,” possesses good resistance to heat aging when properly compounded because it possesses a saturated backbone. Because of this fact, EVM is being used more in automotive seal and gasket applications where good heat aging resistance is needed. The EVM grades that contain a vinyl acetate content between 40 and 80% are good elastomers for rubber applications. GEN: R. Pazur, L. Ferrari, H. Meisenheimer (Bayer Inc.), “Ethylene Vinyl Acetate Copolymers: The Forgotten Rubber,” Paper No. XVI presented at the Spring Meeting of the Rubber Division, ACS, May 17–19, 2004, Grand Rapids, MI.

EPDM

EPDM reportedly can be compounded to have heat resistance up to 125°C (257°F). GEN: K. Dominic, V. Kothari, “Overview of Automotive Wire and Cable and Recent Advances,” ACS Rubber Division Meeting, Spring, 1998, Paper No. 32, p. 13.

Using peroxide to cure an EPDM compound will improve its heat aging resistance. RT: Chapter 6, “Elastomer Selection,” R. School, p. 132.

Low-Viscosity, Gas-Phase EPDM Needs Less Oil

Try compounding with an ultra-low Mooney viscosity gas-phase polymerized EPDM with very high ethylene content and filler loading. Higher ethylene content reportedly improves the processability of the compound without dependency on the use of traditional processing oils and plasticizers, which can sometimes impart poor hot air aging properties. GEN: A. Paeglis, “Very Low Mooney Granular Gas-Phase EPDM,” Presented at ACS Rubber Div. Meeting, Fall, 2000, Paper No. 12.

■ EPDM/CR

Consider adding a small quantity of CR (or other chlorinated polymer) to a peroxide-cured EPDM compound to improve the compound's heat resistance. GEN: R. Ohm, R. Annicelli, T. Jablonowski, C. Lahiri, R. Mazzeo, "Optimizing the Heat Resistance of EPDM and NBR," ACS Rubber Div. Meeting, Fall, 2000, Paper No. 99, p. 5.

■ EPDM/CR Alloy

Consider developing a rubber compound based on a blend of 70 phr of Neoprene GRT, 30 phr of EPDM, with a compatibilizer of escor acid terpolymer at 10 phr (ethylene-methacrylate-acrylic acid terpolymer), which displays superior DeMattia cut growth resistance, heat resistance, and ozone resistance, which is claimed to be good for many power transmission belt applications. GEN: P. Arjunan, R. Kuszniir, A. Dekmezian, "Compatibilization of CR/EPM Blends for Power Transmission Belt Applications," *Rubber World*, February, 1997, p. 21.

■ EPDM/POE

EPDM compound heat aging resistance can be improved by blending with polyolefin elastomer (POE). RT: Chapter 6, "Elastomer Selection," R. School, p. 139.

■ Butyl and Halobutyl

Consider using compounds based on butyl and halobutyl rubber instead of general purpose rubber. RT: Chapter 8, "Specialty Elastomers," G. Jones, D. Tracey, A. Tesler, p. 174.

ExxonMobil's Exxpro (BIMSM, brominated copolymer of isobutylene and paramethylstyrene) has no unsaturation in its backbone. Therefore, BIMSM has more heat resistance than halobutyl rubbers, which do possess a small level of unsaturation in their backbone. Therefore, using BIMSM in place of halobutyl rubber in the tire innerliner may result in the innerliner being more heat resistant, thus improving the service life of the tire innerliner under severe service conditions. GEN: G. Jones, "Exxon's Exxpro Innerliner for Severe Service Tire Applications," Presented at the 1996 ITEC Meeting, September, 1996, Akron, OH.

■ HIIR

Halobutyl rubber may provide better resistance to heat aging than regular butyl rubber cured with a conventional sulfur vulcanization system. RT: Chapter 8, "Specialty Elastomers," G. Jones, D. Tracey, A. Tisler, p. 185.

Higher heat resistance is obtained with halobutyl rubber when cured with bis-maleimide (HVA-2) either with or without peroxide. RT: Chapter 8, "Specialty Elastomers," G. Jones, D. Tracey, A. Tisler, p. 186.

