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Compounding Precipitated Silica in Elastomers

Norman Hewitt

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COMPOUNDING PRECIPITATED SILICA IN ELASTOMERS

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CHAPTER 1

SILICA AS A REINFORCING FILLER

1.1 INTRODUCTION

The subject of this chapter is fine particle, precipitated, hydrated silica and its use as a reinforcing filler for elastomer compounds. A more complete definition, relative to its position in the family of silicas, relies on a classification of commercial silicon dioxide, based on origin and primary particle size. Table 1.1 is a partial listing of the many varieties used in rubber compounding under the word “silica”.

Table 1.1 Forms and Properties of Silica Used in Rubber Compounding

	Primary Size, μm	**Function in Rubber**
Natural (crystalline):		
Ground quartz	1-10	Extending
Diatomite	1-5	Processing; Extending
Neuberg silica	1-5	Extending
Synthetic (amorphous):		
Fumed	0.005-0.02	Reinforcing
Precipitated	0.01-0.03	Reinforcing
Precipitated	0.04	Semi-reinforcing
Precipitated	0.08	Processing; Color
Ferro-silicon by-product	0.10	Extending

The two major classes, based on origin, are natural and synthetic. This distinction translates to a division between crystalline and amorphous forms, and, of equal importance, to a substantial division between coarse and fine primary particles.

Among the natural, non-reinforcing materials, the term “ground quartz” includes a number of variously named grades which are defined in respect to their geographic and geologic origin. For example, the grade known as “tripoli” is quartz mined mainly in southern Illinois, USA. The adaptability of this material to fine grinding has led to an erroneous classification as an amorphous type. Neuberg silica, better known as Sillitin™, derives from a German deposit of corpuscular quartz and kaolin. Quartz fillers find their principal use as extenders in silicone compounds, and elsewhere, to provide transparency.

Among the synthetic group, rubber reinforcement, in terms of enhanced abrasion resistance and tear and tensile strengths, is supplied only by those precipitated and fumed silicas with primary particle diameters below 40 nanometers (0.040 microns). The larger particle size grades (above 40 nanometers) are noted for their contribution to nerve reduction and smooth, extruded surfaces during compound processing operations.

The largest particle material, used only as an extender, is a furnace type, sometimes called microsilica. It is formed as a by-product during the manufacture of ferro-silicon alloy or silicon metal.

Fumed or pyrogenic silicas offer the smallest particle sizes and, therefore, the highest degree of reinforcement. They are produced by the high temperature hydrolysis of silicon tetrachloride, a process which results in a pure silica with low silanol and water content. Processing problems and high prices have limited fumed silica markets to silicone compounds and other specialty elastomers.

The ensuing compounding discussions and formula recommendations in Chapters 2 to 7 are centered on the reinforcing grades of precipitated silicas in the 15 to 20 nanometer size range.

1.2 MANUFACTURE OF PRECIPITATED SILICA

Precipitated silica is produced by the controlled neutralization of dilute sodium silicate (waterglass) by either concentrated sulfuric, hydrochloric, or carbonic acids. The raw materials are those required for the silicate: sand, soda ash, caustic soda, and water. The silicate can be produced in furnace or digester operations, but in either case the ratio of SiO_2 to Na_2O is generally within a range of 2.5 to 3.5. Dilution with water provides relatively low silicate concentrations, which, together with moderate acidification rates, produce a precipitate of particulates rather than gel agglomerates. A minor amount of gel is usually present. Reaction temperature is the major determinant of primary particle size.

Precipitation produces a low solids content slurry of hydrated silica and residual salts, either sodium sulfate, sodium chloride or sodium carbonate. The salts are removed by washing in either a counter-current decantation system or by filter press. Washing reduces the salt content to 1 or 2%. Further concentration in rotary or plate and frame filters produces a solid wet cake which still contains only 15 to 25% silica. Because of this high water content, the final drying step, whether by rotary, tray, belt or spray dryers, is a large consumer of energy. Due to lower investment and operating costs, spray drying has become the dominant drying process. In all cases the final product still contains about 6% free water, which is roughly the equilibrium free water content at 50% relative humidity. The end product is often milled and compacted to attain an optimum balance between the absence of visible particles and minimal dustiness during rubber mixing.

Precipitation, if carried out with too rapid addition of concentrated acids, produces a small amount of silica gel. Gel content generally has no adverse effect on reinforcement, but it can be a significant source of undispersed, visible particles in the mixed elastomer compound. Visible dispersion is discussed further in Section 1.6.

Silica manufacturing stages can be related to rubber processing and compound properties. Reinforcement potential depends entirely on primary particle size, which is fixed during the early stages of neutralization. Precipitation parameters involved in setting particle size include temperature, silicate ratio, reaction rate, reactant concentrations, and the presence of additives. Precipitation temperature correlates with size; low temperatures produce small particles. Slow rates of neutralization reduce gel formation. Silicate and acid concentrations also relate to gel formation; high concentrations produce more gel. These relationships are summarized in Table 1.2.

Table 1.2 Manufacture and Compounding

Silica operation	**Behavior in rubber**
Precipitation	Reinforcement
Precipitation; drying; milling; compaction	Visible dispersion
Drying; milling; compaction	Dustiness

1.3 SILICA AND CARBON BLACK

A description of fine particle precipitated silica will benefit from a comparison to carbon black, the major reinforcing filler for many rubber compounds. Carbon blacks are manufactured in a wide range of primary particle sizes (surface areas). This provides the basis for classifying the various commercial grades. Classification by size is accompanied by a second basic property, termed structure. Structure in this case refers to chain-like forms which have a significant influence on processing and vulcanizate properties of a black reinforced elastomer compound. The third basic characteristic is surface activity, which denotes the presence of functional groups on the black particle surface. These groups enable chemical bonding of the carbon black to the polymer. Their importance in the reinforcing function is evident in a comparison to graphite of comparable particle size where the lack of these surface groups renders the graphite non-reinforcing.

These three characteristics also apply to precipitated silica, but with significant modification. Primary particle size, generally indicated by surface area measurement, is, as for carbon black, the most important factor in predicting reinforcement. As noted elsewhere, the term reinforcement is defined here as superior values of abrasion resistance, tensile strength and tear strength in the vulcanizate. High surface area values predict a high level of reinforcement. Silica surface area values are higher than those of blacks of comparable particle size.

Efficient reinforcing action, however, requires the presence of surface functional groups (surface activity) which provide a substantial bond of filler to elastomer. In contrast to the organic nature of the black surface, the silica surface is inorganic, saturated with silanols (SiOH). A model view is seen in Figure 1.1.

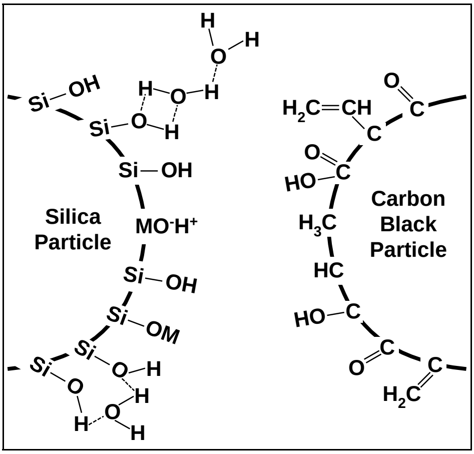


Figure 1.1 Hydrophilic Silica Surface; Hydrophobic Carbon Black Surface

These silanols produce the hydrophilic reactivity of precipitated silica. They also attract a transient cloud of free water, described in detail in a following section. Unfortunately, this silanol-water surface is incapable of forming a strong bond with organic elastomers. The compounding results of this inadequate polymer bonding include low values for high extension (>50%) modulus, poor abrasion resistance, excellent tear strength and excessive heat build-up, all relative to comparable black reinforced compounds. This situation can be completely reversed when the silanol surface has been reacted, either before or during mixing, with a mercaptosilane. Silane modification is discussed in several of the compounding chapters.

Perhaps the most interesting difference between carbon black and silica resides in the term structure. Black structure can be regarded as the formation of chain or branched configurations during manufacture. These are permanent features, unchanged by compound mixing, and are the basis for classifying blacks as high or low structure grades. In contrast, silica structure refers to the hydrogen bonding of individual particles to form clusters, not chains. This structure is transient and is easily modified or removed during mixing and by the use of additives. It is responsible for the stiff or boardy nature of some silica reinforced compounds. A related effect is the hardening of silica compounds during bin storage.

Differences in surface chemistry and structure between carbon black and silica can be readily related to compound characteristics. Silica surface silanols produce a low degree of silica-elastomer bonding, which leads to low abrasion resistance, high elongation, and low modulus in silica compounds. As noted in the chapters on solution polymers, zinc contamination of the silica surface is also involved in these deficiencies. The silica silanol surface reaction with soluble zinc is the major influence on the low cure states (reduced crosslinking) associated with silica compounds. Silica's cluster structure relates to high viscosity during processing and higher hardness after curing. The transient nature of this structure has become a significant factor in reducing energy consumption in dynamic applications. An pertinent example is the tread of the "green" tire, which can significantly reduce gas consumption.

1.4 SILICA SURFACE AREA

A typical commercial specification or description of a precipitated silica will include the properties noted in Table 1.3.

Table 1.3 Specification Properties of Precipitated Silica

Property	**Range**
N_2SA*, single point, m^2/g:	
Reinforcing	125-250
Semi-reinforcing	35-100
Free water, % loss @ 105°C	6 ±3
Bound water, % (silanols)	3 ±0.5
pH: Reinforcing	5-7
Semi-reinforcing	6-9
Salt content, %	0.5-2.5
Specific gravity in rubber	2.0 ± 0.05

*BET nitrogen surface area

Surface area, determined by BET (Brunauer, Emmett, Teller) nitrogen (N_2SA) or CTAB (cetyl trimethyl ammonium bromide) methods, is essentially a stand-in for primary particle size, measurement of which requires time consuming and expensive electron microscopy. Large surface areas denote small particles. The reinforcing range for particle diameter size is 10 to 30 nanometers. This generally corresponds to surface areas of 250 to 125 square meters per gram (exceptions noted in the Section 1.7 on silanols). This relationship between size and area works fairly well for particulate particles, but can be quite misleading if applied to silica gel. Silica gel agglomerates, although characterized by surface areas as high as 1000 m^2/g, are too large to provide rubber reinforcing properties. Physical form – powder, pellet or flake – bears no relation to primary particle size.

Fine primary particle size, together with surface activity (functional groups noted in Figure 1.1) comprise the basic requirements for rubber reinforcement for both silica and carbon black. The actual size of the reinforcing unit is, however, not only that of the individual particle but, more often, that of small agglomerates. Electron micrographs of a cured rubber compound which contains silica of 20 nanometers average primary particle diameter will show many agglomerates (or aggregates) 40 to 100 nanometers in diameter.

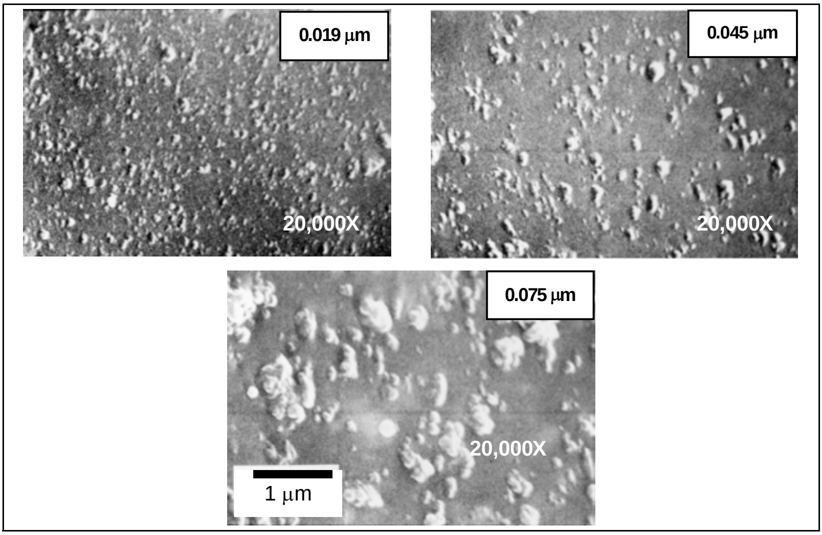


Figure 1.2. Ultimate Particle and Agglomerate Size; 30 phr in NR

This cluster structure is quite different from the chain structure characteristic of reinforcing furnace blacks. Silica agglomerate structure is present in milled and vulcanized compounds, although mixing conditions, water content and various compound additives influence the size of the agglomerates and, thereby, compound properties. The electron micrographs in Figure 1.2 illustrate the situation for three silicas of different surface area compounded at 30 parts per hundred parts (phr) in natural rubber.

Small particles (high surface area) produce small agglomerates; large particles produce large agglomerates with larger filler-free areas. The latter observation is helpful in explaining the ability of semi-reinforcing silica to maintain flow while reducing nerve in extruding and calendering operations. Particle size influence on compound properties is discussed in each of the separate polymer chapters.

1.5 SILICA FREE WATER

Free water content reflects the hydrophilic nature of silica and its tendency to adsorb moisture to attain equilibrium with the relative humidity of its environment, as illustrated in Figure 1.3.

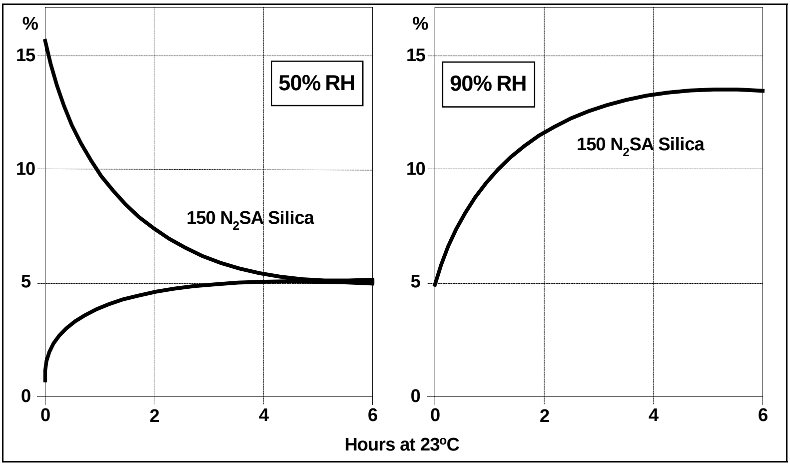


Figure1.3 Equilibrium Moisture Content

During manufacture, water or steam is sometimes added to the dried product to reduce electrostatic charges on fine particles and to alleviate the cure retarding effects of dry silica. The latter phenomenon is responsible for much of the processing and vulcanizate variability associated with silica reinforced compounds. Free water acts as a barrier to reduce the attachment of silica surface silanols (SiOH) to soluble zinc and hydrogen bonded materials. In particular, this removal of zinc from its cure activating function has a profound retarding effect on cure rate. Since variable amounts of free water can be lost during mixing, cure rates will, of necessity, vary. Use of permanent barrier materials such as glycols provides a partial solution to this problem. Free water content is generally determined by moisture balance at 160-200ºC or in a vacuum oven at 105ºC.

Unfortunately, the barrier effect of water on soluble zinc attachment is also a cause of reduced bonding of silica to elastomer. This effect is obviously a hindrance to reinforcement, and is partially the cause of lower than expected abrasion resistance and high-strain modulus in silica reinforced compounds. Later discussions of “zinc-free” acceleration describe a compounding approach to the barrier problem.

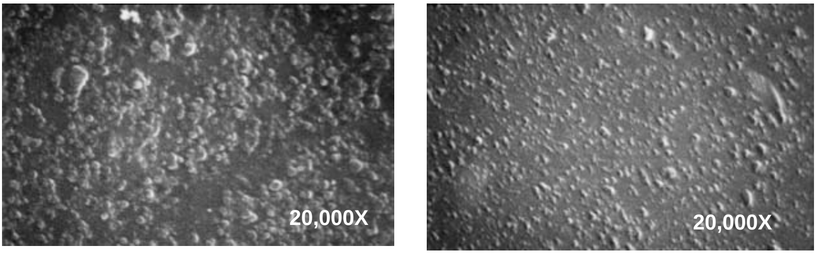
Table 1.4 illustrates the effects of free water variation in a peroxide cured natural rubber reinforced with 30 phr silica, adjusted to maintain equal SiO_2 content.

Table 1.4 Free Water Content; Peroxide Cure

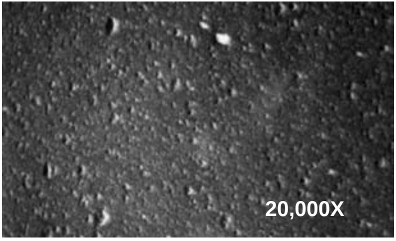
	A	**B**	**C**
Silica free water, %	6.0	0.2	0.2
160 m^2/g N_2SA Silica, phr	30	28	28
Mercaptosilane	-	-	1
ODR cure at 160ºC, T_{90}, minutes	18	16	22
ODR Mh-ML crosslinks, dN-m	61	52	52
Mooney viscosity, ML_4100	66	90	74
Durometer hardness	60	57	53
300% modulus, MPa	6.9	7.8	9.2
Elongation, %	495	490	430
Pendulum rebound, 100ºC	84.1	86.5	88.4
SEM predominant silica size range in vulcanizates, nm	30-100	30-70	30-50
Other ingredients: SMR CV60 NR- 100; ODPA- 1; paraffinic oil- 3; Dicumyl peroxide- 2.4			

The major changes due to “dry” silica (less than 1% water) include increased viscosity (50% increase), reduced hardness and increased high-strain modulus. The combination of higher viscosity and lower hardness is probably unique to hydrated silica and calls for explanation. In this case, the inclusion of silane coupling effects (compound C) and the scanning electron micrographs of these three compounds, in Figure 1.4, provide enlightenment.

It is evident in Table 1.4 that an increase in viscosity with dryness involves a loss of plasticization in the absence of the cloud of water which normally surrounds the silica particle. Also, agglomerate size is reduced (Figure 1.4), possibly the result of higher shear forces during mixing. The disappearance of higher viscosity values when the silanol surface is modified by silane indicates that resulting loss in hydrogen bonded structure is the major effect. It should be noted that dry silica is defined here as water content less than 1%. Normal water content is in the range of 3 to 7%. At water contents above 7% plasticization predominates, with a resulting decrease in viscosity, in terms of either Mooney or rheometer minimums.



Untreated Silica, ~5% Water **Untreated Silica, <1% Water**



Silane-Treated Silica, <1% Water

Figure 1.4 Effect of Water Content on Agglomerate Size; 150 m^2/g Silica in NR

In the peroxide cured compounds in Table 1.4, the contrast of increased viscosity and reduced hardness reflects the test parameters involved. The low strain deformation of durometer and 20% modulus testing of the vulcanizate is far removed from the continuous shear deformation involved in measuring the viscosity of the uncured compounds. Under the static, low strain conditions of durometer tests, hardness reduction occurs when the silanol-water structure is largely eliminated, without change in crosslinking. This structure and hardness loss is increased further when silanol bonding is removed by silane modification of the silica surface. Reduced structure, (smaller agglomerates), is quite apparent in the Figure 1.4 photomicrographs where the average diameter size of the larger particle agglomerates is reduced from 100 to 70 nanometers with dry silica. These smaller agglomerates, together with the removal of the free water barrier, are largely responsible for the increase in 300% modulus and, frequently, abrasion resistance.

The use of a peroxide cure system in exploring water effects allows the separation of filler reinforcement mechanisms from the silica surface reactions which occur with zinc-sulfur crosslinking. As noted elsewhere, these reactions of silica with soluble zinc produce a significant increase in polysulfide crosslinks and reduced filler-polymer bonding, which in themselves are sufficient to overshadow water effects. In Table 1.5 the data for dry silica effects in sulfur cured SBR combine both crosslinking and polymer bonding effects.

The doubling of viscosity together with increased 300% modulus in the dry silica compound are similar to those effects seen in the peroxide cured, zinc-free natural rubber compounds. However, other property effects here are all influenced by changes in sulfur crosslinks and filler-polymer bonding. Higher set, modulus and durometer are all evidence of an increase in polysulfide crosslinks, the result of zinc removal from its accelerator activating function (by attachment to silanols). Increased abrasion resistance (50% improvement) and modulus indicate improved silica-polymer bonding in the absence of barrier water.

Table 1.5 Free Water Content; Sulfur Cure

	A	**B**
Silica water content, %	3.8	0.7
MDR cure rate, 150°C, T_{90}, minutes	17	30
MDR crosslinks, dN-m	21	18
Mooney viscosity, ML_4100	57	112
Durometer	61	64
300% modulus, MPa	2.3	3.0
Compression set:70hrs,100°C	69	77
PICO abrasion index	45	68
Other ingredients: SBR 1502-100; Hi-Sil180H- 50; C.I.resin-10; oil- 5; Zinc oxide- 3; stearic acid- 2; ODPA-1; PEG3350-2; Sulfur- 2; MBS- 2; TMTM- 0.6		

Similar behavior of BR and solution SBR compounds is summarized, together with a comparison to an HAF control compound, in Table 1.6.

In view of the predominantly beneficial reinforcement effects of dry silica, it is reasonable to ask why commercial products with less than 1 % free water are not readily available. Two major obstacles must be overcome. As noted above, the free water content of precipitated silica is in equilibrium with relative humidity. Since the equilibrium values vary from 1% to more than 20% over the possible humidity range, it is apparent that maintaining less than 1% water, particularly in bulk shipping, would be very difficult. The electrostatic charges and associated dusting which are characteristic of dry silicas also raise formidable problems in handling and shipping. From the compounding standpoint, cure retardation in sulfur systems with dry silica must be countered with adjusted acceleration.