Cure bromobutyl-based compound with a proprietary curative called Vanax 189 from R. T. Vanderbilt for significantly improved heat aging resistance. Vanax 189 is a derivative of 1,2-dimercapto-1,3,4-thiadiazole. GEN: R. Ohm, "New Developments in Curing Halogen-Containing Polymers," Presented at ACS Rubber Div. Education Symposium No. 45, "Automotive Applications II," Spring, 1998, p. 4.

Consider curing a halobutyl compound with zinc oxide and certain diamine AOs such as di-beta-naphthyl-*p*-phenylenediamine (Agerite White[®]). This may improve the compound's heat resistance. (The mechanism may involve a Friedel-Crafts alkylation reaction.) GEN: J. Dunn, "Compounding Elastomers for Tomorrow's Automotive Market, Part II," *Elastomerics*, 1989, p. 28.

Using a substituted *p*-phenylenediamine AO such as *N,N'*-di-beta-naphthyl-*p*-phenylene-diamine (DNPD or Agerite White[®]) and zinc oxide as crosslinking agents for a bromobutyl-based compound may improve air aging resistance. GEN: D. Edwards, "A High-Pressure Curing System for Halobutyl Elastomers," *Rubber Chemistry and Technology*, March-April, 1987, Vol. 60, p. 62.

In tire innerliner compounds, use less natural rubber and more halobutyl rubber to improve heat resistance. GEN: W. Waddell, R. Napler, D. Tracey, "Nitrogen Inflation of Tires," Paper No. 45 presented at the Fall Meeting of the Rubber Division, ACS, October 14-16, 2008, Louisville, KY.

BIIR vs. CIIR

Compounds based on BIIR may give slightly better heat resistance than those based on CIIR. GEN: J. Fusco, "New Isobutylene Polymers for Improved Tire Processing," Presented at the Akron Rubber Group Meeting, January 24, 1991, Akron, OH.

BIMS

Use Exxon's EXXPRO[®] (polyisobutylene with brominated *p*-methylstyrene cure site) for further heat resistance over regular halobutyl rubber, which relies on unsaturation sites as cure sites. GEN: R. Ohm, "New Developments in Curing Halogen-Containing Polymers," Presented at ACS Rubber Div. Education Symposium No. 45, "Automotive Applications II," Spring, 1998, p. 5.

Brominated isobutylene-co-*p*-methylstyrene (BIMS)-based compounds may have better heat aging properties than a conventional halobutyl rubber compound under more severe temperatures such as 125°C (257°F) or 150°C (302°F). GEN: G. Jones, "Exxpro Innerliners for Severe Service Tire Applications," Presented at ITEC, 1998, Paper No. 7A.

■ Avoid Zinc for CM and CSM

For compounds based on chlorinated polyethylene (CM) or chlorosulfonated polyethylene (CSM), *avoid* incorporating *any* zinc-containing materials into the formulations or in any way using any zinc-containing coatings or dusting agents that might come in contact with these formulations because they will seriously degrade heat resistance and state of cure. RT: Chapter 8, “Specialty Elastomers,” L. Weaver, C. Baddorf, pp. 212, 215.

■ CR

Generally, mercaptan-modified neoprene has better heat resistance than the sulfur-modified or xanthate-modified neoprene. GEN: Nobuhiko Fujii, Denki Kagaku Kogyo K. K. (Denka), “Recent Technical Improvements of CR and ER in Industrial Applications,” Denka Literature, 2011.

■ CSM

Epoxidized soybean oil (ESO) and sometimes epoxidized glycerol dioleate (EpGdO) reportedly impart better stability from exposure to air oven aging of chlorosulfonated polyethylene (CSM)-based compounds. RT: Chapter 14, “Ester Plasticizers and Processing Additives,” W. Whittington, p. 358.

Nickel dibutyldithiocarbamate (NBC) reportedly may improve the heat resistance of Hypalon[®]. RT: Chapter 19, “Antidegradants,” F. Ignatz-Hoover, p. 453.

■ CPE

Selecting grades of chlorinated polyethylene with lower percentage of chlorine may allow better resistance to heat aging. RT: Chapter 8, “Specialty Elastomers,” L. Weaver, p. 213.