Table 1.6 Dry Silica Effects, With and Without Silane

N_2SA Silica / HAF Black	**135**	**135**	**135**	**135**	**N330**
Free water, %	6	6	1	1	0.4
Mercaptosilane	0	1	0	1	0
ODR cure rate, 160°C, T_{90}, minutes	28	19	27	22	3.5
ODR crosslinks, dN-m	62	68	62	65	74
Mooney viscosity, $ML_4$100	122	103	112	116	67
Durometer	80	74	79	77	73
300% modulus, MPa	7.7	13	8.7	12	13
Tensile, MPa	15	16	16	17	16
Elongation, %, Original	660	400	630	445	410
Elongation, %, 96 hrs, 100°C	280	250	210	230	300
PICO abrasion index	96	130	104	144	100
Compression set: 70hrs, 100°C	75	49	70	50	62
Pendulum rebound (Z), %:					
23°C	55	59	55	57	63
100°C	59	65	60	63	67
Goodrich flexometer: 100°C, 22.5%, 1 MPa:					
Set, %	24	14	20	14	25
Heat build-up, °C	47	40	48	48	68
Other ingredients: BR1220-50; SBR1250-50; 100°C resin-12; ODPA-1; ZnO-3; Sulfur-2.5; MBTS-1; DOTG-1.59; (with black only: stearic acid-1)					

1.6 SILICA FREE WATER, EFFECT ON VISIBLE DISPERSION

Free water content has a significant influence on visible dispersion, that is, the appearance of silica particles greater than 300 microns in mixed and cured compounds. As noted previously, minute amounts of gel (generally under 0.1%) can be formed during precipitation. Under certain drying conditions this gel contracts to become hard, undispersed white particles. Although poorly dispersed silica particles of this sort have not been found to affect vulcanizate properties or performance adversely, their presence is a severe marketing handicap. This has been a particular problem for one widely used 150 m^2/g non-dusting pelleted silica grade [1]. One method of improving the visible dispersion of this material involves its free water content and the use of water as a compounding ingredient. Table 1.7 provides a comparison of water, several silica modifying ingredients and resin softeners in natural rubber reinforced with 35 phr of this silica. In this case, only water addition is significantly effective in breaking up visible silica gel particles.

Table 1.7 Visible Dispersion Additives [1]

Additive Type	Amount, phr	Particles observed in 63 cm^2
None	-	16
Water	5	1
Mercaptosilane	0.5	17
Polyethylene glycol	2	10
Ethylene glycol	5	16
CI resin	5	21
Rosin ester	5	14

Mixing order represents an equally important technique to attain a reduction in visible silica particles. Early silica addition to the Banbury mixer is recommended. Zinc oxide is withheld until a second stage or at the end of a single stage mixing procedure. Resulting higher mixing temperatures can be assuaged by the concurrent addition of resin or oil solteners with a portion of the silica. Unlike carbon black, silica is not subject to loss of reinforcement by direct mixing with oils and resins.

As noted in the previous section and in the scanning electron micrographs (Figure 1.4), *ultimate* silica dispersion (in the nanometer range) is adversely affected by water content, and must be considered as a phenomenon separate from visible dispersion.

1.7 SILICA SURFACE SILANOL GROUPS

In contrast to the ephemeral nature of free water, bound, hydrated water is held firmly in place as silanol groups until temperatures rise above 250ºC. This is well above rubber processing temperatures, and thus allows the silanol surface to be considered a permanent silica characteristic. Silanols are responsible for the hydrophilic nature of silica and its unique (versus carbon black) reactivity with water, soluble zinc and other compounding ingredients as well as elastomers. The network of hydrogen bonded silanols leads to higher viscosity, hardness and stiffness in silica reinforced compounds, in contrast to those based on carbon black. This network is essentially a definition of silica structure. This type of structure, unlike that of carbon blacks, is not permanent, and can be significantly removed by addition of the materials described below.

Examination of a model that contrasts the surface make-up of silica and carbon black [2] reveals the source of their widely divergent behavior in rubber. As illustrated in Figure 1.1, silanol groups provide a hydrophilic surface; carbon black is hydrophobic, and therefore more compatible with organic polymers. Silanols react readily with oxygen- or nitrogen-containing compounds such as glycols, water, alcohols, amines, divalent metal salts and with each other. Among these reactions, that with soluble zinc is the major source of silica's unique compounding characteristics. The reaction, as shown in Figure 1.5, takes place in two steps. First, reaction of zinc oxide with a fatty acid produces soluble zinc ion; second, zinc becomes securely bound to one or two silanols. Zinc attachment displaces part of the free water and creates a heterogeneous surface in which the ratio of zinc-to-water is variable. This ratio will increase when water is driven off by high mixing temperatures or when zinc oxide is added early in the mixing schedule. The ratio will decrease when the addition of glycols or other buffering chemicals compete with soluble zinc for silanol attachment. High ratios of zinc-to-water lead to a loss of soluble zinc from its cure activating function and lead to reductions in cure rate, mono and disulfide crosslinks, and high strain modulus. These effects are accompanied by excessive elongation, set and heat build-up. At the same time, the presence of zinc on the silica surface reduces silica-polymer bond strength with a resulting loss in abrasion resistance. A zinc-free cure system used with solution polymers has been effective in overcoming these characteristic silica compounding problems. Alternate compounding solutions are discussed in subsequent chapters.

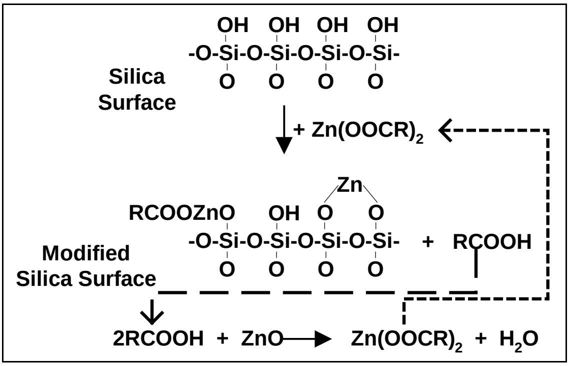


Figure 1.5 Soluble Zinc Reaction with Silica

Determination of silanol content is made by incineration above 900°C, a method somewhat complicated by the loss of volatile salts.

Other methods include reacting silanols with a variety of organic compounds [3]. The surface of precipitated silica is considered to be completely saturated with silanol groups. At 200ºC these are present in the range of 4 to 5 per square nanometer (some determinations at lower temperatures put the value between 8 and 12). Of greater importance to rubber reinforcement is the position of -OH in respect to a surface silicon. Analysis with photoacoustic FTIR by J. R. Parker [5] has done much to reveal the nature of the silica surface. Three positions are recognized: isolated, vicinal and geminal, modeled in Figure 1.6. A vicinal grouping refers to adjacent silanols (-SiOH), hydrogen bonded. Geminal refers to two -OH groups attached to one silicon. The isolated silanol is the most reactive, and is the principal location for bonding to soluble zinc, amine derivatives, glycols and other additives. The photoacoustic infrared spectrum of silica in Figure 1.7 identifies the silanol types and other surface groups.

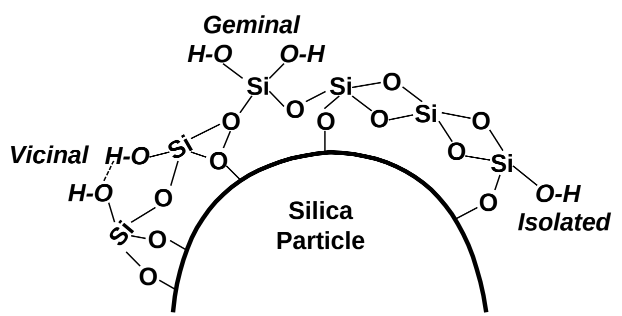


Figure 1.6 Types of Silica Surface Silanols

Most commercial precipitated silicas show little difference in the relative amounts of these three silanol types. A possible exception is the product Zeosil® 1165. A comparison of the infrared characterization of this silica with that of a silica of comparable surface area show fewer than normal isolated silanols. This difference might explain the higher MDR (moving die rheometer) crosslinks and 300% modulus found in many sulfur cured compounds based on 1165. Fewer isolated silanols result in less removal of soluble zinc from its crosslinking function.

Of greater interest is the possible influence of reduced isolated silanols on surface area measurements. Both CTAB and BET procedures give subnormal values for 1165 in respect to its actual agglomerate size in vulcanizates. The Figure 1.8 scanning electron micrographs of 1165 and other silicas in a zinc-free BR/NR formula show that only the silica with an average CTAB area of 170 m^2/g (Hi-Sil® 190G) has agglomerates similar in size to those of the CTAB 155 m^2/g Zeosil 1165.

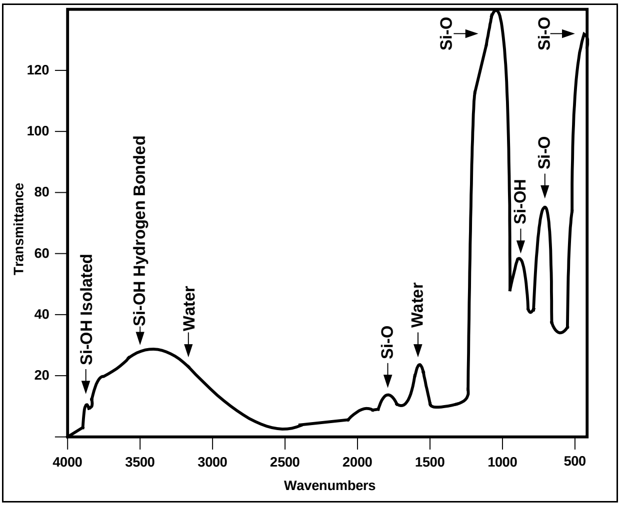
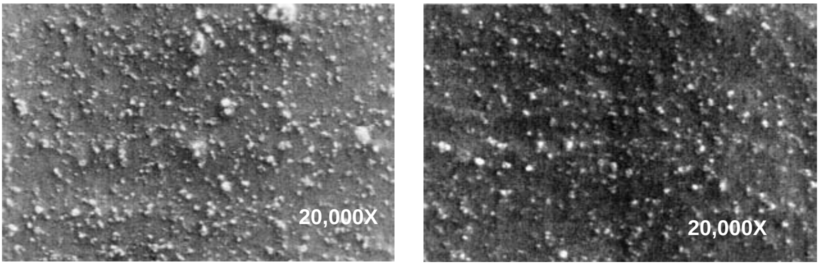
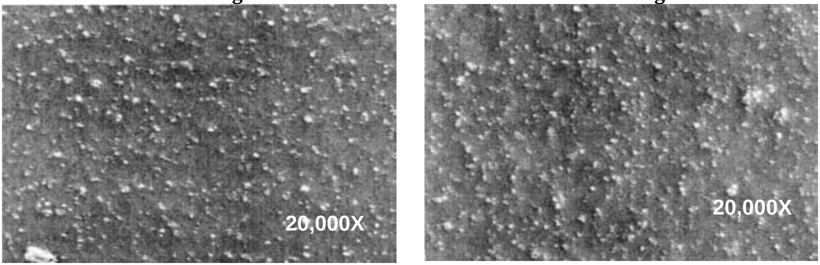


Figure 1.7 Silica Photoacoustic IR Spectrum



CTAB 125 m^2/g Silica

CTAB 130 m^2/g Silica



CTAB 155 m^2/g Silica

CTAB 170 m^2/g Silica

Figure 1.8 Isolated Silanol Content vs Agglomerate Size; 45 phr in BR/NR

BET single point (N_2SA) values show a wider gap of 217 to 173 m^2/g. The inference here is that a reduction in silanol reactivity (fewer isolated groups) has also reduced surface area values. Confirmation of this failure of surface area to predict particle size is seen in Table 1.8 in a comparison of the processing and vulcanizate properties of 190G and 1165 compounds. There are no significant differences between the two silica compounds.

Table 1.8 Surface Area Anomaly of Zeosil 1165

	A	B
Silica	190G	1165
CTAB, m^2/g	170	155
MDR crosslinks, dN-m	13	13
Mooney viscosity, ML_4100	115	111
Durometer:		
23°C/100°C	70/66	69/62
300% modulus, MPa	6.8	6.7
DIN abrasion loss, ml	71	71
Pendulum rebound (Z), %		
23°C/100°C	61/64	60/62
DMA dynamic modulus: 60°C; 1 Hz:		
E", MPa	0.63	0.66
E', MPa	6.5	6.3
Tangent delta	0.098	0.105

Other ingredients: BR1220-70; SMR-30; silica-45; Vestenamer 8012-15; Resin-10; ODPA-1;ZnO-1; Sulfur-2.7; MBTS-2; DPTH-0.5; single pass to 130°C; sulfur on mill.

In this case (Table 1.8) the normal prediction that high surface areas produce small agglomerates and high reinforcement is completely at odds with the data. That prediction appears to be valid only for silicas of similar silanol type distribution. Fortunately, this is still the situation for most commercial silicas.

The “zinc-free” formula used in Table 1.8 uses a cure system which excludes soluble zinc, that is, one without fatty acid. It has been effective in solution polymers, raising the abrasion resistance of silica reinforced compounds very close to that of comparable carbon black compounds. Zinc-free curing systems are discussed at length in Chapter 4 on solution polymers.

1.8 SILICA pH

The pH values for reinforcing grades of precipitated silicas generally lie within a range of 6.0 to 7.5, adjusted by acid addition after precipitation and partial removal of soluble salts. Over this range the effect of pH variation on processing and vulcanizate properties is negligible. When the range is somewhat extended to a higher pH of 8.6 (compound C in Table 1.9), a comparative evaluation in SBR compounds indicates improved crosslinking with the more alkaline silica.

Table 1.9 Effect of Silica pH on Compound Characteristics

	A	**B**	**C**
Silica pH	5.8	7.3	8.6
surface area (BET-1), m^2/g	154	153	148
Compound.pH: Uncured	6.8	7.3	7.6
Compound pH Cured	7.3	7.3	7.4
MDR cure rate, 150°C, T_{90}, min.	9.0	9.4	7.6
MDR crosslinks, dN-m	24.3	22.0	25.5
Mooney viscosity, ML_4100	137	130	126
Durometer	76	75	75
M300, MPa	4.9	5.0	5.6
PICO abrasion index	64	66	62
Compression set, %	48.9	45.6	39.4
Flexometer heat build-up,°C	38	37	33
DMA loss modulus, MPa	3.2	2.8	3.0
DMA tan delta, 30°C	0.111	0.111	0.113
100C rebound, %	62.0	60.2	67.0
Other ingredients: SBR-100; silica -50; resin-10; oil-3; Stearic acid-2; HPPD-2; Zinc oxide-3; Sulfur-2; MOR-1.5; TMTM-0.6; PEG-1.5			

The trend at higher pH is to faster cure rate and increased crosslinking, which result in increased modulus and rebound resilience with lower compression set. Slightly higher compression set and loss modulus with the low pH silica indicates an increase in polysulfide crosslinks. It is interesting to note that the pH of the *compounds* (water extraction 2 hours at 70°C) before curing follows the ranking of the silica pH, but with a tendency to reach an equilibrium at pH 7.3.

When a silica of pH 3.2 is evaluated (Table 1.10), unusual behavior in respect to transparency and strain whitening is observed.

Translucency in silica reinforced compounds is the result of zinc oxide removal through attachment to the silica surface. Complete removal produces a transparent compound. In this case it appears that the extremely low pH has activated the silanol-zinc ion reaction and thereby eliminated insoluble zinc oxide. Absence of the opacifying effect of insoluble zinc oxide produces a transparent compound. Removal of accelerator activating zinc with low pH silica is in agreement with the reduction in rheometer crosslinks and modulus. The phenomenon of extension whitening in non-black mineral filled compounds is generally attributed to poor filler-polymer bonding. When, as in this case, whitening has been eliminated, one must conclude that the silica-SBR bond has improved. Although the abrasion index is unchanged in the example above, its retention, notwithstanding modulus and crosslink losses, indicates that the filler-polymer bond has indeed strengthened.

Table 1.10 Low pH Effects [11]

Compound Characteristics	Compound A	Compound B
Silica pH	3.2	6.5
NaCl in silica, %	1.71	1.74
CaO in silica, %	0.52	0.67
Transparent	Yes	no
Extension whitening	none	much
Mooney viscosity, ML_4100	122	121
ODR crosslinks, dN-m	84	89
Durometer	69	70
M300, MPa	12.5	13
Elongation at Break, %	670	645
PICO abrasion index	60	61
Other ingredients: SBR 1502-100; silica-55; resin-20; ZnO-3; S.A.-0.5; Sulfur-2.7; MOR-1.2; DPG-0.4; TMTM-0.6; PEG-1.		

The acidic silicas in these examples were produced by the addition of HCl to washed slurries. An alternative method involves extended leaching of soluble salts. Complete removal of both salts and free water produces a relatively pure silica of pH 3.5. Although a *compound* pH of 4.5 can be obtained by the addition of benzoic acid during mixing, the resulting loss of 300% modulus and abrasion resistance is completely at odds with the increase found to take place with low pH silica.

Semi-reinforcing grades in the surface area range of 25 to 70 m^2/g are available with pH values as high as 9.8. The maximum basic side of the silica pH spectrum is 10.7, the point at which appreciable silica solubility occurs. As a result of this sensitivity to highly alkaline environments, particularly at high temperatures, silica reinforced compounds are not suitable for such applications as textile processing rolls used in caustic soda treatments.

1.9 SOLUBLE SALTS IN SILICA

Commercial grades of precipitated silica are marketed with salt contents of up to 3% by weight. There are three sources of non-silica ingredients: (1) sodium sulfate or chloride from silicate neutralization and pH adjustment, (2) calcium and magnesium salts from processing water and (3) aluminum and iron in sand used for silicate production. The amount of sodium sulfate is generally between 1 and 2%. Extended washing or ion exchange can reduce this to less than 0.05%, but production cost limitations are the major factor in maintaining the higher content.

With one exception, compound processing and reinforcement properties are not significantly altered by salt reduction. The exception is *water sensitivity* (swelling during water immersion). Compound resistance to swelling in water is proportional to soluble salt content; swelling is negligible when salt content is below 0.05%. During water immersion the relatively loose silica-polymer bond aids salt leaching, which, over several days at 70°C, reduces the high initial swell to values lower than those obtained with black and mineral fillers. Thus, pre-leaching of silica reinforced products can provide highly water resistant behavior. Salt leaching is adversely affected by silica surface modification. An interesting example is the use of silane coupling agents, the presence of which usually produces higher swelling compounds. Salt influence on water absorption was thoroughly studied by Briggs, Edwards and Storey [6].

Ion exchange is effective in removing soluble salts. A discontinued ion exchanged silica product (Hi-Sil X303) with a salt content less than 0.04% was effective in providing silicone compounds with excellent water resistance and electrical properties.

The salt induced water content of silica compounds has proved to be a restricting factor in pressureless, continuous curing applications. Cured compounds which contain more than 12 phr silica show unacceptable porosity. The addition of calcium oxide in the formula is seldom effective in reducing porosity. Pricing considerations and marketing conservatism have prevented the introduction of a low salt, low water speciality silica for low pressure curing.

Electrical insulating applications are sensitive to the nature of the salt anion. Sodium chloride, as opposed to sodium sulfate, can reduce dielectric strength by an order of magnitude (and considerably more at 70°C). Only one series of commercial silicas, Hi-Sil 210, 233 and 243, contain sodium chloride rather then sodium sulfate.

1.10 PHYSICAL FORM AND DENSITY OF SILICA

The density of precipitated silica after incorporation in elastomers is generally calculated from the density of the mixed and cured compound. Values range from 1.95 to 2.05 g/cc, dependent on the initial free water content of the silica. The density values are the same for all surface area grades. This value is significantly lower than the 2.5 to 2.7 range of mineral fillers such as clay, whiting and talc. The density of carbon black grades is 1.80, a number that gives black an advantage in calculating pound-volume material costs.

The physical forms of commercial silica fillers include dusty milled powders, compacted nuggets, spray dried powders and non-dusting rotary dried pellets. Gross particle size and screen analyses, where the minus 100 mesh fraction is considered to be dust, are summarized in Table 1.11

Table 1.11 Gross Particle Size of Silica Forms [2]

		Screen fractions, %	
	Size range, mm	**+100 Mesh**	**-100 Mesh**
Powder, milled	0.010 - 0.020*	0	100
Powder, spray dry	0.025 - 0.100*	60 - 95	5 - 40
Pellets, rotary dry	0.5 - 2.0	98 - 100	0 - 2
Granular, compacted	5 - 15	75 - 90	10 - 25
	*Coulter counter		

Wide variation in the –100 mesh screen fraction (dust) is seen among spray dried forms and, to a lesser extent, in granular forms. Notwithstanding the dust content, spray dried silicas have become the preferred form in the world market. The rotary dried pellet form can in most cases be considered dust free. The only product In this category is Hi-Sil 210. It is particularly well suited to bulk shipment and is the predominant form used in the North American tire industry. Wider use has been somewhat restricted because of the presence of visible white particles in the cured compound. In all cases, the selection of physical form is a compromise between dustiness and dispersion, where dispersion is defined by the appearance of visible white particles. These particles, formed from gel or dryer scale, account for less than 0.1% of total filler and have little or no effect on vulcanizate properties. They do, however, represent a serious cosmetic problem. Ultimate dispersion, measured by SEM and defined in terms of nanometer sized agglomerates, bears little or no relation to the presence or absence of visible or micron sized particles. In this respect, silica differs markedly from carbon black. In black reinforced compounds, micron sized areas of poor dispersion can have an adverse effect on vulcanizate properties and product performance.

Testing of silica to predict visible dispersion can be done by ball milling and by counting the number of residual particles on a 50 mesh screen (300 micron particles). Particle counts of 0 to 2 indicate acceptable dispersion. Measuring the crushing strength of granules or pellets has shown little or no correlation with silica dispersion .

Properties of interest in bulk handling situations include bulk density, static configuration and flow characteristics. All silica forms noted above have bulk densities between 0.12 and 0.33 g/cc. Milled powders are the lowest and most subject to air inclusion during movement. Angles of repose range from 35° for spray dried forms, to 39° for rotary dried pellets, and to 52° for a milled powder.

1.11 OTHER SILICA PROPERTIES

The refractive index for precipitated silica is 1.45, the lowest among all mineral fillers. This value, compared to 1.56 for clay, 2.00 for zinc oxide and 2.71 for titanium dioxide, is of basic importance in the use of reinforcing silica grades in translucent and transparent compounds. However, to attain any degree of transparency, a low refractive index must be accompanied by removal of zinc oxide through reaction with silica silanols.

Pore volume or diameter is a measurement by mercury porosimetry of the gross agglomerate structure of various silicone reinforcing grades of both precipitated and fumed silicas. There is little application to the reinforcement of organic polymers. Pore structure varies widely among silicas of the same surface area which have undergone different drying and compaction treatments. The shear forces involved in Banbury mixing are sufficient to obliterate all structure identified by porosimetry measurements.

These considerations also apply to the use of oil or DBP absorption data to predict the processing or vulcanizate properties of silica compounds. Absorption measurements reflect only the physical form. Their influence disappears during mixing and milling operations.

1.12 SILANE TREATED SILICAS

A very important surface modification for precipitated silicas, as well as for many mineral extender fillers, has been the treatment by organic silanes to enhance filler-polymer bonding and, thereby, reinforcement. Publications which discussed the use of silanes with silica first appeared in the early 1960’s [8]. The coupling mechanism involves hydrolysis of the silane alkoxy groups, and subsequent bonding to silica silanols. However, the second part of the coupling reaction to organic polymers requires a functionality compatible with polymer unsaturation. Only a mercaptosilane will meet this requirement for sulfur vulcanized natural and synthetic rubbers, and it was not until mercaptopropyltrimethoxy silane (MPTS) became available that commercial development of silane coupled silica in rubber compounds became a standard feature of compounding technology.

The efficiency of mercapto functionality is easily seen in Table 1.12 compiled from data developed by M.P.Wagner for an SBR tread compound [4].

Table 1.12 Silane Coupling Agents in SBR

Silane Function	**Viscosity ML_4100**	**M300, MPa**	**Heat Build-up Index,°C**	**Tread Wear Index**
None	168	4.9	49	100
Methyl	80	3.7	42	95
Vinyl	125	5.2	38	98
Glycidyl	86	5.2	34	100
Amino	112	6.5	31	104
Mercapto	77	12.0	28	140

Although all alkoxy silanes have a positive influence in lowering viscosity, through reducing silica network structure, only the mercapto function is capable of producing increased modulus and abrasion index, through silica-polymer bonding. Unfortunately, the unmodified mercapto silane carries with it a strong odor which is highly objectionable to many factory personnel. The most successful of several attempts to reduce the odor is the bis polysulfide modification, triethoxysilylpropyltetrasulfide silane (TESPT). Molecular weight differences make this silane only half as efficient as MPTS. In addition, Banbury mixing temperatures involve a minimum, to insure breakdown into the active mercapto function, and a maximum, to avoid scorching.

The obvious alternative to silane modification is pre-treatment of the silica. This procedure, involving room temperature blending with MPTS, was successful in producing a treated silica with no offensive odor or mixing temperature sensitivity [9]. These products are marketed under the trade name, Ciptane®. Silicas treated with TESPT and other silanes are known as Coupsil®.

More detailed examination of silane coupling is taken up in each of the polymer chapters.

References

References 1 to 4 provide a valuable introduction to a study of the relationship of silica properties to elastomer compounding technology

1. J.H.Bachmann et al, “Fine Particle Reinforcing Silica and Silicates”, Rubber Chem. Technol. 32, 1286 (1959)
2. H.J.Wartmann & C.R.Strauss, “Analysis of Cure Parameters to Define Vulcanization and Reinforcement”, paper presented at ACS Rubber Division, spring meeting, 1965
3. D.B.Russell, “Activator Interactions Affecting Vulcanizate Properties of Silica filled SBR”, paper presented at ACS Rubber Division spring meeting, 1966
4. M.P.Wagner, “Reinforcing Silica and Silicates”, Rubber Chem. Technol. Vol 49,No.3 (1976)
5. J.R.Parker, unpublished paper
6. Briggs et al, “Salt Content of Precipitated Silica”, Rubber Chem. Technol. 1963, p 621
7. Education Symposium #34, Silica Fillers, ACS Rub. Div. Meeting #147, (1995)
8. Schwaber & Rodriguez, “Silane Coupling Agents”, Rubber & Plastics Age, 48, 1081 (1967)
9. PPG Industries Technical Service bulletin “Ciptane”, 2000
10. PPG Technical Service bulletin 150-G-50
11. J.D.Boroff, unpublished, “Effect of pH on Properties of Rubber”.

CHAPTER 2

COMPOUNDING PRECIPITATED SILICA IN NATURAL RUBBER

2.1 INTRODUCTION

Commercial production of the first grades of precipitated silica took place in 1948. At this time, natural rubber had barely relinquished its position as the principal, if not only, elastomer in commercial use. In these circumstances, most of the early compound development work involved natural rubber as the base polymer. In some respects this was a fortunate situation for silica. In comparison to carbon black, abrasion resistance was only slightly reduced; high viscosity and slow cure rates, which appear in synthetic elastomers, were not significant problems. The major silica attributes of tear strength, heat resistance and adhesion to fabrics and metals were very much in evidence in natural rubber compounds. It was not until the development of sophisticated dynamic testing procedures that the superiority of silica, frequently silane coupled, in the reduction of tire rolling resistance was discovered and put to commercial use.

2.2 SILICA AND CARBON BLACK

High surface area grades of precipitated silica provide an alternative to carbon black as a source of reinforcement for natural and synthetic rubber compounds. Among the criteria for reinforcement – abrasion resistance, tear and tensile strengths – unmodified silica is inferior only in respect to smooth surface abrasion resistance. This deficiency, together with higher prices, has confined silica production and consumption to roughly 10% of that of carbon black in the U.S. market. In view of this preponderance of carbon black compounding usage, it is appropriate to begin a compounding appraisal of silica in terms of silica’s relation to black.

Valid comparisons in respect to both filler and compound properties are best made on a basis of comparable filler particle size or compound hardness. In the following tables, 2.1a through 2.1c, a silica of 19 nanometers average particle size (180 m^2/g N_2SA silica) and an ISAF carbon black of 22 nanometers (N220) are compared at 40 phr in compounds of equal hardness with appropriate changes in acceleration:

Table 2.1a A Comparison of Silica and Carbon Black Fillers

	180 m^2/g N_2SA Silica	**N220 Carbon Black**
TBBS, phr	3	1
Polyethylene glycol, phr	1	--
ODR cure rate, 150°C, T_{90} minutes	20	13
ODR crosslinks, MH-ML, dN-m	75	73
Mooney scorch, 121°C, T_5 minutes	30+	24
Mooney viscosity, ML_4 100	58	48
Other Ingredients: SMR-100; Filler-40; ODPA-1; ZnO-4; Stearic acid-2; Sulfur-2.8		

Table 2.1b Static Properties of Silica and Carbon Black Compounds

	180 m^2/g N_2SA Silica	**N220 Carbon Black**
Durometer hardness	64	64
M300, MPa	5.8	12.6
Tensile, MPa:		
Original	28	29
Aged 480 hours, 85°C	15	6.1
Elongation, %:		
Original	600	540
Aged	430	140
MG Trouser tear, kN/m	19	4.7
PICO abrasion index	97	113
Compression set, 72 hrs, 100°C, %	56	54

Table 2.1c Dynamic Properties of Silica and Carbon Black Compounds

	180 m^2/g N_2SA Silica	**N220 Carbon Black**
Pendulum rebound (Z), %		
at 23°C	78	74
at 100°C	85	84
Goodrich flexometer: 100°C; 22.5%; 1 MPa		
% set	5.1	4.6
Heat build-up, ºC	15	16
DeMattia cut growth, kc to 500%	15	15
DMA dynamic modulus: 30°C; 1 Hz; 20% strain		
E', MPa	7.0	7.2
E"	0.38	0.64
Tangent delta	0.55	0.89

The use of 3 phr TBBS and, less importantly, polyethylene glycol produces nearly equivalent cure and scorch behavior, including rheometer crosslinks, for both compounds. These comparable properties, together with equivalent hardness, form a sound basis to make legitimate comparisons between silica and black fillers. The selection of TBBS, at higher than normal concentration, is discussed at length in the accelerator section of this chapter.

The stress-strain path leading to tensile and elongation values shows the typically low 300% modulus for silica, noted previously in Chapter 1. This phenomenon is related to low silica-polymer bonding and cannot be corrected with increased acceleration. The solution to this – and the associated deficit in abrasion resistance – lies in the use of silane coupling or zinc-free cure systems, discussed elsewhere. Major contributions of silica are seen in trouser tear strength, and, with additional TBBS, in resistance to degradation during extended heat aging at 85°C. Comparable compression set values are a good indication of the power of added TBBS to eliminate the tendency of normally accelerated silica compounds to form polysulfide crosslinks. Although polysulfide crosslinks usually favor trouser tear strength, their reduction has not detracted significantly from the remarkably high tear values of this compound.

Beginning with rebound, particularly at room temperature, the superiority of effectively accelerated silica (vs. carbon black) in dynamic behavior is fully evident. This is most significant in terms of loss modulus (E") and tan delta where carbon black values are reduced by almost 50% with silica. In natural rubber, unlike SBR, this dynamic improvement is obtained without the use of silane coupling. The structural basis for silica’s dynamic behavior is discussed in Chapter 1. The practical outcome has been, among several applications, the replacement of carbon black by silane-modified silica in low rolling resistance passenger treads, illustrated in this chapter’s formulary section by compounds NR 30, NR 34 and NR 59.

It needs to be noted that, at the 40 phr filler content in this example, there is little difference in Mooney viscosity between silica and carbon black. At higher filler contents, however, silica compound viscosity will increase substantially and in many cases this increase will require added plasticization. Higher silica content, particularly for silica surface area grades of 180 m^2/g or more, will also tend to increase heat build-up and set, although this increase is largely mitigated by an acceleration of 3 to 4 phr TBBS. Partial replacement of HAF (N330) carbon black by silica is illustrated in formulary compound NR 59.

2.3 ACTIVATION: ZINC OXIDE

Zinc oxide solubilized with stearic or other organic acid provides accelerator activation through the formation of intermediate accelerator complexes. In earlier, less regulated times, lead oxides were a source of more effective crosslinking with silica [1]. More recently, a "zinc-free" system has been successful in modulating the normal zinc oxide activating function in the presence of certain accelerators [2]. Examples are discussed in a later section.

The essential requirement for activation by zinc oxide is that it be solubilized in situ by a fatty acid. Addition of zinc stearate as a formula ingredient fails to produce adequate crosslinking and vulcanizate properties, as shown in Table 2.2.

Table 2.2 Effect of Zinc Oxide and Zinc Stearate on NR Compounds

	A	B	C
Zinc oxide	3	3	--
Stearic acid	2	2	--
Zinc stearate	--	--	5
Polyethylene glycol	--	1	1
Crosslinks, dN-m	33	36	24
Compression set, 70 hrs, 100°C, %	74	78	86
Durometer hardness	70	70	65
M300, MPa	6.8	6.3	3.7
Tensile Strength, MPa, 500 hrs, 90°C	14	11	2.3
Pendulum Rebound (Zwick), %	57	55	43
Other Ingredients: 180 m^2/g N_2SA Silica-50; ODPA-1; sulfur-2.8; TBBS-3			

Even with the activating assistance of polyethylene glycol, zinc stearate is relatively ineffective. The almost total loss of heat aging resistance in the stearate compound reflects the role of the zinc ion in an antioxidant function. It should be noted that, in this example, the use of a relatively high TBBS concentration (3 phr) mitigated the usual activation effects of polyethylene glycol.

As discussed previously, soluble zinc reacts with silica silanols, and this reaction competes with the zinc activating function. Evidence of this competition is seen by varying the zinc oxide order of addition during Banbury mixing, as shown in Table 2.3.

The mechanism here involves zinc ion attachment to silica silanols, which reduces silica network formation and results in lower viscosity, increased nerve and roughness. At the same time, removal of zinc from accelerator complexing retards the cure rate. With accelerators other than the delayed action TBBS (e.g. CBS), second stage addition of zinc oxide alters the shape of the rheometer curve, providing both improved scorch safety and faster crosslinking.

Table 2.3 Mixing Order for Zinc Oxide (two stage mixing) Addition

Zinc Oxide Addition, stage	**First**	**Second**
Mooney Viscosity, ML_4 100	52	72
Milled Surface Quality	Rough	Smooth
ODR cure rate, 138°C, T_{90} minutes	41	32
NR-100; 150 m^2/g N_2SA Silica -50; ZnO-5; S.A.-1; PEG-2.5; Sulfur-3; TBBS-2; DPG-0.6; ODPA-1; tall oil-5		

2.4 CURE ACTIVATION: GLYCOLS

Glycols and amines, through hydrogen bonding, generally provide a buffer layer to reduce the silica–zinc reaction. Polyethylene glycol is the most frequently used additive because of results such as shown in Table 2.4.

Table 2.4 Cure Activation by Polyethylene Glycol

	PEG 3350, phr		
	0	**2**	**4**
ODR cure rate, 144°C, T_{90} minutes			
Original	34	19	16
Remilled	42	21	16
Mooney Viscosity, ML_4 100	51	41	39
Durometer hardness	59	66	60
Flexometer Heat Build-up, ^{o}C	32	29	22
NR-100; 150 m^2/g N_2SA Silica - 30; 35 m^2/g N_2SA Silica -45; Sulfur- 2.8; MBS- 1.5; DPG- 0.3; ZnO- 5; Stearic acid-3)			

In addition to cure acceleration, PEG eliminates the loss in cure rate which can occur during re-milling of silica reinforced natural rubber. Although PEG is the preferred buffer/activator because of its low volatility, other materials such as triethanolamine, glycerin, and diethyleneglycol (DEG) are suitable for buffering. DEG finds considerable use at 3 to 5 phr in footwear production where it also functions as a plasticizer. DEG also inhibits sunlight discoloration of white compounds. Comparisons among PEG, DEG and TEA, on an equal part basis, indicate that PEG is 20 to 30% faster curing than DEG and slower than TEA. PEG produces higher hardness and higher viscosity with vulcanizates that are less susceptible to swelling in water. Glycol order of addition during mixing is not critical.

In general, glycol and other activators affect compound properties through crosslink modification, filler network formation and filler agglomeration. However, their presence on the silica surface can interfere with silica–polymer bonding. Evidence of this is demonstrated in Table 2.5 through examination of a peroxide cured formula where sulfur crosslinking modification is absent.

Table 2.5 Effects of Glycol Modification on Compound

	Diethylene Glycol, phr	
	0	**3**
Agglomerate size range, SEM 20,000X, nm (Figure 2-1)	50-100	100-150
MDR cure rate, 160°C, T_{90} minutes	3.6	3.9
MDR Mh-ML crosslinks, dN-m	27	25
Mooney viscosity, ML_4 100	58	42
Durometer hardness	55	53
M300, MPa	5.7	3.2
Tensile, MPa	24	20
Elongation, %	560	570
Compression set, 70hrs, 100°C, %	31.6	33.5
Pendulum rebound,%		
23°C	61	59
100°C	66	62
Other Ingredients: SMR-100; 150 m^2/g N_2SA Silica-30; Oil-3; ODPA-1; DCP-2.4		

Losses in hardness, modulus and tensile in the presence of DEG are readily explained by the SEM views in Figure 2.1 where DEG interference with silica–polymer and silica–silica bonding has prevented a complete break-up of reinforcing silica agglomerates.

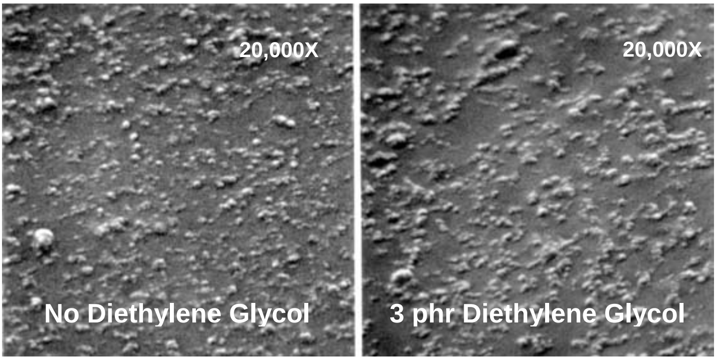


Figure 2.1 Effect of DEG on Silica Agglomeration in NR

In the absence of any significant change in crosslinking, all property changes can be related to filler–polymer bonding interference. Similar behavior, somewhat less severe, is seen with polyethylene glycol in place of DEG. In polyisoprene the role of glycol activation is more important than in natural rubber. With 50 phr silica reinforcement, even strong acceleration systems require the use of PEG to attain a satisfactory state of cure.

2.5 ACCELERATION WITH SECONDARY ACCELERATORS IN NORMAL SULFUR SYSTEMS

General compounding practice requires the use of 1 to 2 phr of a primary accelerator such as MBTS or a sulfenamide, with smaller concentrations of a secondary accelerator to regulate curing and vulcanizate properties. Cure rate, scorch safety and viscosity undergo considerable change due to the type and amount of secondary accelerator. Modulus, tensile, set and heat build-up are also affected. The results of a study of several secondary accelerators at 0.3 and 0.6 phr are illustrated by means of trend lines, in Figures 2.2, 2.3, 2.4, that indicate property ranking as well as concentration effects. The natural rubber formula for this and other studies includes the following: 150 m^2/g N_2SA Silica-50; Resins-15; ODPA-1.5; Stearic acid-2; PEG-3; Zinc oxide-3; Sulfur-3; MBS-1.2; secondary accelerator-0.3 and 0.6

Cure rate and scorch safety rankings must be considered together to determine the fastest secondary, which also provides adequate scorch safety. Secondaries, TMTM, DPTH and BDMDC all fall in this category. Lack of scorch safety with PPDC and DETU make their use questionable in this context. None of the secondary accelerators in this study had any adverse effect on the knotty form of tearing, characteristic of silica reinforcement of natural rubber.

Viscosity is a critical factor in processing silica compounds, but one not usually associated with secondary accelerators. In this case, substantial reduction in ML_4100 values is produced by the amine derivatives, diphenyl guanidine, trimene base, and diethyl thiourea, as well as the dithiocarbamate PPDC. The mechanism involves the reduction in silica network and agglomeration forces produced by accelerator modification of the silica surface. Major improvements in vulcanizate properties include reduced heat build-up and set in the compounds accelerated by 0.6 phr of TMTM, DPTH or BDMDC. These secondaries have also proved to be beneficial in eliminating excess surface tack of hot air cured sheeting.

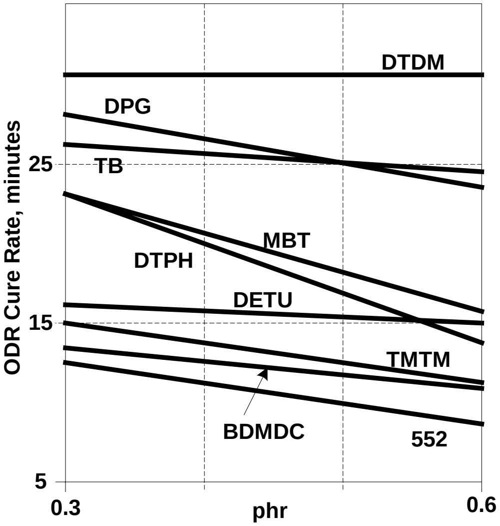


Figure 2.2. ODR Cure Rate at 144°C

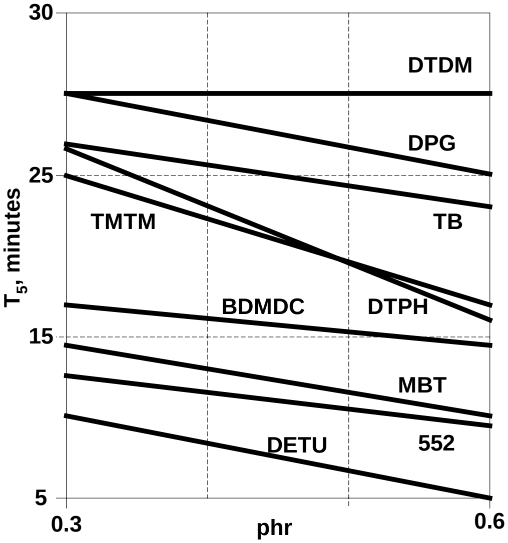


Figure 2.3. Mooney Scorch at 121°C

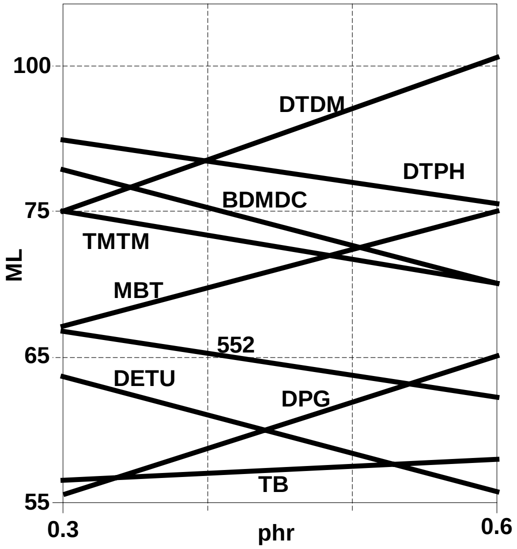


Figure 2.4. Mooney Viscosity at 100°C

2.6 ACCELERATION: SINGLE ACCELERATORS IN NORMAL SULFUR SYSTEMS

In terms of vulcanizate properties such as compression set, high strain modulus and heat build-up, which reflect the number and type of crosslinks, silica reinforced natural rubber compounds, for reasons discussed previously, have rarely been equal to those based on carbon black reinforcement. This deficiency in cure state persists even with the use of glycol activation and relatively large concentrations of two or more accelerators. Most normal sulfur cure systems in natural rubber have consisted of thiazole–guanidine or sulfenamide–thiuram combinations. In more recent work a different approach involves the evaluation of individual accelerators at concentrations of 1 to 4 phr. Included are representatives of guanidine, urea, sulfenamide, thiazole, dithiocarbamate and thiuram types:

DPG	Diphenyl guanidine
DETU	Diethyl thiourea
DCBS	Dicyclohexyl benzothiazole sulfenamide
MBTS	Benzothiazole disulfide
MBS	Morpholinothio benzothiazole
TBBS	T-butyl benzothiazole sulfenamide

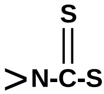
TCS (OTOS)	Thiocarbamyl sulfenamide
TMTM	Tetramethylthiuram monosulfide
ZBDC	Zinc dibutyl dithiocarbamate
ZEPDC	Zinc ethylphenyl dithiocarbamate

A typical silica characteristic is its susceptibility to rheological change by materials other than conventional softeners. In this study, substantial viscosity reduction appears in the presence of guanidine, urea and ZBDC accelerators. These lower viscosities associated with amine derivatives and zinc alkyldithiocarbamates are the result of their deactivating effect on the silica–silica hydrogen bonded network. MBTS, for no apparent reason, occupies an intermediate position in this respect.