Epoxidized ester plasticizers reportedly impart better stability from exposure to air oven aging of CPE-based compounds. RT: Chapter 14, “Ester Plasticizers and Processing Additives,” W. Whittington, p. 359.

A four-way comparison of compounds based on CM, CSM, GECO, and NBR/PVC found that CM gave superior heat resistance in relation to the other three elastomers. GEN: C. Hooker, R. Vara, “A Comparison of Chlorinated and Chlorosulfonated Polyethylene Elastomers with Other Materials for Automotive Fuel Hose Covers,” Presented at ACS Rubber Div. Meeting, Fall, 2000, Paper No. 128.

■ Avoid High-Styrene Resins

High-styrene resins should be avoided for compounds that will be used in service at high temperatures. RT: Chapter 18, “Tackifying, Curing, and Reinforcing Resins,” B. Stuck, p. 446.

Silicone Rubber

PVMQ silicone gums impart to a rubber compound somewhat better resistance to heat than do VMQ silicone gums. RT: Chapter 8, "Specialty Elastomers," J. R. Halladay, p. 235.

In silicone rubber compounding, precipitated silica can impart superior heat aging properties above 200°C (392°F). RT: Chapter 8, J. R. Halladay, "Specialty Elastomers," p. 236.

In silicone compounding, traditional antioxidants are not used; however, heat stabilizers are used. Red iron oxide (at 1 to 2 phr) is an inexpensive heat stabilizer that is sometimes used in silicone rubber compounding. Barium zirconate at about 4 phr is also an important stabilizer for light-colored compounds. Many commercial silicone bases already have heat stabilizers and may not require additional stabilizers. RT: Chapter 8, J. R. Halladay, "Specialty Elastomers," p. 236.

Reportedly, some silicones can be compounded to display heat resistance up to 260°C (500°F). GEN: M. Chase, "Roll Coverings Past, Present, and Future," Presented at Rubber Roller Group Meeting, New Orleans, May 15-17, 1996, p. 7.

Polyurethane

Polyurethanes are in general not considered "high-temperature materials." However, usually, but not always, selecting a polyurethane based on a TDI prepolymer will give better high-temperature properties. In addition, selecting an ester-type polyurethane will usually give better heat aging resistance in demanding applications. RT: Chapter 9, "Polyurethane Elastomers," R. W. Fuest, p. 257.

Castable polyurethane fabricators using MDI prepolymer systems may be able to increase their product's tolerance to high-temperature exposure by trying to use aromatic diol chain extenders such as bis(hydroxyethyl) ether of resorcinol (HER) and hydroquinone (HQEE). The use of these chain extenders will create hard domains that have higher melting points. GEN: R. Durairaj, "Chain Extenders Increase Heat Tolerance," *Rubber & Plastics News*, November 29, 1999.

A novel polyurethane elastomer based on *p*-phenylene diisocyanate (PPDI) has been reported to give very good aging property retention at 150°C. GEN: Z. Zhu, R. Rosenberg, V. Gajewski, G. Nybakken, M. Ferrandino (Chemtura Corp.), "High Performance Polyurethane Elastomers," Paper No. 31 presented at the Fall Meeting of the Rubber Division, ACS, November 1-3, 2005, Pittsburgh, PA.

XLPE

Reportedly, XLPE can be compounded to have heat resistance up to 125 to 150°C (257 to 302°F). GEN: K. Dominic, V. Kothari, “Overview of Automotive Wire and Cable and Recent Advances,” Presented at ACS Rubber Div. Meeting, Spring, 1998, Paper No. 32, p. 13.

Silicone/EPDM

Using compounds based on silicone-EPDM in place of straight EPDM compounds can enable heat resistance up to 204°C (399°F). GEN: M. Chase, “Roll Coverings Past, Present, and Future,” Presented at Rubber Roller Group Meeting, New Orleans, May 15-17, 1996, p. 7.

TPV

Thermoplastic vulcanizates (TPVs) based on EPDM and polypropylene (PP) compositions provide excellent retention of physical properties at elevated temperatures with aging, provided the service temperatures are sufficiently below the melt transition temperature of the TPV. RT: Chapter 10, “Thermoplastic Elastomers,” C. P. Rader, p. 274.

High-temperature limits for TPVs are determined by the susceptibility to oxidative attack by the thermoplastic phase. For polypropylene (PP), this oxidative limit may be approximately 125 to 135°C (257 to 275°F). RT: Chapter 10, “Thermoplastic Elastomers,” C. P. Rader, p. 276.

Thermoplastic vulcanizate alloys consisting of dynamically vulcanized polyacrylate rubber (ACM) with polyamide (PA) provide material that can withstand long-term exposure to temperatures around 150°C. GEN: Jiri G. Drobay, “High Performance Thermoplastic Elastomers: A Review,” Paper No. 69 presented at the Fall Meeting of the Rubber Division ACS, October 14-16, 2008, Louisville, KY.

Also, consider using Dupont’s thermoplastic elastomers called the ETPV family consisting of a copolyester matrix with highly crosslinked AEM (modified ethylene-acrylate rubber), which reportedly may handle temperatures of 135°C continuously and peaks that are as high as 180°C. GEN: J. Drobny (Drobny Polymer Associates), “High Performance Thermoplastic Elastomers: A Review,” Paper No. 69 presented at the Fall Meeting of the Rubber Division, ACS, October 14-16, 2008, Louisville, KY.

Silica

Consider using precipitated silica in a rubber compound where an improvement in heat aging resistance is needed. RT: Chapter 13, “Precipitated Silica and Non-black Fillers,” W. Waddell, L. Evans, p. 331.

Carbon Nanotubes

Reportedly, from the use of multiwalled carbon nanotubes (MWCNT) in an NBR formulation, the percent retention in ultimate tensile strength from high-temperature exposure was significantly improved. GEN: Steve Driscoll, Status Report titled "U. Mass. Lowell Today"; N. Warasitthinon, L. Schulte, A. Erley, A. Hope, et al., "Nanocomposites of Nitrile Rubber with Multi-walled Carbon Nanotubes," Presented at the India Rubber Expo 2011, January 2011, Chennai, India.

CPE Nanoclay composites

Consider using organically modified clay montmorillonite (such as natural montmorillonite modified with quaternary ammonium salts) dispersed in a CPE compound. Reportedly this improves heat resistance. GEN: S. Kar, K. Bhowmick, "Thermal Mechanical Behavior of Chlorinated Polyethylene Nanocomposites," Paper No. 56 presented at the Fall Meeting of the Rubber Division, ACS, October 14–16, 2008, Louisville, KY.

Talc

It has been reported that substituting 40% of the carbon black in an EPDM hose compound with talc resulted in an improvement in heat aging resistance. Certain grades of talc may show a significant advantage over treated and untreated clay as well. GEN: O. Noel, unpublished draft, "Talc Synergy with Carbon Black in Sulfur Donor Cured EPDM," June, 2003; H. Bertram, "Influence of Light Colored Fillers on the Aging Behavior of NBR Vulcanizates," Bayer TIB 17. RP: O. Noel.

Plasticizers

Polymeric plasticizers should be considered instead of monomeric plasticizers for better heat aging and permanence. RT: Chapter 14, "Ester Plasticizers and Processing Additives," W. Whittington, pp. 356, 362.

Synthetic plasticizers with higher viscosity, such as polymeric plasticizers, impart better permanence and aging properties to a rubber compound than monomeric synthetic plasticizers generally do. RT: Chapter 14, "Ester Plasticizers and Processing Additives," W. Whittington, p. 362.

Consider substituting hydrocarbon resins in place of the more volatile plasticizers and processing oils to retain better permanence and impart better heat aging resistance. GEN: "Hydrocarbon Resins for Rubber Compounding," Neville Literature, 2008, Neville Chemical Co.

■ High-Viscosity Oils

For good heat aging resistance, use processing oils with high-viscosity properties because they usually have fewer low molecular weight components and better permanence (less volatility) in a compound than a low-viscosity oil. GEN: R. Tabar, P. Killgoar, R. Pett, "A Fatigue Resistant Polychloroprene Compound for High Temperature Dynamic Applications," *Rubber Chemistry and Technology*, September–October, 1979, Vol. 52, p. 781.