Crosslink formation in respect to both rate and extent is a major criterion of accelerator activity. Although swelling measurements have frequently provided a measure of crosslink density, a more rapid evaluation with less involvement with filler–polymer bonding can be obtained from oscillating disc (ODR) or moving die rheometers (MDR). The difference between maximum and minimum torque values (MH-ML) reflects the amount, but not the length, of sulfur crosslinks formed at a given temperature. In the Figure 2.5 plot of rheometer crosslinks and accelerator concentration, the thiocarbamyl and benzothiazole sulfenamides (TCS, TBBS, and MBTS) attain highest delta torque values. As seen in Figure 2.6, TCS is faster and reaches a plateau at 3 phr, but at the same time produces greater reversion than the others.

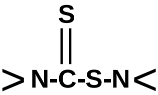
Rheometer crosslinks frequently show a linear relationship to high strain modulus (M300% modulus) of the vulcanizate. Thus the plot in Figure 2.7 of M300 versus concentration is almost a duplicate of that for crosslinks versus concentration. It is likely that this and other crosslinking studies are, in part, a reflection of accelerator solubility and its dependence on elastomer type and processing temperatures. Thus, accelerator optimization conclusions reached for natural rubber may not accurately predict performance in other elastomers.

Total crosslinks are not necessarily related to the rate at which they develop. In the Figure 2.8 comparison of rheometer cure rates, the fastest accelerators, TMTM, ZBDC and TBTD, were unable to produce high torque levels. Only TCS, at 2.5 phr combines both speed and a high state of cure. Examination of the structural formulas shows that curing speed is associated with the dithiocarbamate group (1) and total crosslinks with the sulfenamide group (2). The success of TCS in providing both speed and high crosslink density has been achieved by combining (1) and (2) in one product (3), known as thiocarbamylbenzothiazolesulfonamide (TCS) or N-oxydiethylenethiocarbamyl-N'-oxydiethylenesulfenamide (OTOS):

(1) 

$>N-\overset{\overset{S}{\|}}{C}-S$

(2) $S-N<$

(3) 

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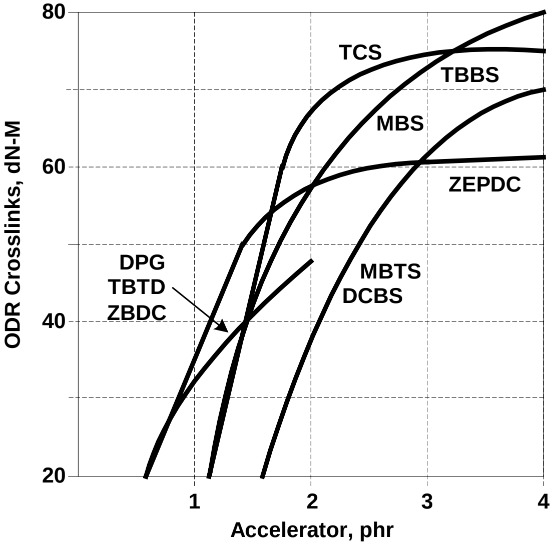


Figure 2.5. Effect of Accelerator Concentration on Crosslinks

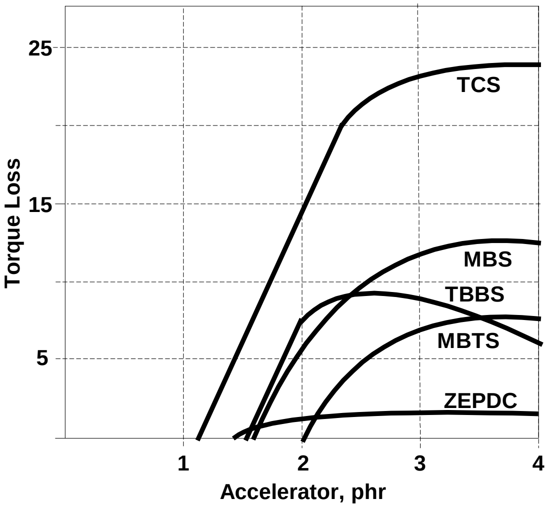


Figure 2.6. Effect of Accelerator Concentration on Rheometer Torque Loss, 1 Hour at 150°C

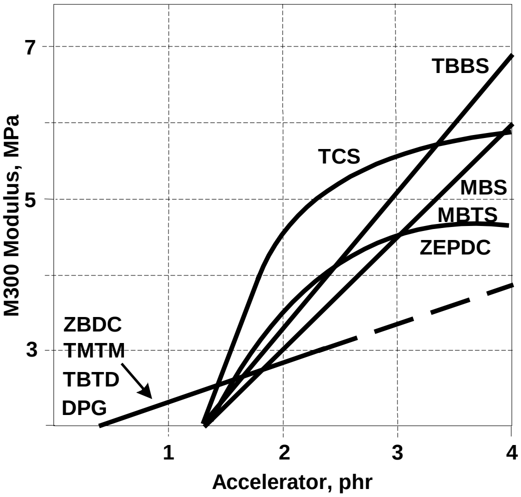


Figure 2.7. Effect of Accelerator Concentration on Modulus

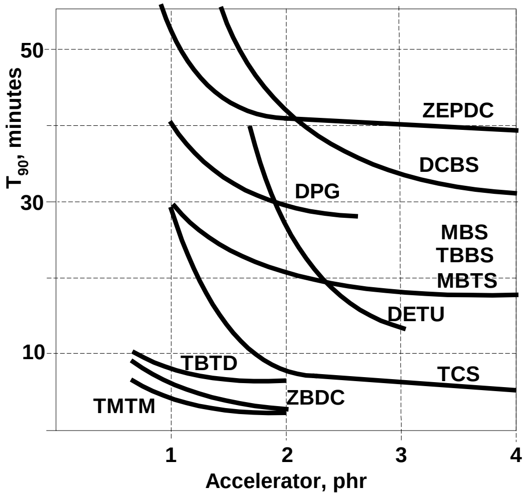


Figure 2.8. Effect of Accelerator Concentration on Cure Rate

An exception to the cure rate–structure relationship among the dithiocarbamate accelerators is ZEPDC, where the phenyl group evidently hinders one or more steps of the crosslinking mechanism. These relationships also apply to non-silica reinforcement, but scorching of carbon black compounds at high accelerator concentrations precludes similar investigations in the absence of silica.

Cure rate and state alone do not supply sufficient information for a practical evaluation of accelerators. Adequate resistance to pre-cure at processing temperatures (scorch safety) must be considered in concert with activity at curing temperatures. Scorch testing can take place on various instruments at temperatures from 121°C to 150°C. In these studies, shown in Figure 2.9, scorch tendency is expressed as the T_2 value from ODR cure curves at 150°C. Under these conditions the minimum acceptable T_2 for most factory operations would be from 2 to 3 minutes. By this criterion it appears that, in a normal sulfur system, TMTM, ZBDC as well as DPG and DETU, might be excluded from use at concentrations that provide the most effective crosslinking.

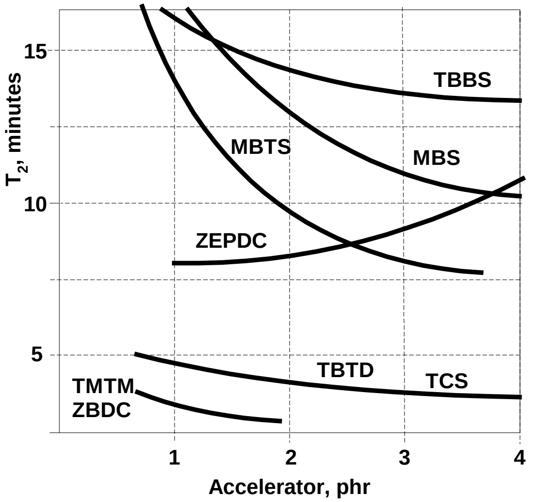


Figure 2.9. Effect of Accelerator Concentration on Scorch Delay

2.7 ACCELERATION: SINGLE ACCELERATORS; VULCANIZATE PROPERTIES

Curing reactions determine compound properties not only by crosslink density but also by crosslink length in terms of mono-, di-, or polysulfides. Short crosslinks generally produce low set and heat build-up together with improved heat aging resistance. In the absence of analytical data, compression set testing can provide a reliable indication of crosslink type as influenced by accelerator activity. In the Figure 2.10 plot of compression set vs rheometer torque, only TBBS, TCS and the thiurams attain a compression set of 60% or lower, behavior which predicts that only these accelerators are capable of producing mono and disulfide crosslink types. A related plot, Figure 2.11, of compression set versus accelerator concentration demonstrates the need for 3 or 4 phr concentrations to reach the 50–60% range. TCS is the most effective.

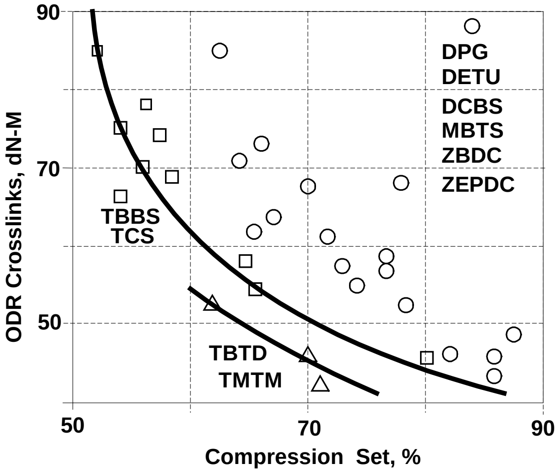


Figure 2.10. Effect of Accelerators on Crosslinks vs Set

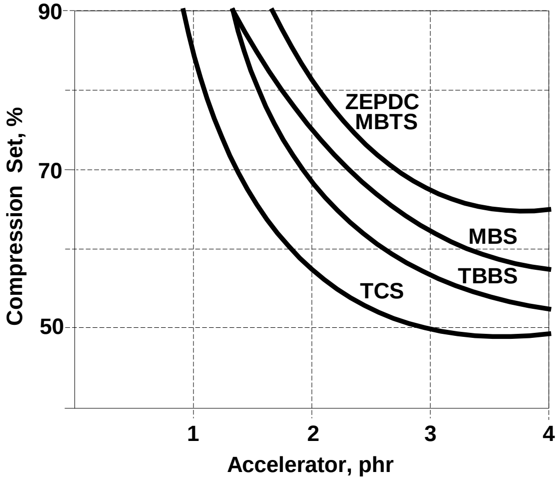


Figure 2.11 Effect of Accelerator Concentration on Set; 3 Days at 100°C

Flexometer heat build-up evaluations, in Figure 2.12, show a linear decrease for MBTS, MBS and ZEPDC up to 4 phr and, at a faster rate, for TCS and TBBS up to 3 phr. At concentrations of 3 phr the latter two accelerators provide values that are equal to those typical of black filled compounds. The 40°C drop in HBU attained by increasing TBBS from 2 to 3 phr is especially significant. Dynamic evaluation for tan delta offers a similar picture in Figure 2.13. However, at comparable crosslinking, the value for the N220 black control is considerably greater than those of the effectively accelerated silica compounds. In this comparison the most effective, TBBS, has provided a reduction in tan delta of almost 40%.

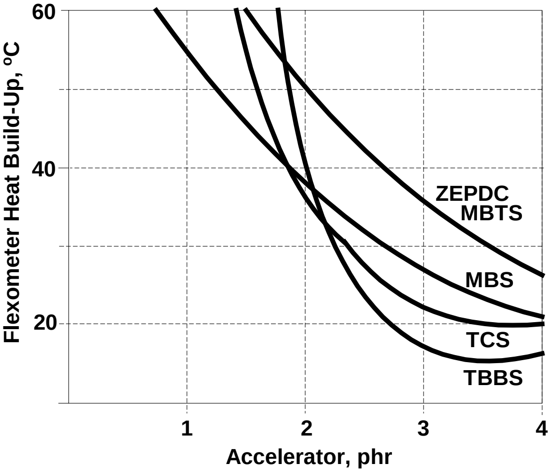


Figure 2.12. Effect of Accelerator Concentration on Heat Build-Up

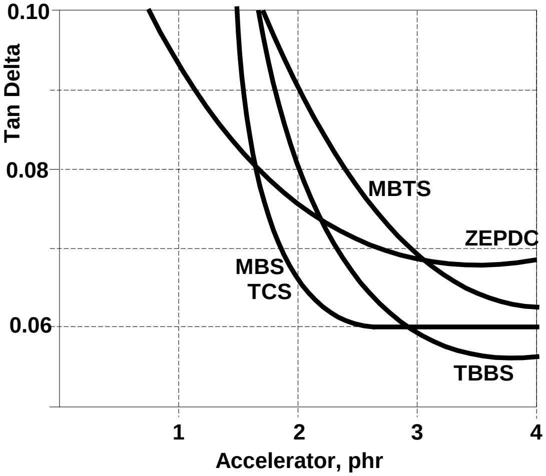


Figure 2.13. Effect of Accelerator Concentration on Tan Delta; 60°C, 1 Hz

In respect to the properties normally associated with precipitated silica, any cure system modification should retain the high resistance to tear (cutting, chipping and chunk-out), which is the hallmark of silica reinforcement. In this and other studies, tear strength is defined by the PPG trouser mode of testing (MG trouser tear) in which a trouser type tear is confined in grooves molded lengthwise in the 1x6 inch specimen, as shown in Figure 2.14.

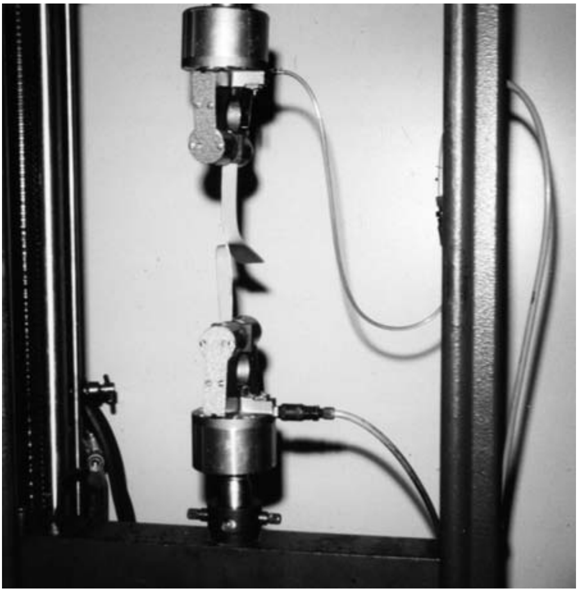


Figure 2-14. MG Trouser Tear

Although effective acceleration produces some loss in tear strength, in no case are the values reduced to the level typical of black reinforcement, as seen in Table 2.6.

Table 2.6 Effect of Accelerator Type and Amount on Tear Strength

Accelerator (phr)	MG Trouser Tear, kN/m
TBBS (3)	18.5
TBBS (4)	8.8
MBS (4)	14.1
TCS (4)	16.6
TCS (3)	16.6
Black Control, MBS (1)	4.4

Silica enhances heat resistance in almost all polymers. This behavior is most apparent when aged elongation is the criterion used to evaluate the condition of a compound after exposure to heat. A large part of improved aged flexibility (higher aged elongation) is due to the high *original* elongation characteristic of silica reinforcement. In many cases the percent elongation retained after aging is also found to increase as silica replaces black. Among the accelerators in this study, Table 2.7, TBBS at 4 phr is particularly effective in providing heat resistance at both 85°C and 100°C.

Table 2.7 Aging Resistance of Silica and Black

	180 m²/g N_2SA Silica		**N220 Carbon Black**
Accelerator Type/phr	TBBS/4	TCS/3	TBBS/2
Original Stress/Strain:			
Durometer hardness	68	64	64
Tensile, MPa	27	27	29
Elongation, %	605	660	540
Aged 500 hours, 85°C:			
Tensile, MPa	14	13	6.2
Elongation, %	360	300	140

In addition to tear strength and heat resistance, further comparisons to a carbon black reinforced control indicate that silica compounds accelerated with TBBS or TCS provide distinct advantages in scorch safety, set, heat build-up and resilience. Cure and scorch activity are the major factors in distinguishing between TBBS and TCS. As previously noted, the scorch safety of the faster curing TCS is marginal. One remedy to this shortcoming is a 2 to 2 blend with TBBS, by which scorch safety is increased from 16 to 27 T_5 minutes. At the same time, beneficial synergistic effects appear in both static and dynamic modulus, while tear strength declines precipitously, as seen in Table 2.8.

Table 2.8 Effect of Accelerator Blends on Elastomer Characteristics

	Accelerator amount, phr		
TBBS	4	2	0
TCS	0	2	4
Mooney scorch, 121°C, T_5 minutes	30+	27	16
MDR cure rate, 150°C, T_{90} minutes	19	6.5	6.0
M300, MPa	6.6	7.3	5.7
Dynamic Modulus E’ MPa	9.8	16.5	14.6
MG Trouser tear, kN/m	8.8	4.2	15.7

In this and other studies of accelerator effects in silica reinforced natural rubber, no influence on laboratory abrasion test results has ever been detected. Abrasion resistance appears to be related solely to silica–polymer bonding, and any improvement in this property must rely on silane coupling or on the zinc-free cure system.

Accelerator solubility and bloom are practical aspects of higher-than-normal accelerator concentrations. The use of accelerators at the 3 and 4 phr level is feasible only if bloom residues do not appear during shelf aging. Although low hydrocarbon solubility data indicate that TCS and MBTS may be sparingly soluble in rubber, no signs of bloom have been observed on vulcanizates shelf aged for several years. Adsorption by the highly active silica surface is likely to alter bloom and migration.

2.8 ACCELERATION: LOW SULFUR/SULFUR DONOR SYSTEMS

Substantial improvement in heat resistance can generally be obtained by reducing sulfur content to 1 phr or less and adding sulfur donors, as demonstrated in Table 2.9.

Table 2.9 Characteristics of Low Sulfur/Sulfur Donor Systems

Sulfur	0.5	1.0	2.0	3.0	4.5
DPTH	0.7	0.7	0.5	0.3	0.3
MDB	1.5	1.0	0.5	0.5	0.5
ODR cure rate, 150°C, T_{90} minutes	15	17	18	16	15
Durometer: Original	59	56	59	60	65
700 hrs, 100°C	57	50	55	71	84
Tensile, MPa: Original	18	18	18	17	16
700 hrs, 100°C	9.1	6.7	4.5	3.1	1.8
Elongation, %: Original	500	540	580	540	530
700 hrs, 100°C	460	430	230	80	50
Other Ingredients: NR-100; 60 m^2/g N_2SA Silica -60; Resins-10; TMQ-1; Stearic acid-3; ZnO-5; MBS-0.5					

With sulfur content of about 0.5, the selection of a suitable sulfur donor becomes an important exercise. At this sulfur level, line graphs (not shown) have been used to classify sulfur donors in respect to their influence on cure rate, scorch safety, tear strength, heat aging, and, of most significance, heat build-up and set properties. Two sulfur donors, DTDM and MDB, have little or no accelerating effect, and as a consequence, produce flexometer blow-out under severe test conditions. Among a number of interesting relationships, those in Table 2.10 are noteworthy.

There is a wide divergence in cure rates, due mainly to the lack of any accelerating effect by DTDM or MDB. DPTH is not only the fastest but also the only donor to show increased activity at the higher concentration. However, scorch safety may be a problem with this accelerator. DTDM actually retards cure rate, and in many cases, scorch as well. TBTD appears to offer the best combination of properties. TBzTD, which offers less nitrosamine generation, is a suitable alternative to TBTD, although slightly less effective in reducing heat build-up. Extended cures of 200 minutes at 138°C do not alter these relationships.

Table 2.10 Sulfur Donor Accelerators and Their Characteristics

Characteristics	**Sulfur Donor**
Fast cure rate	DPTH; TMETD
Scorch safety	TBTD; DTDM
Heat Aging Resistance	MDB; TMETD
Trouser Tear Strength	MDB
Low Compression Set	TBTD; DPTH; TMETD
Low Dynamic Set	TBTD; DPTH
Ingredients: SMR-100; 150 m^2/g N_2SA Silica-50; Resins-13; TMQ-2; HPPD-2; PEG3350-2; ZnO-4; Stearic acid.-2; Sulfur-0.5; TBBS- 2	

A most suitable application of sulfur donor systems in silica reinforced natural rubber is their use in OTR (off-the-road) earthmover tire treads. With normal sulfur cures, higher silica content, although contributing to improved cut resistance, will also produce high heat build-up. This impasse can be largely resolved by the use of the sulfur donor compounding principles described above. Illustrative comparisons are given in Table 2.11.

Table 2.11 Sulfur Donor Acceleration, OTR Tread, High Silica Content

Compound System	**Normal**	**Donor**
150 m^2/g N_2SA Silica	13	32
Carbon Black N231	52	25
Sulfur	2.0	0.3
MBS (MOR)	1.3	2.0
MDB	--	2.0
TBTD	--	0.2
ODR cure rate, 140°C, T_{90} minutes	22	27
Mooney Viscosity ML_4 100	45	37
Cure: 200 minutes, 140°C		
Durometer hardness	67	67
M300% modulus, MPa	8.0	5.5
Tensile, MPa	19	24
Elongation, %	560	640
MG Trouser Tear, kN/m	11	28
Flexometer HBU, °C	45	36

The application of the sulfur donor principle to the single accelerator systems discussed above can be expected to provide the ultimate in heat resistant natural rubber. A successful application based on sulfur-0.4 phr, donor-1.5 phr, and TBBS-4 phr achieves excellent property retention after oven aging of 28 days at 100°C. In this compound, tear strength remains at an extremely high level. Results for both TBBS and TCS are compared with those for a primary/secondary system in Table 2.12.

Table 2.12 Effect of Single, Double Accelerator on Rubber Properties

	Accelerator System		
	Single	**Single**	**Double**
TBBS	4	--	2
TCS	--	2.3	--
TMTD	--	--	0.4
ODR cure rate, 150°C, T_{90} minutes	28	9	13
Durometer: Original	58	62	60
700 hours, 100°C	70	85	73
Tensile, MPa: Original	20	20	6.4
700 hours, 100°C	9.6	40	740
Elongation, %: Original	715	640	740
700 hours, 100°C	350	45	235
Pendulum Rebound (Zwick):			
23°C/100°C	56.4/65.2	58.0/69.1	54.8/63.6
Compression Set: 70 hrs, 100°C, %	62	47	53
Goodrich Flexometer: 100°C; 25%	1.6 MPa		
HBU, °C	68	62	Blow
DMA Tangent Delta, 30°C	0.114	0.099	0.121

Other ingredients: NR-80; BR1220-20; 180 m^2/g N_2SA Silica -45; 100C resin-5; TMQ-4; HPPD-2; Stearic acid-2; PEG-2; ZnO-8; Sulfur-0.4; MDB(donor)-1.5

A further refinement of this formula to attain the aging performance of TBBS combined with the excellent dynamic properties of TCS is carried out by means of a response surface design. Contour curves based on varying concentrations of TCS and TBBS, Figures 2.15 to 2.18, afford a selection of optimum blends of these two powerful accelerators in respect to age resistance, tear strength and flexometer heat build-up. An optimum area appears in the vicinity of TBBS-4 phr and TCS-0.6 phr.

The merits of this system are better demonstrated if it is compared to a black control of equal hardness. Substantial advantages in heat resistance, tear strength and dynamic properties are apparent in Table 2.13.

Table 2.13 Silica and Carbon Black Compounds of Equivalent Hardness

150 m^2/g N_2SA Silica	50	-
Carbon Black N220	-	45
TBBS	4	2
TCS	0.6	-
MDR cure rate, 150°C, T_{90} minutes	17	14
Mooney scorch, 121°C, T_5 minutes	30+	24
Mooney viscosity, ML_4 100	86	54
Durometer hardness	67	66
Tensile, MPa, Original	20	26
Aged 700 hrs, 100°C	12	9.9
Elongation, %, Original	660	615
Aged 700 hrs, 100°C	405	185
Trouser Tear Strength, kN/m	17	11
Flexometer Heat Build-up, ^{o}C	51	55
DMA Tangent Delta, $30^{o}C$	0.137	0.230
Other ingredients: NR-80; BR1220-20; 100C resin-5; TMQ-4; HPPD-2; PEG-2; Stearic acid-2; ZnO-8; Sulfur-0.4; Vultac 710 (donor)-1.5		

These improvements in heat resistance furnish a strong indication that the usual $70^{o}C$ service limit for natural rubber can, with silica reinforcement, be significantly extended to approach the abilities of some synthetic elastomers.

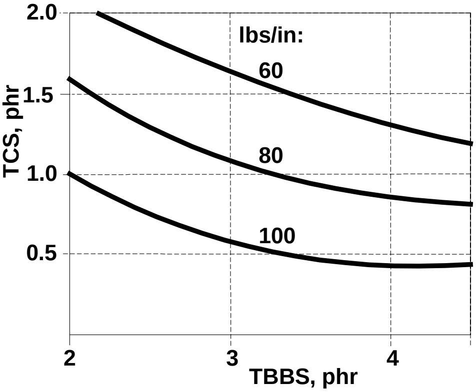


Figure 2.15 Low Sulfur Acceleration: Trouser Tear

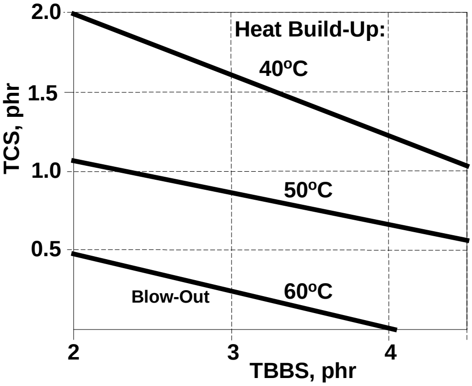


Figure 2.16 Flexometer HBU; 93°C, 25%, 1.6 MPa

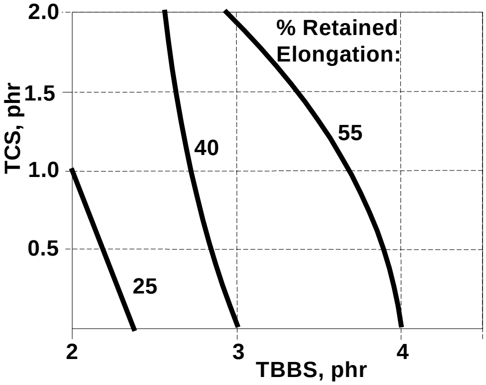


Figure 2.17 Retained Elongation; Aged 28 Days, 100°C

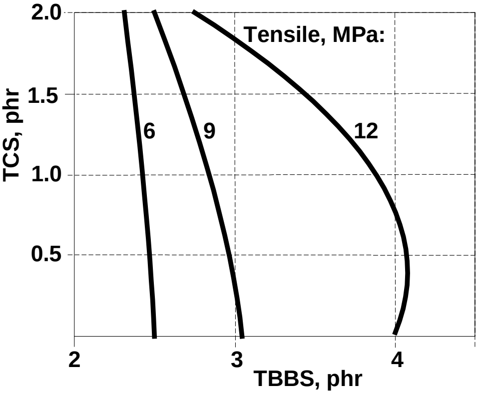


Figure 2.18 Tensile Strength; Aged 28 Days, 100°C

2.9 REVERSION

The term reversion is applied mainly to natural rubber compounds and refers to a decrease in extension modulus and hardness after extended cure times or higher cure temperatures. These and related changes in other vulcanizate properties can be predicted from the shape of the rheometer cure curve where torque values fail to maintain their maximum or plateau range, and decline, to an extent determined by the cure system. In chemical terms, the cause of reversion is generally explained by the breaking and reformation of polysulfide crosslinks and their replacement by shorter, and possibly fewer, monosulfide and disulfide bonds. The chain scission behavior characteristic of natural rubber may also be involved in the reversion phenomenon. Most synthetic elastomers are not usually subject to reversion.

On the basis of a polysulfide breakdown mechanism, it could be anticipated that the usual high polysulfide bond content of silica reinforced natural rubber would lead to an increased likelihood of reversion. However, a comparison of silica and carbon black in the NR/BR formula on an equal hardness basis, in Table 2.14, shows this to be true only at 160°C; at 175°C, silica is superior. At the high cure temperature (175°C) the silica compound is considerably more resistant to physical degradation in terms of retained stress/strain properties.

Table 2.14 Reversion Characteristics of Silica and Black Compounds.

	Cure Conditions	**220 m^2/g N_2SA Silica**	**Carbon Black HAF N330**
20% Modulus, MPa	25min / 150°C	0.86	0.79
	90 min / 160°C	0.97	0.75
	25 min / 175°C	0.85	0.65
300% Modulus, MPa	25 min / 150°C	3.1	11.5
	90 min / 160°C	2.1	9.3
	25 min / 175°C	2.2	4.2
Tensile Strength, MPa	25 min / 150°C	22.7	24.4
	90 min / 160°C	17.0	17.0
	25 min / 175°C	17.0	12.1
Elongation, %	25 min / 150°C	830	525
	90 min / 160°C	905	455
	25 min / 175°C	895	385
MDR 150°C Loss, dN-m (MH10 - MH60)		0.5	0.0
Other ingredients: NR-70; BR-30; Filler-50; resin-8; ZnO-3; Stearic acid-2; Sulfur-2.5; TBBS-3 (0.8 with HAF); PEG-1			

Three major approaches to combating reversion in silica reinforced natural rubber include 1. blending with synthetic elastomers, 2.use of sulfur donor accelerator systems, and 3. use of cross-linking additives. The blending method is illustrated in Table 2.15 by compounds in which 15 or 25 phr SBR replace natural rubber in a compound reinforced in part by a silanized silica (Ciptane®) and accelerated with 3 phr TBBS. It is apparent that the reversion effects in M20% and M300% modulus have been significantly reduced by the presence of solution SBR. Unfortunately a sharp loss in abrasion index remains.

Sulfur donor and crosslinking additives are both effective in combating reversion. A thiuram sulfur donor such as TMETD produces a preponderance of mono- and disulfide crosslinks that are already in the stable state to which polysulfide bonds rearrange during reversion. This state of reduced sulfur bond length produces lower hardness and dynamic stiffness than does a normal sulfur cure.

Table 2.15 Reversion Resistance by Polymer Blending

SMR CV60	100	85	75
SSBR 715	--	15	25
20% Modulus, MPa			
15min / 150°C	1.3	1.3	1.2
90 min / 160°C	1.2	1.3	1.4
300% Modulus, MPa			
15 min / 150°C	8.2	8.1	8.0
90 min / 160°C	5.9	7.0	7.1
MG TrouserTear, kN/m			
15 min /150°C	20	15	12
90 min / 160°C	19	15	13
PICO Abrasion Index			
15 min / 150°C	79	78	76
90 min / 160°C	47	47	51
Other ingredients: 220 m^2/g N_2SA Silica-30; Ciptane-20; resin-10; ZMTI-1; ODPA-1; ZnO-5; Stearic acid-2; Sulfur-2.5; TBBS-3; PEG-1.5			

The crosslinking additives HTS (hexamethylenebisthiosulfate disodium salt dihydrate) and BCI (1,3 bis(citroconimidomethyl) benzene), in contrast to the donor mechanism, produce additional crosslinks during periods of over-curing, which counteract the reduction in polysulfide bonds. Rheometer characterization of these systems in Table 2.16 was obtained in a partially silane coupled 50 phr silica reinforced natural rubber.

At 150°C both donor and additive systems significantly reduce reversion in terms of maximum torque loss. However, at 175°C only the donor system is effective. This reversal in the action of the additives may be caused, at least in part, by increased natural rubber chain scission at the higher temperature. In any case, it presents an example of the uncertainties associated with accelerated evaluations at temperatures higher than those encountered in normal processing or service.

Comparison of net rheometer crosslink data at two temperatures shows changes that relate to reversion mechanisms. Both thiuram containing compounds have lower torque at 175°C which relates to the *decrease* in sulfur bond length from polysulfide to monosulfide; the torque of HTS and BCI additive compounds increases due to the formation of *additional* crosslinks. Only the TBBS system maintains torque at both cure temperatures.

Table 2.16 Reversion Resistance: Crosslinking Additives and Sulfur Donor

Cure system	**A (Control)**	**B**	**C**	**D**	**E**
Sulfur	2.5	2.5	0.4	2.5	2.5
TBBS	2.0	3.0	1.5	3.0	3.0
TMETD	0.3	-	1.5	-	-
HTS	-	-	-	2.0	-
BCI	-	-	-	-	2.0
MDR reversion*, dN-m					
150°C	4.0	4.0	1.7	0.8	1.5
175°C	1.5	5.0	0.0	5.5	3.0
MDR crosslinks:					
MH - ML, dN-m					
150°C	26	25	21	24	23
175°C	19	25	16	29	26

* loss in maximum torque at 60 minutes

Other ingredients: NR-100; 150 m^2/g N_2SA Silica -30 (220 m^2/g N_2SA Silica in A and B); Ciptane 1-20; 100ºC resin-10; ODPA-1; ZMTI-1; ZnO-5; Stearic acid-2; PEG 3350-1.5

Examination of the physical properties of these compounds in normal and over-cured states (15 minutes at 150°C and 90 minutes at 160°C) illustrates the more important compounding aspects of reversion in Table 2.17.

The control, as expected, shows the greatest loss in durometer and 300% modulus as a result of overcure. The accelerator modifications

(TBBS and TMETD) succeed in stabilizing hardness, but not M300; note that rheometer indications of significant reversion with TBBS (above) are not seen here in terms of compound physical properties. Crosslinking additives raise durometer hardness and maintain M300. The principal over-cure change, which appears to occur independently in respect to other properties, is the severe loss in the PICO abrasion index in all systems. Polymer degradation is a likely explanation.

Table 2.17 Properties of Compounds Described in Table 2.16

	A (Control)	**B**	**C**	**D**	**E**
Durometer					
15 min / 150°C	70	70	64	68	70
90 min / 160°C	66	69	64	77	74
M300% modulus, MPa					
15 min / 150°C	7.2	8.5	7.2	7.8	8.4
90 min / 160°C	4.6	5.2	5.2	6.7	7.9
MG.trouser tear,kN/m					
15 min / 150°C	22	20	16	16	20
90 min / 160°C	50	19	23	20	14
PICO abrasion index					
15 min / 150°C	87	78	63	81	76
90 min / 160°C	56	47	54	46	53
Flexometer, HBU °C					
15 min / 150°C	29	23	23	24	23
90 min / 160°C	36	28	33	25	24

A combination of a 25 phr replacement of NR by SSBR 715 with TBBS at 3 phr and HTS at 2 phr provides a compound with over-cured hardness of +5 and no degradation in other properties, except abrasion.

A summary of compounding for reversion resistance includes:

1. 15-25 phr replacement of NR by SBR or SSBR
2. A sulfur donor or 3 phr TBBS cure system
3. Crosslinking additives HTS or BCI
4. Combinations of 1, 2, and 3.

2.10 ANTIOXIDANT SYSTEMS: NON-STAINING

Evaluation of antioxidants in connection with resistance to degradation of tensile properties during heat aging involves side reactions with silica as well as polymer degradation. The summary in Table 2.18 includes the accelerator TBBS and several amine antioxidants in a normal sulfur compound reinforced with a 220 m^2/g N_2SA silica. Addition of one phr

TBBS (from 2 to 3) produces a significant improvement in aged tensile properties as well as a large reduction in heat build-up and set. Increased scorch safety is an anomalous benefit. The ZMTI/ODPA combination offers the best tensile retention, with a sacrifice in scorch safety. TMQ is somewhat less effective than ODPA. Silica surface area can also influence aging behavior (see formulary compound NR 38). Surface areas above 150 m^2/g offer improved tensile properties after accelerated aging at 85°C.

Table 2.18 Antioxidant Systems: Non-staining

TBBS	2	3	3	3
TMTD	0.5	--	--	--
ODPA	1.5	1.5	1.5	--
ZMTI	--	--	1.5	--
TMQ	--	--	--	1.5
ODR cure rate, 150°C, T_{90} minutes	3.1	7.4	3.6	8.1
Mooney scorch, 30°C, T_5 minutes	7.5	15	7.0	17
Durometer:				
Original	60	60	59	60
700 hours, 85°C	68	70	72	72
Tensile Strength, MPa				
Original	28	36	36	34
700 hours, 85°C	14	26	29	20
Elongation, %				
Original	745	735	720	685
700 hours, 85°C	390	570	645	465
Goodrich flexometer: 100°C; 22.5%; 1 Mpa:				
Set, %	36	11	17	15
HBU, °C	44	18	26	20
Compression.set: 70.hrs, 100°C, %	87	71	84	73
PICO abrasion index	59	88	103	100
Other ingredients: SMR-100; Silica-40; 100C resin-5; Stearic acid-1; PEG-1; Sulfur-2.8; Zinc oxide-3				

2.11 PLASTICIZATION

Plasticizing silica reinforced natural rubber and other elastomers is primarily a matter of breaking up the silica network agglomerates formed by hydrogen bonding of surface silanols. Plasticizing the elastomer itself is a separate function, related to the chemical nature of the elastomer. In some cases, notably natural rubber, certain plasticizing materials perform both functions. These materials are generally vegetable in origin.

Tall oil and rosin derivatives are the most effective in terms of viscosity reduction. An example which compares tall oil and naphthenic oil, formulary compound NR 28, demonstrates that 5 phr tall oil provides viscosity and hardness reductions equal to those obtained with 30 phr naphthenic oil. Elimination of the relatively large oil content results in improved stress/strain properties at equal hardness. Other examples in the formulary, compounds NR 19, NR 29, NR 31 and NR 37, illustrate tall oil effects on a wide range of properties. Of major interest here is the large viscosity reduction achieved with no loss in abrasion resistance. In another example, formulary compound NR 68, a combination of tall oil and silane produces low viscosity and good mold flow in an 80 durometer compound. Recommended mixing procedures call for concurrent addition of silica and tall oil, but extending this approach to the use of a pre-blended silica-tall oil masterbatch shows an unexpected decrease in plasticizing efficiency.

When plasticizer evaluations are made in respect to mold flow, tall oil is also quite effective. This is seen in its action in the bushing example, NR64 in the Formulary section, where 3 phr has more than doubled flow length in the spider mold flow apparatus.

A rosin ester (Staybelite® resin) is equal to tall oil in viscosity reduction, used in the 3 to 6 phr range. An equal hardness evaluation of several de-agglomerating plasticizers in an OTR tread formula with both silica and ISAF carbon black reinforcement illustrates, in Table 2.19, viscosity reduction and physical properties. All compounds provide an unusual combination of extremely high tear strength with strong PICO abrasion index values.

Table 2.19 Plasticizers for Silica Reinforced Natural Rubber

	Plasticizer Type (6 phr)			
	Tall oil	**Rosin ester**	**Pine tar**	**Naph. oil**
Mooney viscosity, ML_4 100	70	71	80	110
Durometer hardness	69	69	69	69
M300% modulus, MPa	12	12	10	13
Trouser tear, kN/m	21	24	26	24
PICO abrasion index	135	140	130	140

As noted in Chapter 1, many soluble zinc compounds are capable of reacting with the silica surface silanols to effect breakdown of silica agglomerates and thus reduce compound viscosity. The most effective of these materials include the zinc methacrylates, zinc octoate, and the in situ formed zinc stearate. In the latter case the point at which zinc oxide is added to the Banbury mixer becomes an important consideration.

Early zinc oxide addition with or directly following silica allows complete solubilization by stearic acid with resulting de-agglomeration and effective viscosity reduction.

Removal of silica agglomerates is also achieved by reaction with silane coupling agents and amine derivatives such as hexamethylene tetramine (HMT), triethanolamine and the guanidine accelerators (noted in the accelerator section). De-agglomeration and viscosity reduction is a by-product of the silane coupling of silica to improve abrasion resistance. In this case the silane modification of the silica surface has displaced the hydrogen bonded silanol network agglomerate.

Among conventional rubber plasticizers or softeners, aromatic and petroleum resins are particularly well suited for silica fillers in their ability to maintain a higher level of compound physical properties than that obtained with mineral oils. In the Table 2.20 example a natural rubber/polybutadiene compound reinforced with a silica/ HAF carbon black blend and plasticized with 8 phr aromatic oil is compared to one in which the oil has been replaced by a blend of aromatic and rosin ester resins.

Table 2.20 Effect of Oil and Resin Plasticizers on Properties

Aromatic oil, phr	8	-
100ºC Coumarone indene resin, phr	-	7
Rosin ester resin, phr	-	5
ODR cure rate, 138°C, T_{90} minutes	35	30
Mooney scorch, 130°C, T_5 minutes	14	16
Mooney viscosity, ML_4 100	76	62
Durometer hardness	70	70
Tensile, MPa	19	22
Elongation, %	510	560
Trouser tear, kN/m	7.2	9.9
DeMattia cut growth, kc to 500%	8	28
Goodrich flexometer HBU, ºC	36	34
PICO abrasion index	103	98

With hardness unchanged and viscosity reduced, significant positive reinforcement property changes are found in the resin plasticized compound. Numerous other examples of resin plasticization are contained in the formulary section.

2.12 TEAR RESISTANCE

Tear strength, in common with other rubber compound properties, is largely defined by the test method itself. In recent years, laboratory and product evaluations have demonstrated that a trouser tear geometry offers by far the most relevant means of defining the property called tear strength and predicting tear related product performance. This conclusion has been well substantiated by the correlation found between cut and chip ratings of OTR treads with trouser tear values, as in Table 2.21.