■ Rapeseed Oil for CR

For the best neoprene compound resiliency, consider using rapeseed oil because it has low viscosity for hysteresis and low volatility for good aging properties. GEN: R. Tabar, P. Killgoar, R. Pett, "A Fatigue Resistant Polychloroprene Compound for High Temperature Dynamic Applications," *Rubber Chemistry and Technology*, September–October, 1979, Vol. 52, p. 781.

■ Vulcanized Vegetable Oil

If a brown vulcanized vegetable oil (VVO) is being used in a natural rubber compound, it may be better to use a VVO based on soybean oil rather than on boiled linseed oil for the better retention of compound air aging properties. GEN: S. Botros, F. El-Mohsen, E. Meinecke, "Effect of Brown Vulcanized Vegetable Oil on Ozone Resistance, Aging, and Flow Properties of Rubber Compounds," *Rubber Chemistry and Technology*, March–April, 1987, p. 159.

If an NR compound contains a brown vulcanized vegetable oil (VVO), the compound's heat resistance will increase if VVOs are used that contain lower percent free sulfur levels or lower percent acetone extract values. GEN: S. Botros, F. El-Mohsen, E. Meinecke, "Effect of Brown Vulcanized Vegetable Oil on Ozone Resistance, Aging, and Flow Properties of Rubber Compounds," *Rubber Chemistry and Technology*, March–April, 1987, p. 159.

■ Ultra-accelerators

Cure systems based on ultra-accelerators such as thiurams and dithiocarbamates tend to impart higher percentages of monosulfidic crosslinks compared to thiazole or amine-type accelerators. Therefore these ultra-accelerators often will impart better aging properties to their vulcanizates. GEN: M. Studebaker, J. R. Beatty, "Vulcanization," *Elastomerics*, February, 1977, p. 41.

■ EV/Semi-EV Cures

Use compounds based on an efficient vulcanization (EV) or semi-efficient (semi-EV) cure system where the ratio of accelerator to sulfur is high and sulfur

donors are sometimes used in place of free sulfur. These cure systems generate a higher preponderance of monosulfidic and disulfidic crosslinks, which are thermodynamically more stable than polysulfidic crosslinks. Therefore, semi-EV and EV cures impart better heat aging properties to a rubber compound and better thermal stability than conventional sulfur cures. RT: Chapter 15, "Sulfur Cure Systems," B. H. To, p. 387.

HTS

Hexamethylene-1,6-bisthiosulfate (HTS), a post-vulcanization stabilizer, reportedly forms special hybrid crosslinks when it is used as a supplement to a sulfenamide cure to impart better heat aging resistance to a natural rubber compound and good flex fatigue resistance. RT: Chapter 15, "Sulfur Cure Systems," B. H. To, p. 391. Similar effects may be achieved if Perkalink 900[®] (from Flexsys) is considered for use. RP: B. H. To.

Thiuram Cure

Consider using a "thiuram cure" for improved heat aging resistance provided that environmental problems with nitrosamines can be avoided through good ventilation and so forth. GEN: T. Kempermann, "Sulfur-Free Vulcanization Systems for Diene Rubber," *Rubber Chemistry and Technology*, July–August, 1988, Vol. 61, p. 422.

Dithiophosphates vs. Dithiocarbamates

Functionally, dithiophosphate rubber accelerators are similar to dithiocarbamate accelerators except the phosphorus atoms replace the nitrogen atoms for these traditional dithiocarbamate cure packages. The dithiophosphate cures reportedly give potentially better heat aging resistance and reversion resistance as well compared to a dithiocarbamate. GEN: S. Monthey, M. Saewe, V. Meenenga (Rhein Chemie), "Using Dithiophosphate Accelerators to Improve Dynamic Properties in Vibration Isolation Applications," Presented at the Spring Southern Rubber Group, June 11–14, 2012, Myrtle Beach, SC.

DIPDIS Cure

Consider the use of an experimental accelerator, bis(diisopropyl)thiophosphoryl disulfide (DIPDIS), with synergistic combinations of conventional thiazole-type accelerators to produce NR vulcanizates with more stable crosslinks and better aging properties. GEN: S. Mandal, R. Datta, D. Basu, "Studies of Cure Synergism, Part 1: Effect of Bis(diisopropyl)thiophosphoryl Disulfide and Thiazole-Based Accelerators in the Vulcanization of NR," *Rubber Chemistry and Technology*, September–October, 1989, Vol. 62, p. 569.