The trouser specimen used in this work is based on a design suggested by A.G. Vieth and modified by M. P. Wagner in which two opposing molded grooves run the length of a 150 x 25 mm slab. The tear takes place in the web between the grooves, usually one mm thick, in a stress/strain tester at a rate of 50 cm/minute (see Figure 2.14). Specimens are prepared so that the tear occurs with the mill grain. Cases of knotty tear, which occur most often in natural rubber compounds, are noted when maximum values are double the minimums. Knotty tear behavior is significant in its ability to resist tear propagation.

Table 2.21 Correlation of Tear Strength and Tire Tread Cut/Chip Rating

150 m^2/g N_2SA Silica	--	35	45
Carbon Black HAF N330	55	20	10
Rosin ester resin	3	5	6
With sulfur donor cure system:			
ODR cure rate, 138°C, T_{90} minutes	27	31	31
Mooney viscosity, ML_4 100	67	59	58
Durometer hardness	72	66	68
MG trouser tear, kN/m	8.6	13	17
Cut/chip rating, rock surface (1= excellent; 4= poor)	4	2.5	2

Tear data must be interpreted with due regard to state of cure. This is a particular consideration for compounds designed for use in thick articles where curing involves periods of several hours at low temperatures. In the example in Table 2.22, based on a filler blend of 30 phr silica and 27 phr N231 carbon black, variations in sulfur and TBTD produce significant tear variation at differing cure conditions. Here a cure of 60 minutes at 138°C gives a false representation of the actual tear strength at 200 minutes, particularly for 0.3-phr sulfur content. Elimination of TBTD provides best tear stability but heat build-up is excessive. Examples based on these relationships are described in the formulary compounds NR 48 and NR 54.

Trouser tear strength has a close relationship to certain other compound properties, particularly elongation at break and hysteresis. Of most practical interest is that between tear and elongation, as illustrated in Figure 2.19, in which higher elongations predict high tear strength. An inverse relationship obtains between tear and flexometer heat build-up.

Table 2.22 Sulfur and Accelerator Effects on Tear Strength.

Sulfur	0.3	0.7	1.0	1.0
TBTD	0.5	0.5	0.5	--
(TBBS-2; MDB-1 in all)				
MG Trouser tear, kN/m				
60 min / 138°C	41	44	27	35
200 min / 38°C	21	25	13	35
300 min / 127°C	40	18	11	35
Durometer hardness				
60 min / 138°C	71	73	75	74
200 min / 138°C	73	76	76	74
Elongation, %				
60 min / 138°C	590	550	500	630
200 min / 138°C	600	560	500	630
Goodrich flexometer: 100°C; 22.5%; 1 Mpa:				
HBU, ºC, 60 min / 138°C	71	63	56	Blow out

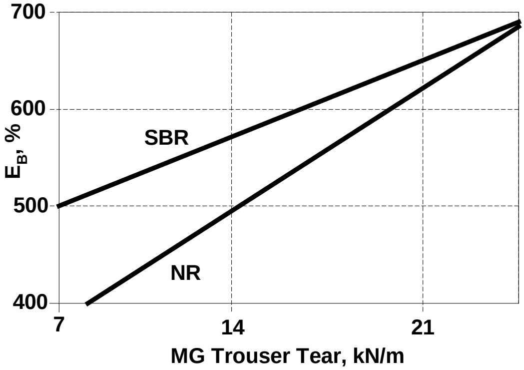


Figure 2.19 Ultimate Elongation vs Trouser Tear

Attempts to reconcile good tear strength with low heat build-up have been more successful with silica than with carbon black reinforcement [4]. These relationships appear to be completely logical when regarded in terms of a stress relaxation mechanism for tearing. Significant stress relaxation relates to a low level of crosslinking and predominantly polysulfide linkages. These properties are typical of many silica reinforced compounds, which produce both high elongation and heat build-up in vulcanizates. Stress relaxation at an advancing tear tip requires high tearing forces to maintain continuing fracture.

Exploration of the interaction of tear strength with other properties has made use of a "viscoelastic" ranking of compounds [5]. This term is useful as a reference to the plastic or elastic nature of common test properties. When the plastic or irreversible flow behavior of a viscoelastic material outweighs the elastic behavior, the results are high values of tear strength, elongation and heat build-up. An example of a viscoelastic ranking of a group of silica reinforced compounds is based on a fairly wide range of tear strength and other property values which are obtained from variations in silica:carbon black ratio, silica surface area (BET N_2SA), silane coupled silica or cure systems. Variations in these compound components produce a group of compounds, which *without significant change in hardness,* can be ranked in terms of tear strength and related properties, as in Table 2.23.

Table 2.23 Viscoelastic Relationship Among Tear Strength, Elongation and Heat Build-up (HBU)

Rank (highest = 1)			Silica/ N231 Black	Silica N_2SA, m^2/g	TBTD, phr	Silane*
Tear	**Elong.**	**HBU**				
1	1	1	50/0	180	0.3	-
2	2	1	50/0	140	0.3	-
2	3	3	50/0	150	0.3	-
4	4	3	30/18	150	0.3	-
5	5	5	18/30	150	.0.2	-
6	6	6	24/24	150	0.3	-
7	7	7	50/0	150	0.3	+
8	8	8	0/50	-	0.1	-

*3% mercaptopropyltrimethoxysilane

Notwithstanding an occasional juxtaposition due to surface area or TBTD concentration, the ranking of these 8 compounds presents a convincing picture of the linear relationship of trouser tear strength, elongation and flexometer heat build-up. Among the all-silica compounds, only the silane-coupled silica (3% mercaptopropyltrimethoxysilane) shows a large loss in tear strength rank, with predicted reductions in elongation and heat build-up. Its rank is, however, still superior to that of the N231 carbon black control. A ranking presentation also demonstrates in convincing fashion the problem of mitigating high heat build-up in tear resistant compounds. Some solutions to this dilemma are discussed in the following sections.

The first principle in compounding for tear strength is the replacement of carbon blacks by reinforcing silica. The effectiveness of silica has been well demonstrated in designing treads for earth mover and heavy duty truck tires, conveyor belt covers, hose and compounds for intricate molding operations where hot tear strength is a factor. The finest particle carbon blacks, such as ISAF and SAF N100 grades, can favorably alter tear strength, but these effects are less substantial than those imparted by silica. Silica driven improvement in tear strength is demonstrated by progressive increases in silica:ISAF ratio in natural rubber tread formulas with low sulfur acceleration in Table 2.24.

Table 2.24 Silica Content Influence on Trouser Tear Strength

150 m^2/g N_2SA Silica	0	12	20	30
ISAF N231 Carbon Black	55	46	40	27
ODR cure rate, 138°C, T_{90} minutes	17	18	30	36
Durometer hardness	72	72	70	68
M300% modulus, MPa	13	11	9	6
MG Trouser tear, kN/m	8.9	9.6	13	20
Flexometer Heat build-up, ºC				
22.5%; 1 MPa	35	35	40	41
25%; 1.6 MPa	46	50	75	70
Cure system: Sulfur1; MDB-1; MBS-2; PEG-1.5				

It appears that a substantial improvement in tear strength is achieved at 20 phr silica; at 30 phr silica the increase is more than 100%. The silica tear strength margin is maintained in testing at 100°C (not shown). Heat build-up with a 200 minute cure remains a problem. The cure system described in Table 2.25 offers a solution.

Silica concentrations of at least 25–30 phr are also important in maintaining high tear strength during the extended cure times required for large truck, OTR, and solid tires. In the compounds in Table 2.25, 13 phr of silica are obviously inadequate to maintain tear strength during a 200 minute cure; 32 phr silica together with a reduction in total filler from 65 to 57 phr, provide a marked improvement. A sulfur donor system (compound C) provides further resistance to tear degradation during a cure time of 200 minutes, together with a reduction in HBU

The data in Table 2.25 also offer an opportunity to compare compound properties characteristic of normal and a low sulfur cure system that includes the accelerator TBTD (compounds B and C). In this case, the major change is a significant loss in hardness when sulfur is reduced to 0.3 phr, even with added donors and TBTD. However, the lower viscosity of compound C will allow a reduction in softener content with a resulting improvement in hardness. In respect to attaining the elusive combination of high tear strength (particularly for the 200 minute cure) and low heat build-up, compound C represents a modest success.

Table 2.25 Cure System and Filler Content Modification for High Tear Strength and Low Heat Build-up

	A	**B**	**C**
150 m^2/g N_2SA Silica	13	32	32
ISAF N231 Carbon Black	52	25	25
Rosin ester resin	--	5	5
Sulfur	2	2.5	0.3
MDB	--	--	2
MBS	--	--	2
TBTD	--	--	0.2
ODR cure rate, 141°C, T_{90} minutes	22	31	27
Mooney viscosity, ML_4 100	45	36	37
Durometer hardness	67	73	67
MG Trouser tear, kN/m			
Cure 40 min / 141°C	19	15	17
Cure 200 min / 141°C	10	20	28k
M300% modulus, MPa			
Cure 40 min / 141°C	11	6.4	5.9
Cure 200 min / 141°C	8.0	5.4	5.6
Goodrich flexometer: 22.5%; 1 MPa			
Permanent set, %	20	18	12
Heat build-up, ºC	45	38	36

A further look at the effectiveness of TBTD (tetrabutylthiuram disulfide) in reducing heat build-up without significant loss of tear strength appears in Table 2.26. It is apparent that the improvement in dynamic behavior from TBTD addition has brought the heat build-up (blow-out conditions) into an acceptable area without a major sacrifice in tear strength. The relatively low tear values at 100°C reflect the low (50 phr) filler loading; at 60 and 70 total filler phr, 100°C tear values for the silica blends rise to 15–20 kN/m, with some accompanying rise in flexometer HBU. PICO abrasion indexes remain relatively unchanged at 87, 94 and 81 respectively.

Other examples of the effectiveness of TBTD, at concentrations of 0.3 and 1.0, in reducing heat build-up are seen in formulary compounds NR 40 and NR 53. The nitrosoamine-reducing thiuram, TBzTD, performs similarly to TBTD. Properties of a TBzTD accelerated compound are described in formulary compound NR 48.

Table 2.26 Reduced Heat Build-up (HBU) with TBTD

	A	B	C
150 m^2/g N_2SA Silica	0	15	25
ISAF N231 Carbon Black	50	25	25
TBTD	0	0.1	0.2
PEG 3350	0	0.5	0.8
Aromatic oil	9	6	3
ODR cure rate, 138°C, T_{90} minutes	27	26	28
ODR crosslinks, MH-ML, dN-m	47	44	46
Mooney scorch, 130°C, T_5 minutes	17	17	20
Durometer hardness	64	63	64
M300% modulus, MPa	11	9	12
MG Trouser tear, cure 200 min / 138°C, kN/m			
23°C	8.4	11.6	14.9
100°C	4.6	3.7	7.1
Flexometer, 25%; 1.6MPa (blow-out conditions)			
HBU, °C	45	46	58

Some help in determining optimum values for sulfur and TBTD can be found in the Figure 2.20 contour graphs for tear and HBU within ranges for sulfur from 0 to 2.5 and for TBTD from 0 to 1 phr. Fortunately, minor variation in slope provides an opportunity to optimize the combined properties, i.e., high trouser tear and low HBU. On this basis, a compound based on 2 phr sulfur and 0.2 phr TBTD has been evaluated and is described as formulary compound NR 63.

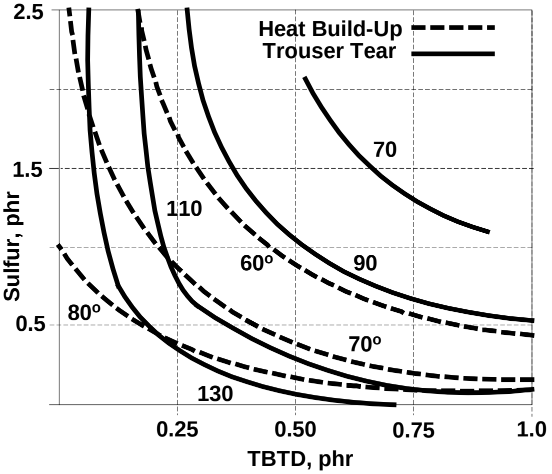


Figure 2.20 Optimizing Trouser Tear and Heat Build-Up

Another example of the benefits available from carbon black replacement by silica is seen in the natural rubber/polybutadiene 60/40 blend of formulary compound NR 53 where replacement of 27 phr HAF by a 150 m^2/g N_2SA silica has been effective in changing the normally brittle nature of this BR blend. Formulas and results are summarized in Table 2.27.

In summary, the preceding discussion of reconciling high tear strength with low heat build-up is based on three compounding solutions:

1. Sulfur reduction with addition of sulfur donors
2. A modest reduction in total filler content of silica-black blends
3. Addition of accelerator TBTD.

Examples of these compounding rules, as noted above, are found in the tables and the formulary compounds.

Table 2.27 Tear Strength Improvement in a BR/NR Blend

	A	**B**
HAF N330 Carbon Black	57	30
150 m^2/g N_2SA Silica	--	27
Aromatic oil	8	4
100ºC resin	--	6
Cure System:	Sulfur donor with TBTD (NR53)	
Mooney scorch, 130°C, T_5 minutes	6	16
Mooney viscosity, ML_4 100	64	70
Durometer hardness	70	70
Trouser tear, kN/m	3.5	8.7
Elongation, %	350	500
DeMattia cut growth, kc to 500%	2	16
PICO abrasion index	131	100
Flexometer HBU, ºC	34	35

2.13 TEAR RESISTANCE: CONTOUR CURVE STUDIES OF SILICA CONTENT EFFECTS

Contour curve studies offer a very useful tool for designing rubber compounds. Generally, a group of 8 to 12 compounds in which concentrations of two components are varied will provide a sufficient number of data points to fit the curves. Each curve represents a constant value of one compound property; the two graph coordinates are selected from variable formula components such as fillers, elastomers, and curatives, fitted with a practical range of phr values. Graphs can be analyzed for individual property responses (through slope or orientation to axis) or can be superimposed to reveal optimum areas for a combination of two or more properties (note description of sulfur and TBTD above). Superimposition is particularly useful in reconciling properties, which are, in the viscoelastic sense, opposites. In all cases it is extremely important to maintain equal or nearly equal hardness among the compounds. This requirement is especially important in studies of filler effects where hardness variation will, in itself, influence dynamic and static test properties. Thus, in the example below, filler variation is accompanied by changes in oil content to control hardness (within experimental variation). Similar considerations in respect to cure rate and crosslink density lead to additions of polyethylene glycol and TBTD at higher silica contents.

Table 2.28 describes a contour curve study in which the compounding variables are 180 m^2/g N_2SA silica content and total filler (silica and carbon black) content.

Table 2.28 Results of Contour Curve Study

Compound Formula Variables				**Controlled Compound Properties**		
Silica*/N231	Oil	TBTD	PEG	Durometer	T_{90}, min	Xlink, dN-m
0/50	9	0	0	64	27	54
0/70	23	0	0	66	27	50
1 /35	6	0.5	0.5	63	26	54
15/45	12	0.5	0.5	63	26	51
15/55	20	0.5	0.5	64	27	48
25/25	3	0.8	0.8	64	28	58
25/40	15	0.8	0.8	65	27	51
25/55	26	0.8	0.8	67	27	49

*180 m^2/g N_2SA Silica

Contour curve graphs, Figures 2.21 to 2.25, for trouser tear at ambient and 100°C temperatures, Goodrich flexometer heat build-up, 100°C rebound resilience, and PICO abrasion index illustrate the dependence of these compound properties on silica and total filler content. Although increasing filler with no silica present is helpful, the highest tear strength values can be attained only at silica contents of 20 phr and more.

Tear testing at 100°C shows even greater silica importance. Heat build-up contours, derived from blow-out test conditions, show that both carbon black and silica contribute to higher HBU in equal proportion; at a total filler content of 70 phr, silica has little effect. Any degrading influence from silica is also absent in hot rebound resilience testing at all filler contents and in abrasion testing at 55 phr total filler. At higher filler contents, abrasion resistance loss is slight.

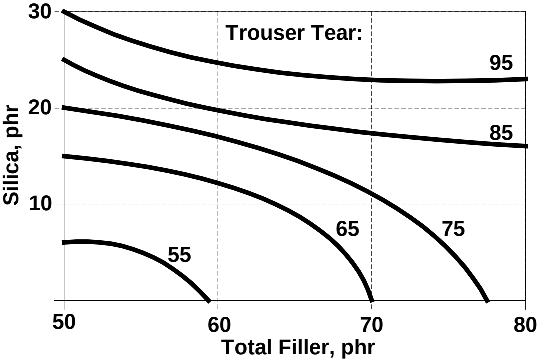


Figure 2.21 Silica vs Total Filler Content: Ambient Trouser Tear

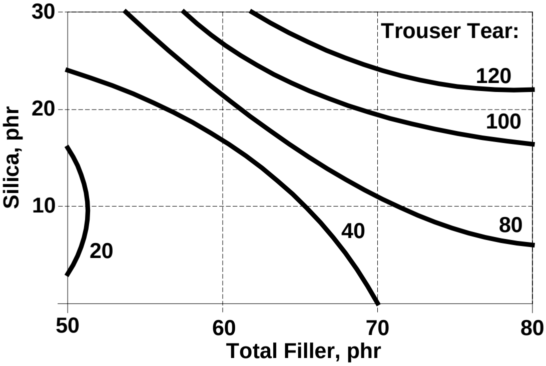


Figure 2.22 Silica vs Total Filler Content: 100°C Trouser Tear

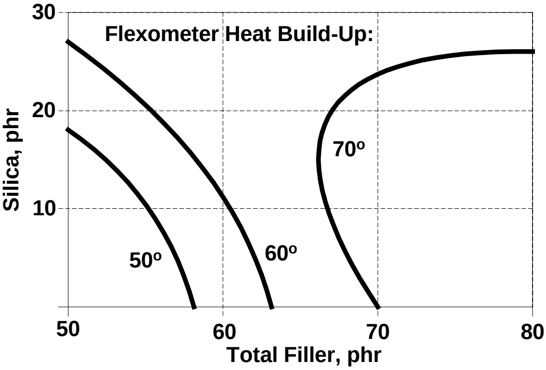


Figure 2.23 Silica vs Total Filler Content: Heat Build-Up

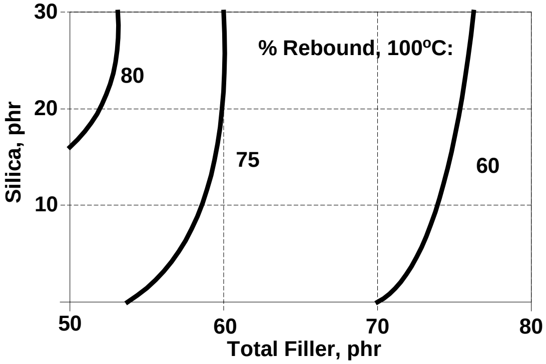


Figure 2.24 Silica vs Total Filler Content: 100°C Rebound

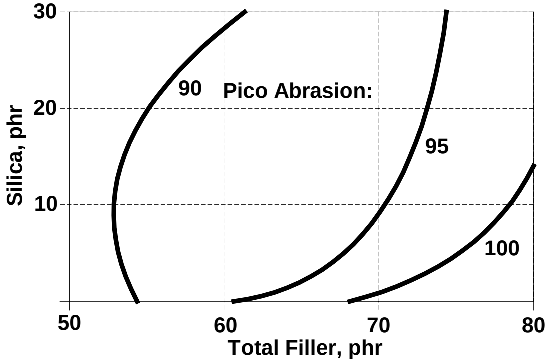


Figure 2.25 Silica vs Total Filler Content: PICO Abrasion

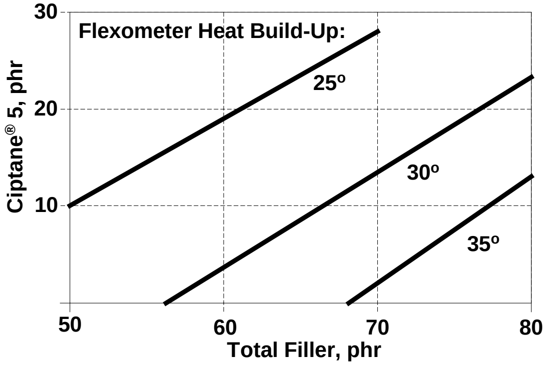


Figure 2.26 Treated Silica vs Total Filler: Heat Build-Up

The silica tendency to reduce abrasion resistance and increase heat build-up can be reversed by blending polybutadiene with natural rubber and by silica modification with a silane coupling agent. A series of silica-black filler variations similar to those above based on a 50/50 blend of BR1245 and SMR with 5% silane treated silica (Ciptane 5) gives a radically different picture of silica effects. In this case the silane treated silica *reduces* tear strength as well as heat build-up. Contour curves, Figures 2.26 to 2.28, illustrate significant reduction in heat build-up and increase in hot rebound resilience as silica content rises. Abrasion resistance responds only to increased filler content.

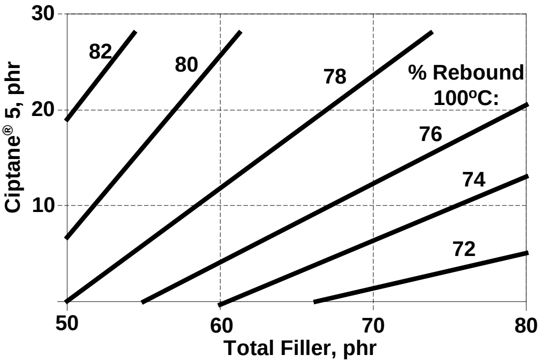


Figure 2.27 Treated Silica vs Total Filler: 100°C Rebound

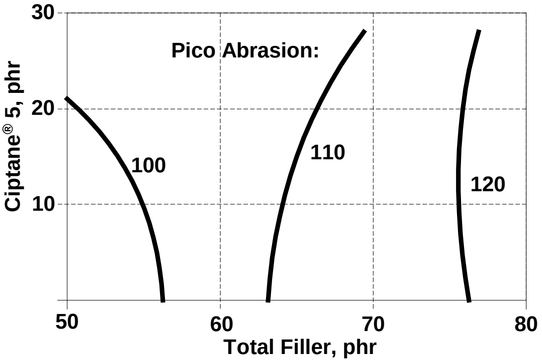


Figure 2.28 Treated Silica vs Total Filler: Pico Abrasion

2.14 TEAR RESISTANCE: SILICA PRIMARY PARTICLE SIZE

Silica particle size, as defined by BET nitrogen surface area (N_2SA), is the property responsible for major changes in tear strength and HBU (see formulary compound NR 38). Over a range of 150 to 250 m^2/g

N_2SA, trouser tear strength increases five fold, while durometer hardness remains unchanged until surface area reaches 250 m^2/g. PICO abrasion index, which depends, in addition to filler particle size, on the strength of the filler–polymer bond, is unaffected. In keeping with the augmentation of silica structure that occurs with increased surface area, Mooney viscosity rises from 36 for 150 m^2/g N_2SA to 102 for 250 m^2/g N_2SA silicas. Both ambient and 100°C rebound values reflect the loss in efficient dynamic behavior, which occurs at the highest surface area. Although flexometer heat build-up shows a significant increase with the 250 m^2/g N_2SA silica, the cure system of 3 phr for both TBBS and sulfur retains HBU within a practical range.

Perhaps the most interesting and most unexpected effect of increased silica surface area is the faster cure rate, greater MDR crosslinking (MH-ML) and increased activity at processing temperatures (scorch safety in formulary compound NR 38). This behavior is completely at odds with that of other silica reinforced elastomers (EPDM excepted) where higher surface areas produce slower cure rates and reduced high strain modulus (M300). This cure retarding behavior is readily explained by more soluble zinc removal (from its accelerator reactions) due to the greater surface area available. With natural rubber the attachment of zinc to silica may make the zinc ion more reactive to accelerator complexing, or, more likely, the increased surface area supplies a base for catalytic reactions. Peroxide cured NR compounds also show this unusual relationship between cure rate and silica surface area.

2.15 TEAR RESISTANCE; NON-MARKING SOLID TIRES

Compounds for non-black industrial tires are based on silica contents of 40 to 60 phr, generally with silane modification. Service requirements are similar to those of pneumatic truck or OTR tire treads, i.e., low heat build-up, resistance to cutting and chipping and abrasive wear resistance. Since solid tires are cured by both compression and injection molding, viscosity and scorch safety are also important factors. These properties involve different, and sometimes conflicting, compounding technologies.

Low heat build-up is attained from low silica content, use of cure systems designed for silica, and silane coupling. Cut resistance, defined by laboratory trouser tear test methods, depends largely on silica content and surface area. Silica contents above 50 phr and surface areas above 150 m^2/g provide the highest trouser tear values. Silane coupling significantly reduces tear strength.

Abrasive wear reinforcement requires the use of high surface area silica accompanied by moderate silane coupling. Partial replacement of natural rubber by BR is also helpful, but results in loss of tear resistance. Compound viscosity can be reduced in two ways, through polymer breakdown or silica structure modification. De-agglomeration of silica structure is one of the characteristics of silane coupling. It is also readily achieved, with or without silane, by the addition of zinc methacrylate or tall oil or their derivatives. The latter materials, in the 1 to 3 phr range, are preferred for viscosity control as they entail few changes in reinforcement.

The effects of a mercaptosilane (TESPT) on relevant properties in a 45 phr 220 m^2/g silica reinforced NR formula are summarized in Table 2.29.

Table 2.29 Effects of Mercaptosilane on Compound Properties

	TESPT Content, phr		
60 min / 140°C cure:	0	1.0	2.5
Mooney Viscosity, ML_4 100	70	70	53
Durometer Hardness	72	72	69
MG Trouser Tear, kN/m	27	12	7
DIN abrasion loss, ml	191	173	158

Present commercial practice frequently favors the use of one solid tire formula for use in all types of service conditions: overloads, cutting surfaces, sliding abrasion, etc. To satisfy this requirement, the following example, based on the compounding technology discussed above, is recommended as a general purpose non-marking industrial tire compound:

Natural Rubber-100; 220 m^2/g N_2SA Silica-45; TESPT-1.0 (or mercaptopropylsilane-0.5); 100ºC resin-7; ZMTI-1.0; ODPA-1.0; Zinc Oxide-3; Stearic acid- 1; PEG 3350-0.5; ZDMA 634-3; Sulfur-3.3; TBBS-3.0

Processing and vulcanizate properties of this compound are described in formulary compound NR 55. To provide maximum tear strength and abrasion resistance a 220 m^2/g N_2SA silica at 45 phr is used. Zinc dimethacrylate (ZDMA 634) maintains suitable viscosity and TBBS at 3 phr insures low HBU and tangent delta. The importance of 3 phr TBBS cannot be overestimated, particularly for tread applications. To illustrate, a reduction of TBBS to 2 or 2.5 phr, using the formula recommendation above, results in the deterioration of crosslinks, abrasion, hardness, tear strength, heat build-up and dynamic modulus shown in Table 2.30.

Table 2.30 Effects of Reduced TBBS

	A	**B**	**C**
TBBS Content, phr	3.0	2.5	2.0
MDR cure rate, 150°C, T_{50} minutes	4.4	5.3	5.5
MDR Crosslinks, 20 minutes, dN-m	32	27	23
Durometer harness	67	63	64
PICO abrasion index	85	81	68
MG trouser tear, kN/m	28k	17k	22
Flexometer HBU, ºC	14	14	32
Dynamic modulus, E', MPa	9.5	5.1	7.3

Although silane coupling of silica is unique in attaining abrasion resistance and is commensurate with that of black reinforcement, in other respects silane effects are similar to those provided by ultra accelerators such as TBzTD. As noted in formulary compound NR 50, this similarity is particularly true for tear resistance, heat build-up and compression set properties, for both medium and high surface area silicas. The significantly higher M300% high strain modulus of the silane coupled compounds is a usual accompaniment of increased abrasion resistance and reflects the coupling improvement in silica–rubber bond strength.

Tear strength is also affected by mixing procedures. A single stage Banbury mixed batch in which curatives are included is compared to one in which curatives are added on a mill (both compounds based on raw natural rubber) in Table 2.31. Mill addition values reflect additional rubber breakdown during milling. Other properties show no significant change.

Table 2.31 Mixing Effect on Tear Strength Using Raw NR

	Banbury	**Mill**
MDR cure rate, 150°C, T_{50} minutes	6.4	7.3
MDR Crosslinks, 30 minutes, dN-m	36	34
Mooney viscosity, ML_4 100	46	42
Durometer (30 min/150°C):		
23°C	72	71
100°C	70	68
MG Trouser tear, kN/m	12	8

Silane pretreated 150 m^2/g N_2SA silica has also been used in non-marking solid tires to provide the necessary combination of tear strength and wear resistance. A typical example is formulary compound NR 47.

2.16 SHELF AGED STIFFNESS AND GREEN STRENGTH

Formula NR 55 was also used in a study of *shelf aged stiffening*, a well known characteristic of precipitated silica tread compounds. After shelf aging, Mooney viscometer readings at 1 minute provide a convenient measure of stiffening effects. In this case a rubber peptizer (2,2'-dibenzoamido diphenyldisulfide, Renacit® 11, 1 phr) was compared to zinc dimethacrylate (ZDMA 634, 3 phr) and tall oil (2 phr). Viscosity is measured at 1 and 4 minutes before and after 4 weeks shelf aging:

	Renacit 11		ZDMA		Tall oil	
ML100	O	A	O	A	O	A
1 minute	71	78	68	63	68	63
4 minutes	59	63	48	44	50	42

O= Original, A= Aged

The decrease in ML_4100 after shelf aging for ZDMA and tall oil indicate that both these materials are effective in preventing silica agglomeration and the accompanying stiffening or boardiness. Prior to this work, polyethylene glycol (present in all of these compounds) was normally recommended to prevent shelf stiffening. The added plasticizing and stabilizing actions of ZDMA and tall oil are of special usefulness in those situations where rubber breakdown is omitted.

The agglomeration tendency of precipitated silica often leads to high viscosity and stiffness with an accompanying increase in *green strength*. However, when the objective is to enhance green strength without significant change in viscosity and hardness, it becomes apparent that silica surface area is considerably more important than silica content. In a green strength plot of tension yield point versus total filler content, based on 0, 15 and 25 phr silica for both medium and high N_2SA silicas, Figure 2.29, only the 200 m^2/g silica is effective is raising the yield point, and this only at total filler content less than 75 phr. Hardness and viscosity of compounds included in this polyisoprene-based study are described in Table 2.32a and 2.32b.

Table 2.32a Effect of Shelf Aging: Black Controls

N299 Black	Oil	**ML_4 100**	**Durometer**
50	0	71	68
60	12	71	69
75	24	71	71
Shelf aged 10 days			

Table 2.32b Effect of Shelf Aging: Silica Surface Area

			ML_4100		Durometer	
Silica	N299 Black	Oil	150*	200*	150*	200*
15	35	0	66	70	65	64
15	45	12	59	70	67	64
15	60	24	62	66	69	65
25	25	0	75	70	66	63
25	35	12	77	70	64	64
25	50	24	61	66	68	64

*Silica surface area (BET), m^2/g

Shelf aged 10 days

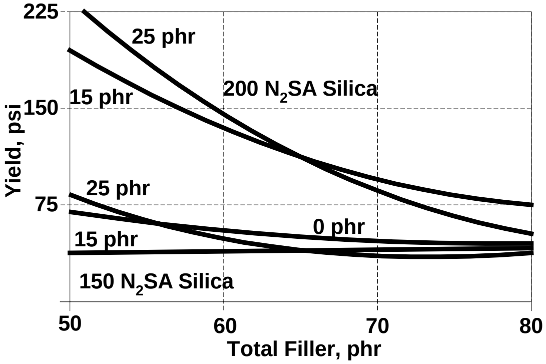


Figure 2.29 Effect of Silica Surface Area and Loading on Green Strength

2.17 PEROXIDE CURE

A major objective of curing silica reinforced natural rubber with peroxides is to obtain low compression set. Other properties such as hardness, resilience, high strain modulus and heat resistance can vary in direction from those of comparable sulfur cured compounds either positively or negatively, depending on ingredient variation. Ultimate elongation and trouser tear strength invariably are lower with peroxides. The comparison of sulfur and peroxide cure systems in formulary compound NR 60 shows a significant reduction in set and an unusual loss in heat resistance with peroxide. The latter is evidently related to the absence of a co-agent, an omission here which makes possible an equal crosslink and hardness comparison.

An equal hardness comparison between silica and carbon black reinforcement, at the 30 phr level in Table 2.33 indicates that ISAF carbon black is still superior to a 135 m^2/g N_2SA silica in respect to attaining low set.

Table 2.33 Properties of Peroxide Cured Compounds: Silica and Black

	N231 Carbon Black	**135 m^2/g N_2SA Silica**
ODR cure rate, 160°C, T_{90} minutes	32	32
ODR crosslinks, MH-ML, dN-m	58	52
Durometer hardness	50	49
M300% modulus, MPa	15	6.6
Elongation, %	310	440
Compression set, 70hrs, 100°C, %	10	21
Pendulum rebound (Z), %:		
23°C	72.4	74.8
100°C	83.4	85.8
Other ingredients: SMR-100; 135 m^2/g N_2SA silica-30;oil-3;ODPA-1;DCP-2.4		

Higher resilience with silica, notwithstanding lower crosslink density, points to a structural explanation. The very significant loss in 300% modulus indicates that even without the silica surface modification by soluble zinc, the silica–rubber bond is still inferior to that of black–rubber. The relationship of these property differences to silica structure is discussed below.

2.18 PEROXIDE CURING: SILICA REINFORCEMENT AND STRUCTURE

A study of peroxide curing of silica filled natural rubber [6] affords an opportunity to explore silica reinforcing mechanisms, free from the constraints and ambiguities present in zinc oxide activated sulfur cure systems. Mechanical properties of sulfur-cured compounds are largely the result of the combined influence of filler–polymer bond strengths and the type and number of sulfur crosslinks. These two factors determine the balance between viscous and elastic responses to deforming forces. Carbon black reinforcement operates primarily through polymer–filler bonding; filler influence on crosslinking is minor. In contrast to this, precipitated silica has, because of its reaction with soluble zinc, a profound and usually degrading effect on crosslinking as well as polymer bonding. Thus, in many sulfur based compounding studies it is not possible to ascertain the true reinforcing function of reinforcing silicas. This silica dilemma has existed ever since the introduction of fine particle precipitated silicas some 60 years ago. Peroxide systems provide a means to evaluate silica and carbon black fillers on a basis of equal cure state, free from sulfur crosslink modification.

The study of silica structure in peroxide cured natural rubber is greatly aided by exploring the effects of silica surface modifying materials on processing and vulcanizate properties. At the same time, SEM micrographs (at 20,000X) make a structural connection in terms of agglomerate size. Zinc ion (soluble zinc oxide) is probably the most common modifier of precipitated silica. In addition to zinc oxide, surface reactants include glycols, amine derivative accelerators and antioxidants, as well as silanes and free water.

Further examination of zinc effects on compression set reveals the silica structure basis of this property. In the formula noted above (with a 150 m^2/g N_2SA silica), addition of zinc oxide with and without stearic acid resulted in a significant lowering of set values. Curing and vulcanizate properties, except for resilience, remain essentially unchanged, as seen in Table 2.34.

Table 2.34 Peroxide Cure: Zinc Oxide Effects

	A	B	C
Zinc oxide	0	3	3
Stearic acid	0	0	2
MDR cure rate, 160°C, T_{90} minutes	3.7	3.9	4.0
MDR crosslinks, dN-m	27	29	27
Durometer hardness	58	61	58
Compression set, %	31.4	18.1	17.6
M300%, modulus, MPa	7.6	7.8	6.1
Elongation, %	500	480	490
Rebound (Zwick), %			
23°C	61	69	70
100°C	69	76	78

In this case, set reduction is unusually large because zinc oxide and stearic acid were added to already mixed and shelf aged compound. Similar results are found with magnesium oxide and stearic acid.

As seen above and in the example below, compression set is not the only test indicator of silica structure. A similar study of silica (30 phr) surface modification by drying and silane addition, which includes the scanning electron micrographs in Figures 2.30 to 2.32, illustrates relationships between agglomerate size and other physical properties. Reduction in maximum agglomerate size is accompanied by lower hardness with increased 300% modulus and resilience, as shown in Table 2.35.

All these data can be taken to illustrate the consequences of changes in silica agglomerate structure. Surface modification of silica by zinc, magnesia, silane attachment or reduction of free water (by drying) hinders the agglomeration of primary particles by hydrogen bonding of surface silanols. With silane attachment or reduced free water, silica-polymer bonding is strengthened.

Reduced hydrogen bonding (reduced agglomerate size) lowers the extent of silica–silica breaking and reformation during a compression set test procedure, and results in lower percent set values. Lower hardness, M20 modulus, and accompanying improved rebound are also indicators of reduced structure strength at low strains. Increased high strain modulus (M300%) indicates improved silica–polymer bonding, notwithstanding the reduction in ODR crosslinks. Here, as in most structure studies, the final structure of silica in a vulcanizate is the result of an equilibrium between silica–polymer and silica–silica bond strengths.

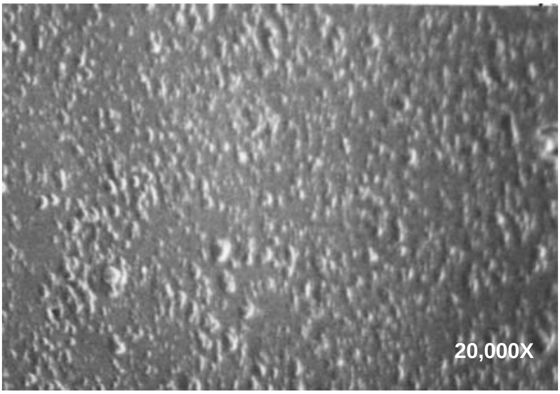


Figure 2.30 Agglomerate Size: Silica with 6% Water

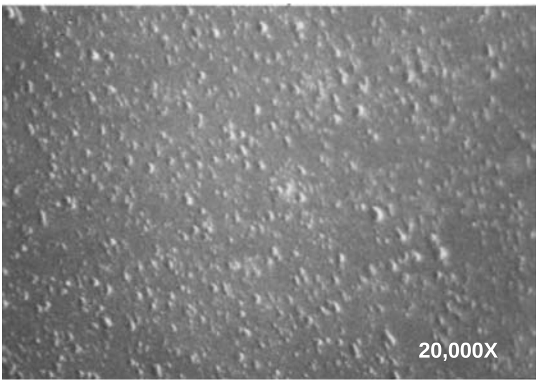


Figure 2.31 Agglomerate Size: Silica with 0.2% Water

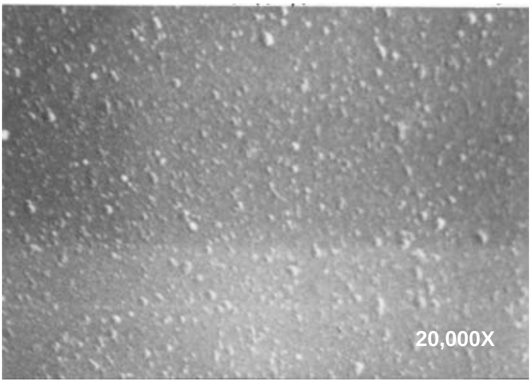


Figure 2.32. Agglomerate Size: Silica, Mercaptosilane and 0.2% Water

Table 2.35 Peroxide Cure: Dry Silica and Silane Coupling

Silica free water, % Mercaptosilane MPTMS	6 (normal) -	0.2 -	0.2 1
Agglomerates, predominant size range, nm			
Minimum	30	30	30
Maximum	100	70	50
ODR cure rate, 150°C, T_{90} minutes	18	16	22
ODR crosslinks, dN-m	61	52	52
Mooney viscosity, ML_4 100	66	90	74
Durometer hardness	60	57	53
M300% modulus, MPa	6.9	7.8	9.2
Pendulum rebound (Goodyear-Healy), %			
23°C	75.2	76.9	79.9
100°C	84.1	86.5	88.4

2.19 PEROXIDE CURING: SILICA SURFACE AREA

Any study of silica surface area effects also benefits from the use of peroxide, rather than sulfur, curing systems. Freedom from sulfur crosslink interference by silica allows a more fundamental approach with peroxide. In addition, in any discussion of surface area effects it is necessary to keep in mind that surface area values are only an indication of primary particle size, the silica characteristic that actually controls reinforcement and crosslinking. Reinforcing primary particle diameters are those in the 12 to 22 nanometer range, determined by electron microscopy.

As noted in the previous chapter, practical testing requirements dictate the use of nitrogen (BET) or cetyltrimethylammonium bromide (CTAB) surface absorption methods as good indicators of particle size. These data, expressed in square meters per gram, generally correlate inversely with particle diameter measurements taken directly from electron micrographs. Smaller particles equal larger surface areas.

A comparison of various surface area commercial silica grades at 30 phr cured with DCP at 2.4 phr, in Table 2.36, reveals only one major property change, viscosity, as surface areas increase. There are, however, some very interesting minor changes in cure rate, crosslinking, heat resistance and compression set.

Table 2.36 Peroxide Cure: Effect of Silica Surface Area on Properties

Silica N_2SA, m^2/g	135	150	190	215	250
MDR cure rate, 150°C, T_{90} minutes	4.2	3.	3.5	3.1	2.7
MDR crosslinks, dN-m	16	17	19	30	31
Mooney viscosity, ML_4 100	60	69	74	85	124
Durometer hardness	55	58	58	58	61
Tensile, MPa, Initial	22	25	25	25	24
Aged 700 hrs, 100°C	1.7	2.0	2.1	3.3	4.7
Compression set, %	25.1	31.4	30.0	33.1	37.5

The modest increase in cure rate and more significant increase in crosslinks are also seen in sulfur systems, formulary compound NR 38 for example. However, with peroxide, the effect is much more pronounced. A possible explanation here is a decrease in heterolytic peroxide decomposition as high surface area silicas sequester organic materials, leading to increased crosslinking. Viscosity escalation is more readily explained in terms of enhanced structure densities with smaller primary particles or agglomerates. As noted above, enhanced structure can also be implicated in rising compression set values. This particular study involves only a relatively low filler level of 30 phr and can therefore not be expected to reveal any substantial distinction in reinforcing properties such as tear strength or abrasion resistance. Regardless of content, other studies that compare surface area effects have detected little influence of surface area on abrasion resistance.

Dynamic modulus testing of these compounds at various temperatures reveals several trends, as seen in Table 2.37. At temperatures of 20°C and above, elastic modulus, E', increases with surface area, in accordance with the hardness increase noted above. However, at -40°C stiffness *declines* with high surface silicas. Loss modulus, E", remains essentially unchanged at 60°C over the entire surface area range.

Similar evaluations of semi-reinforcing silicas, 35 to 70 m^2/g, can best be interpreted by examination of the SEM micrographs in Figure 2.33.