■ New Crosslinking Agent

Reportedly a new crosslinking agent [1,6-bis(*N,N*-dibenzylthiodicarbonyldithio)hexane] gives stable hybrid crosslinks in truck tread compounds for better tread wear properties as well as better heat aging properties. GEN: T. Kleiner (Bayer AG), "Improvements in Abrasion and Heat Resistance by Using a New Crosslink Agent," Paper No. 12A presented at the ITEC 2002 Meeting, September, 2002, Akron, OH.

■ High Zinc Oxide Loading

Sulfur/sulfenamide-cured compounds that contain higher than usual levels of zinc oxide may possess better heat aging characteristics and better resistance to overcure. GEN: W. Hall, H. Jones, "The Effect of Zinc Oxide and Other Curatives on the Physical Properties of a Bus and Truck Tread Compound," Presented at ACS Rubber Div. Meeting, Fall, 1970.

■ NBR Cures

For curing NBR-based formulations, consider using a cure system that uses a lower amount of sulfur and a larger quantity of sulfur donor (such as TMTD or DTDM) as a partial or total replacement for the free sulfur. The use of less elemental sulfur may improve aging resistance in the nitrile compound. RT: Chapter 16, "Cures for Specialty Elastomers," B. H. To, pp. 398–403.

■ Butyl Cure

Select a semi-EV cure system using the sulfur donor DTDM to significantly improve heat aging properties of a butyl compound. RT: Chapter 16, "Cures for Specialty Elastomers," B. H. To, p. 403.

■ EPDM Cure

To improve heat aging as well as improve (i.e., reduce) compression set for EPDM compounds, one should consider a so-called "low-set" cure consisting of sulfur at 0.5 phr, ZBDC at 3.0 phr, ZMDC at 3 phr, DTDM at 2.0 phr, and TMTD at 3.0 phr. RT: Chapter 16, "Cures for Specialty Elastomers," B. H. To, p. 396.

■ ECO Cures

Zinc oxide as an activator in a Hydrin/ECO terpolymer compound has been reported to cause poor hot air oven aging. When service temperatures are near 125°C, perhaps one should consider also using calcium oxide as an activator, perhaps with a reduced quantity of zinc oxide in order to achieve better heat aging resistance. GEN: S. Harber (Zeon Chemical), "Metal Oxide Activation Systems

for Improved Aging in Epichlorohydrin Terpolymer Compounds,” Paper No. 55 presented at the Fall Meeting of the Rubber Division, ACS, October 10–12, 2006, Cincinnati, OH.

■ NR/EPDM Blend

Consider covulcanizing an NR/EPDM blend with a sulfur/peroxide cure. The EPDM will impart better heat aging properties to the compound. GEN: S. Tobing, “Co-vulcanization in NR/EPDM Blends,” *Rubber World*, February, 1988, p. 33.

■ Peroxide Cure for EPDM Compounds

For peroxide cures of EPDM compounds, consider selecting ZMTI as an antioxidant, which should allow good modulus development as well as impart good heat aging. RT: Chapter 17, “Peroxide Cure Systems,” L. Palys, p. 430.

■ Peroxide/Coagent Use

Using a coagent with a peroxide cure may improve heat aging. GEN: P. Dlużneski, “Peroxide Vulcanization of Elastomers,” *Rubber Chemistry and Technology*, July–August, 2001, Vol. 74, p. 451.

For peroxide cures, use a coagent as well to add unsaturation to the system, which results in a higher crosslink density than the peroxide would have generated if used without the coagent. The reason is that it is more efficient and easier to crosslink with a free radical to unsaturation than by hydrogen abstraction to a saturated polymer chain. Because the use of a coagent can lead to different types of crosslink networks, improved heat aging resistance may result. RT: Chapter 17, “Peroxide Cure Systems,” L. Palys, pp. 431–432.

■ Peroxide vs. Sulfur Cure

An advantage of peroxide vs. sulfur cures is that the peroxide cures can more easily be made to impart better heat aging resistance. The reason is that the carbon–carbon bond strength is about 350 kJ/mol vs. sulfur–sulfur bond strength of only 115–270 kJ/mol and carbon–sulfur bond strength of only 285 kJ/mol. RT: Chapter 17, “Peroxide Cure Systems,” L. Palys, p. 434.

■ DBU/MMBI (Heat Stabilizer) Substitute for MgO in CR and HIIR Cures

For halobutyl (HIIR) and polychloroprene (CR) compounds, it has been reported that the presence of magnesium oxide as an acid acceptor actually promotes more C–C bond links than ether and thioether links. By substituting a new heat stabilizer called “DBU/MMBI” in place of magnesium oxide, significantly improved hot air aging properties are reported for polychloroprene-, chloro-

butyl-, and bromobutyl-based compounds. The chemical identity of this “DBU/MMBI” heat stabilizer is only partially disclosed as “DBU: 1,5-diazabicyclo-(4.5.0)-undecen-(11)” or $C_9H_{16}N_2$. GEN: R. Musch, R. Schubart, A. Sumner, “Heat Resistant Curing System for Halogen-Containing Polymers,” Presented at ACS Rubber Div. Meeting, Spring, 1999, Chicago, IL.

■ Use Higher Molecular Weight TMQ

Polymerized 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) is a very cost-effective and widely used general purpose antioxidant. Using a higher molecular weight version of TMQ, such as Flectol H, will provide more antioxidant persistence over time. RT: Chapter 19, “Antidegradants,” F. Ignatz-Hoover, p. 454.

■ TMQ/6PPD

Even though TMQ by itself does not offer ozone or fatigue protection, it is commonly used to extend the effectiveness of 6PPD itself. This is particularly important if the compound is exposed to oxidative aging before exposure to ozone. Therefore it is quite common to see a synergistic combination of TMQ and 6PPD used together to achieve the best combination of both oxidative aging protection as well as protection against ozone attack. RT: Chapter 19, “Antidegradants,” F. Ignatz-Hoover, pp. 454–460.

■ TMQ/BLE

Consider a blend of TMQ and BLE if both good heat aging and flex fatigue properties are needed. GEN: S. Hong, C. Lin, “Improved Flex Fatigue and Dynamic Ozone Crack Resistance Through the Use of Antidegradants or Their Blends in Tire Compounds,” Presented at ACS Rubber Div. Meeting, Fall, 1999, Paper No. 27.

■ Metal “Poisons”

In general, avoid rubber compounding ingredients and raw rubbers themselves that may contain any copper, manganese, nickel, or cobalt. These transition elements can function as pro-oxidants and promote the degradation of the vulcanizate. To some extent, alkyl-aryl PPDs and dihydroquinoline-type AOs in black compounds will react with these “metal poisons.” For nonblack compounds, dinaphthyl-PPD and TMQ can also be used for partial protection. RT: Chapter 19, “Antidegradants,” F. Ignatz-Hoover, pp. 454, 461–462.

■ Bound Antioxidants

Antioxidants can be chemically bound to the backbone of the raw NBR polymer before it is added to the mixing process. This improves the compound’s resist-

ance to heat while also providing resistance to extraction. RT: Chapter 6, "Elastomer Selection," R. School, p. 131.

Some improvement in air oven aging for nitrile-based compounds can be achieved if an NBR is substituted that contains a bound antioxidant; however, the amount of improvement in air oven aging is not even comparable to the much greater improvement achieved by using HNBR instead. RT: Chapter 8, "Specialty Elastomers," M. Gozdoff, p. 199.

Use raw synthetic elastomers in which a hindered phenol or an amine antioxidant is "bound in" to the polymer backbone and can thus impart antioxidant protection to a rubber compound even under harsh environmental conditions. RT: Chapter 19, "Antidegradants," F. Ignatz-Hoover, pp. 454-455.

Use *N*-phenyl-*N'*-1,3-dimethylbutyl-*p*-quinone diimine (6-QDI) in a rubber compound that uses sulfur-vulcanization of a diene rubber base. After vulcanization, a portion of the 6QDI is chemically bonded to the polymer backbone and/or the carbon black and cannot be extracted. Thus this bound antioxidant is reported to perform better than a traditional 6PPD/TMQ combination. RT: Chapter 19, "Antidegradants," F. Ignatz-Hoover, p. 454.

■ Resin Cures

The use of a methylol phenol-formaldehyde resin cure in place of a sulfur cure for a butyl compound should significantly improve the compound's heat aging resistance. These resins can be used to cure some other elastomers as well, not just butyl rubber. RT: Chapter 8, "Specialty Elastomer," G. Jones, D. Tracey, A. Tisler, p. 178; Chapter 18, "Tackifying, Curing and Reinforcing Resins," B. Stuck, p. 443.

■ Bisphenol Cures for FKM

In some situations, for better heat resistance, consider using a bisphenol cure system in place of a traditional peroxide cure system for vulcanizing FKM compounds. GEN: Daikin America Inc., "New DAI-EL Fluoroelastomers for Extreme Environments," Presented at the Fall Meeting of the Energy Rubber Group, September 15-18, 2008, San Antonio, TX.

■ Fibers to Retain Physical Properties

Consider using a low loading of short aramid fiber to improve cured physical property retention at high temperatures such as 150°C (302°F). GEN: K. Watson, A. Frances, "Elastomer Reinforcement with Short Kevlar Aramid Fiber for Wear Applications," *Rubber World*, August, 1988, p. 20.

■ Nitrogen Inflation

Tires inflated with nitrogen instead of air may impart some protection against oxidative aging. GEN: J. MacIsaac, L. Evans, J. Harris, E. Terrill, "The Effects of Inflation Gas on Tire Laboratory Test Performance," Paper No. 18C-1 presented at ITEC 2008, September 16, 2008, Akron, OH; U. Karmarkar, A. Pannikottu (ARDL), "Role of Materials Research in Laboratory Tire Aging and Durability Test Development," Paper No. 17 presented at the Fall Meeting of the Rubber Division ACS, 1999, Cincinnati, OH.

■ 3.2 Improving Ozone Resistance

Ozone attack on a rubber product is usually a surface phenomenon. The average ambient concentration of ozone in the air we breathe has been rising. Ozone attack on certain strained rubber products usually results in cracking. This can severely damage or ruin a rubber product.

*The following **experimental** ideas might improve a cured rubber compound's resistance to ozone attack. Also, all relevant literature sources, including the ones cited below, should be researched and read. **Caution:** these general experimental ideas may not work in all specific situations. Changes to improve ozone resistance will certainly affect other properties as well, for better or for worse, and this book does not purport to show how these other properties are affected. Also, this book does not purport to address safety and health issues.*

■ Waxes

For static ozone protection, it can be important to use a special blend of protective waxes, usually consisting of low molecular weight paraffin, high molecular weight paraffin, and microcrystalline wax. These blends are usually necessary to achieve the proper performance. Wax is used mostly for static protection. In fact if too much wax is used in the formulation, dynamic ozone protection could be harmed. RT: Chapter 3, "Vulcanizate Physical Properties, Performance Characteristics, and Testing," J. S. Dick, p. 64; Chapter 19, "Antidegradants," F. Ignatz-Hoover, p. 456. GEN: R. Layer, R. Lattimer, "Protection of Rubber Against Ozone," *Rubber Chemistry and Technology*, July–August, 1990, Vol. 63, p. 426.

■ PPDs

Paraphenylene diamines (PPDs) are very potent antiozonants providing good dynamic protection. RT: Chapter 19, "Antidegradants," F. Ignatz-Hoover, p. 454. Many times, for good dynamic ozone protection, it is important to use an effective *p*-phenylenediamine antiozonant such as 6PPD. RT: Chapter 3, "Vulcanizate Physical Properties, Performance Characteristics, and Testing," J. S. Dick, p. 64. A combination of 6PPD (for long-term applications) and 77PPD (for short-term applications) is commonly used for better protection from ozone. GEN: L. Walker, J. Luecken, "Antidegradants for Ozone and Fatigue Resistance: Laboratory and Tire Tests," *Elastomerics*, May, 1980, p. 36.

The new high silica loaded tire compounds for lower rolling resistance may require higher loadings of PPD antiozonants because the silica particles absorb some of the PPD antiozonant itself. GEN: F. Ignatz-Hoover, D. Killmeyer,