Table 2.37 Peroxide Cure: Effect of Surface Area on Dynamic Properties

DMA dynamic modulus,		**Silica N_2SA, m^2/g**				
1 Hz, 15%:	**Temp, °C**	**135**	**150**	**190**	**215**	**250**
E', MPa	-40	390	440	460	225	140
	20	10	16	17	15	24
	30	5.0	7.1	7.8	8.1	10.4
	60	4.9	6.7	7.3	7.7	9.7
E",MPa	60	1.19	1.28	1.11	1.12	1.28
Tan delta	60	0.242	1.91	0.151	0.146	0.132

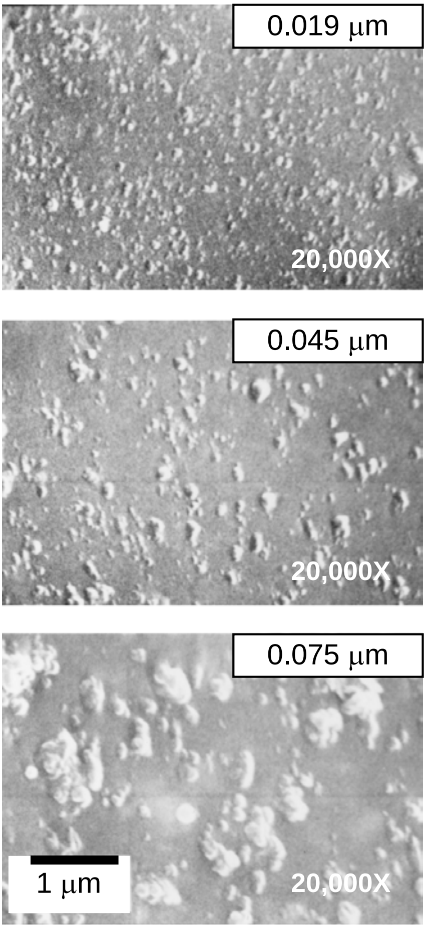


Figure 2.33 Silica vs Agglomerate Size; 30 phr in NR

Here one has a clear picture of the large agglomerates characteristic of low surface areas. The large agglomerates form only weak reinforcement, which translates to lower tensile and tear strengths. More departures from the behavior of high surface area silicas are seen in the low viscosities and high resilience of semi-reinforcing grades. These properties can be predicted from the presence of large areas of unfilled rubber in the SEM micrographs. Although these areas contribute to excellent flow behavior in extrusion, calendering and molding operations, sufficient silica network structure persists to insure low swell and nerve during processing.

2.20 PEROXIDE CURE: SILANE COUPLING

As in the case of the silica structure studies discussed above, peroxide crosslinking allows an unfettered look at silane coupling without the side reactions of sulfur cure systems [7]. At the outset, it must be noted that in natural rubber, silane coupling of silica to polymer is less effective, in terms of abrasion improvement, than in SBR, BR, and other synthetic elastomers. However, in other respects similar compound changes occur. Of greatest significance is the improvement of silica nano-dispersion, seen in the Figure 2.34 electron micrographs of compounds with and without silane.

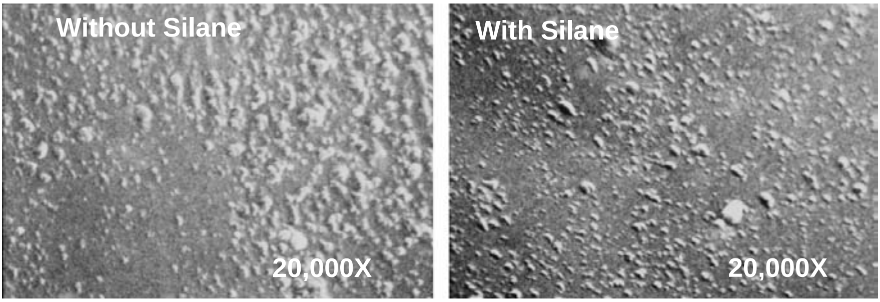


Figure 2.34 Effect of Silane on Nanodispersion of Silica in NR

In dicumyl peroxide cured compounds reinforced with 45 phr of 150 m^2/g N_2SA silica the influence of mercaptosilane on resilience is of particular significance. In Table 2.38 the sulfur donor DTDM has been included in the compound to illustrate a synergy in respect to viscosity and 20% modulus. In spite of a loss in crosslinks, the silane produces a large increase on both 300% modulus and resilience, changes which are due to, respectively, enhanced silica–polymer bonding and reduced silica–silica structure in the vulcanizate. However, in the uncured state the silane shows little silica structural effect, i.e., reduced viscosity, without the presence of the sulfur donor DTDM. This synergism with sulfur has also been found in sulfur cured compounds, accelerated by DOTG, in which zinc oxide is not present, a “zinc-free” system. The conclusion here is that silica structure change by silane MPTMS before crosslinking requires the presence of free sulfur.

Table 2.38 Peroxide Cure: Silane Coupling Effects

Silane MPTMS	0	1.5	1.5	0
Dithiodimorpholine DTDM	0	0	1.5	1.5
ODR cure rate, 160°C, T_2 minutes	1.8	2.0	2.0	1.5
T_{50} minutes	6	7	6	5
ODR crosslinks, MH-ML, dN-m	62	56	48	52
Mooney viscosity, ML_4 100C	108	122	78	110
Durometer hardness	69	67	65	67
Low strain modulus M20%, MPa	1.4	1.4	0.9	1.6
High strain modulus M300%, MPa	8.9	15	10	4.6
Elongation, %	500	375	510	690
Pendulum rebound (Goodyear-Healy), %				
23°C	65.1	70.7	70.7	64.9
100°C	74.0	79.3	78.7	71.8

2.21 SILANE COUPLING: SULFUR CURE SYSTEMS

Modification of the silica surface by silane coupling agents in a sulfur cure system is a reaction somewhat different from that in the peroxide system described above. Here the enhancement of high strain modulus, M300, and dynamic properties has been muted by interference from soluble zinc. Unfortunately, in the Table 2.39 comparison of two mercaptosilanes, mercaptopropyltrimethoxysilane (MPTMS) and triethoxysilylpropyl-tetrasulfidesilane (TESPT), the 130°C stock temperature attained in the single stage Banbury procedure used here is probably not adequate to break down the TESPT completely to a reactive mercaptan state. The noted formula changes in the control are made to maintain an equal hardness basis.

Significant effects of MPTMS include faster cure rate and reduced viscosity. The characteristic coupling effects of increased abrasion resistance, with decreased tear strength and heat build-up are barely visible. However it appears that both mercaptosilanes, probably through decreased polysulfide crosslink formation, have a positive influence on suppressing reversion.

Table 2.39 Silane Coupling Agents with Sulfur Cure

220 m^2/g N$_2$SA Silica, phr	40	45	45
MPTMS (A189)	0	1.5	0
TESPT (SI69)	0	0	1.5
TBBS	3	2	2
MDR cure rate, 150°C, T$_{50}$ minutes	9.2	5.3	8.3
MDR crosslinks, dN-m	31	25	26
Reversion @ 60 minutes	9	4	3
Mooney viscosity, ML$_4$ 100	74	53	81
Cure, 25 min / 150°C:			
Durometer hardness	67	67	70
M300% modulus, MPa	5.9	7.8	7.1
Pendulum rebound, 100°C, %	70	71	70
DIN abrasion loss, ml	176	154	176
Flexometer HBU, °C	17	13	19
MG trouser tear, kN/m	16K	13K	15K
Other ingredients: SMR-100; 100C resin-10; HPPD-2; Stearic acid-2; ZnO-3; PEG 33501; Sulfur- 2.8; TBBS- 2/3.			

2.22 ZINC-FREE CURE SYSTEMS

Although soluble zinc-free systems with precipitated silica are designed primarily for solution polymers, this method of improving reinforcement by silica is also effective in natural rubber compounds. Obviously the fatty acid in natural rubber leads to a certain amount of soluble zinc. As noted below, the “zinc-free” environment is attained by elimination of fatty acid and glycol with reduction of zinc oxide. HMT (hexamethylenetetramine) acts to increase both cure rate and scorch safety, as seen in Table 2.40.

Among many positive items here, the most interesting is the large increase in hardness and dynamic stiffness with zinc-free curing, achieved not from increase in filler or decrease in plasticizer, but from a stronger silica network structure. Higher set values are not reflected by any change in flexometer heat build-up, but they, together with improved trouser tear, can be regarded as reliable indicators of a significant increase in polysulfide crosslinks. The associated increase in dynamic loss modulus and tangent delta is an expected but not desirable consequence.

The relatively modest rise in abrasion index is indicative of natural rubber’s low response to improved silica–polymer bonding. Unmodified silica has always produced better abrasion values in natural rubber than in other elastomers. Although good abrasion resistance is usually accompanied by poor tear strength, the zinc-free system produces improvement in both of these opposing properties. However, reduced availability of soluble zinc leads to a characteristic decline in heat resistance. The solution SBR715 present at 30 phr in these formulas was found to be superior to BR1220, SBR8110 and OE SBR752 in respect to MDR crosslinking, hardness, 300% modulus, PICO abrasion and flexometer heat build-up.

Table 2.40 Zinc-free Cure System

Cure system:	**Normal**	**Zinc-free**
Stearic acid	2	0
Polyethylene glycol	1	0
Zinc oxide	3	0.6
HMT	0	2
MDR cure rate, 150°C, T_{90} minutes	16	7
MDR crosslinks, dN-m	26	29
Mooney scorch, 121°C, T_5 minutes	30+	30+
Mooney viscosity, ML_4 100	98	82
Durometer hardness	66	77
M300% modulus, MPa	5.8	6.4
Tensile, MPa	24	24
Elongation, %: Original	680	705
Aged 700 hrs, 90°C	230	125
PICO abrasion index	75	87
MG trouser tear, kN/m	16	20
Compression set, 70 hrs, 100C,%	71	93
Flexometer HBU, ºC	35	33
DMA dynamic modulus: 60C; 1 Hz		
E', MPa	18	24
E"	1.8	2.9
Tangent delta	0.104	0.123
Other ingredients: NR-70; SBR715-30; 150 m^2/g N_2SA Silica -50; CI resins-17; Sulfur-2; TBBS-3; ODPA-1		

2.23 ZINC-FREE CURE SYSTEMS: POLYISOPRENE (IR)

Since the fatty acid content of natural rubber prevents the establishment of a soluble zinc-free system, an alternative approach in which solution polyisoprene replaces the natural variety is of some interest. The following equal hardness comparison in Table 2.41 is designed to test the ability of a zinc-free system to match the reinforcement of silane coupling in a blend of IR and BR. In this case the zinc-free system not only fails to provide comparable abrasion resistance but also degrades all static and dynamic properties. This failure of polyisoprene to respond to silica reinforcement recalls a similar instance noted in the preceding discussion on glycol activation effects.

The zinc-free approach in natural rubber is effective with blends of silica and carbon black and BR. In the example described in formulary compound NR 62, outstanding hot tear strength and excellent abrasion resistance are combined in a compound based on a 50/50 blend of BR1220 and NR reinforced with 30 phr silica and 33 phr SAF.

Table 2.41 Zinc-free Cure System in Polyisoprene

Stearic acid	2	0
Zinc oxide	3	1
Mercaptosilane	0.5	0
MDR cure rate, 150°C, T_{90} minutes	5.4	3.9
MDR crosslinks, 20 minutes, dN-m	25	23
Mooney scorch, 121°C, T_5 minutes	24	4.2
Durometer hardness	68	67
PICO abrasion index: 23°C	92	81
100°C	66	48
DIN abrasion loss, mg	123	107
Pendulum rebound (Z), %: 23°C	63	60
100°C	70	61
Other ingredients: IR2200 70; BR1220-30; 220 m^2/g N_2SA Silica -45; NS resin-10; Vestenamer 8012-10; ODPA-1; ZMTI-1; Sulfur-2.8; TBBS-2		

Table 2.42 Zinc-free System: Silica Surface Area Effects

	Silica N_2SA, m^2/g		
	150	**190**	**215**
MDR cure rate, 150°C, T_{90} minutes	7.2	8.8	14
MDR crosslinks, dN-m	22	22	25
Mooney scorch, 121°C, T_5 minutes	30+	30+	25
Viscosity, ML_4 100°C	76	76	118
Cure, 35 min / 150°C:			
Durometer hardness	70	67	72
M300% modulus, MPa	4.5	4.2	4.6
Elongation, %	845	870	900
PICO abrasion index	117	128	168
DIN abrasion loss, ml	109	124	98
MG trouser tear, kN/m	32	23	26
Compression set, 70 hrs, 100°C	84	84	84
Flexometer HBU, ºC	37	35	blow
Other ingredients: NR-50; BR-50; Silica-50; 100C resin-15; oil5; ODPA-2; TMQ-1; ZnO-3; Sulfur-2; TBBS-2; HMT-2			

Partial absence of soluble zinc also makes possible a less contaminated silica evaluation of surface area effects, similar to that described in the peroxide section above. In Table 2.42, silicas of several surface areas are compared at 50 phr in a 50/50 BR/NR blend. Higher surface areas lead to improved abrasion resistance, at the expense of viscosity and heat build-up, but with no significant change in other properties, except cure rate. In terms of T_{50} cure rate, the rate with the highest surface area silica is only half that of a 150 m^2/g N_2SA silica. This surface area effect is the reverse of that encountered with normal zinc activated cure systems in natural rubber.

2.24 BRASS ADHESION

Enhanced adhesion to brass coated steel tire cord has been associated with a partial replacement of carbon black by precipitated silica (8 to 15 phr) in radial tire belt compounds. Road and wheel testing, as well as commercial experience demonstrated the effectiveness of silica in reducing separation failures. An example is formulary compound NR 42. Much of the development work associated with brass adhesion was carried out in the PPG Industries rubber laboratories and is available in various publications [8]-[13]. This work, however, differed from other brass adhesion references in respect to the use of dynamic test procedures rather than the static pull-out methods normally in use. The PPG procedure, known as Disc Fatigue, makes use of the Cord Compression Fatigue tester developed by M. W. Wilson and generally used to evaluate the fatigue properties of textile cords [13]. The Disc Fatigue test has been found to predict successfully the dynamic performance, in terms of separation resistance, of tire belt coat and skim compounds. Of even greater importance is its role in compound development and investigating the mechanism by which silica enhances brass adhesion.

There are two unique features of disc fatigue evaluations:

Discrimination - bonding systems which appear to be equal in static pull-out tests are revealed to be distinctly unequal in terms of dynamic fatigue life; disc fatigue life correlation with the incidence of tire belt failures has been demonstrated.

Interfacial separation - bond fatigue separations occur at the rubber–brass interface, leaving a bare metal surface. The absence of adhering skim compound indicates that disc fatigue procedures lead to a true adhesion determination, uncontaminated by a compound cohesion component.

2.25 BRASS ADHESION MECHANISM

The use of silica in brass coat and skim compounds has a fairly extensive commercial history, but no convincing theory of the mechanism involved has been available. For example, a 1991 paper by Hewitt [10] showed that an increase of silica from 0 to 24 phr without the presence of R-F resin and cobalt produced complete resistance to disc fatigue separations after humid aging, but no explanation was apparent.

An early review by Wagner [9] stated that 'the interaction between silica and zinc oxide is important in obtaining maximum adhesion". This conclusion was based, in part, on the observation that addition of zinc oxide *with* silica early in the mix cycle improved static pull-out values and percent coverage. Other proposals invoked silica's wetting effect (low contact angle), water affinity and chemical reactivity.

Hewitt pursued the zinc oxide connection in a series of compounding (as opposed to interfacial analysis) experiments [11]. This work relies in large part on disc fatigue dynamic procedures. Exploration of zinc oxide and silica content effects in response surface designs based on formulas with and without resorcinol and hexamethoxy methylmelamine resins produced contour curves, Figures 2.35 to 2.37, that illustrate the beneficial effect of low zinc oxide and silica concentrations. Optimum concentrations appear at 8 phr for silica and 1 phr for zinc oxide. Formula and properties for this compound are given in formulary compound NR 48a.

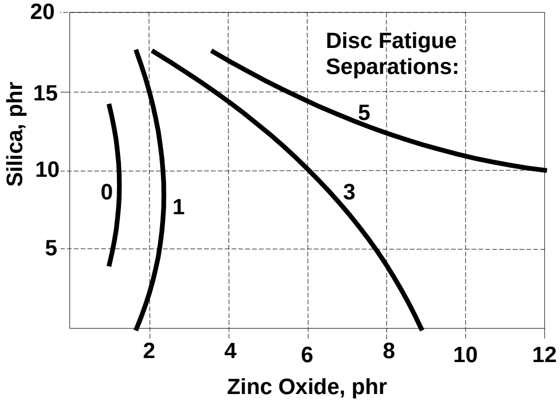


Figure 2.35 With Bonding Resins: Humid Aged 3 Days/50°C Before Curing

These results suggest that the mechanism by which brass adhesion is enhanced in the presence of silica and lower than normal concentrations of zinc oxide is related to the silica–soluble zinc reaction. The role of silica is to repress the availability of zinc in the formation of excess zinc sulfide and zinc oxide at the brass-rubber interface. A similar mechanism appears to apply to the use of cobalt in non-silica compounds. A separate study found that improved aged brass adhesion (pull-out test data) is obtained with cobalt naphthenate and boric acid ester in compounds which produce significantly *lower* zinc oxide concentrations at the brass interface [13].

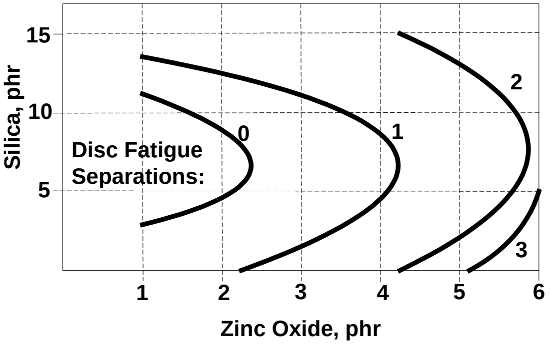


Figure 2.36 Without Bonding Resins

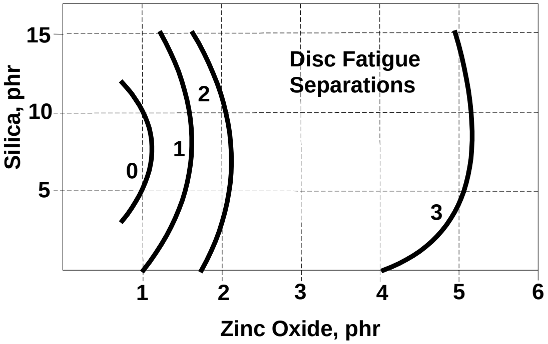


Figure 2.37 With Bonding Resins: Humid Aged 3 Days/90°C After Curing

2.26 ADHESION TO TEXTILE FABRICS; THE HRH SYSTEM

Precipitated silicas have a long history of use to promote cured adhesive bond strengths between elastomer compounds and fabrics. Unlike its function in brass bonds, the role of silica in fabric (treated and untreated) adhesion appears to be one of improving interfacial compatibility or wetting. Silica surface silanols react readily with the oxygenated groups of textiles and resorcinol resins. Thus the presence of silica surface modifying agents such as silanes, glycols and amine derivatives reduces adhesion to fabrics and cords. The wetting function is illustrated (in a non-resin system) in compounds where the silica/black ratio varies from 0/60 to 50/10; as seen in Table 2.43, bond strengths to RFL treated nylon fabric increase in proportion to silica content.

Table 2.43 Bond Strengths to RFL Treated Nylon Fabric

	A	**B**	**C**	**D**
ISAF N231 Carbon Black	60	45	30	10
150 m^2/g N_2SA Silica	0	15	30	50
Strip adhesion, kN/m	5.2	6.4	7.0	7.8
Durometer*	71	71	70	72

*maintained by minor changes in softener & curatives

Since good adhesion requires a strong interfacial bond as well as intimate contact, silica content is generally accompanied by resorcinol or resorcinol resin systems to meet the strength requirement. This combination has been known as the HRH system. With resorcinol present in the compound adherend, it is possible to obtain strong bonds to *untreated* fabric. For treated fabric, the HRH system provides a form of insurance against defective or over-age RFL treatments.

Typical formulas appear in the formulary section, in particular compounds NR 14, NR 21 and NR 29. These demonstrate several empirical rules for attaining optimum adhesion to untreated fabrics:

1. Minimum silica content is one third of total filler (one half for low surface area grades)
2. Minimum zinc oxide and stearic acid contents of 5 and 2 phr respectively
3. Glycols, silanes and other modifiers reduce adhesion
4. Either resorcinol or low molecular weight resorcinol resins in combination with hexa (HMT) or HMMM combinations are suitable, but resorcinol resin with hexa is less effective.

To avoid resin pre-reaction, hexa or HMMM must be added in a second mixing stage with curatives; first stage stock temperatures between 120°C and 175°C have little influence on adhesion. Effective concentrations of resorcinol, R-F resins, HMT (hexa) or HMMM lie within the 1 to 3 phr range, dependent on silica content and cord type.

The reference to required minimum amounts of zinc oxide and stearic acid indicate that more than a direct reaction of resorcinol and formaldehyde is involved in bond formation. A study of the bonding mechanism that indicates that soluble zinc oxide is a vital factor in rubber-to-fabric adhesion is discussed in detail in the SBR chapter.

Crosslinking should be considered as separate from bond formation. Cure rate, as determined by rheometer data, is not a good indicator of bonding rates, particularly to untreated fabric, as seen in Table 2.44.

Complete bond formation to untreated nylon is achieved only at two to three times the optimum rheometer 90% cure time. Increased accelerator content has no significant influence on bonding rates. The separation of crosslinking from bonding reactions is not apparent when R-F dips have already been applied to the fabric.

Table 2.44 Fabric Adhesion: Cure Rate and Bond Formation

R-F resin 1501	0	1	2	3
HMMM resin 634	0	1	2	3
TBBS	1.2	1.4	1.6	1.8
TMTM	0.2	0.4	0.6	0.8
ODR cure rate, 150°C, T_{90} minutes	21	16	12	9
Durometer hardness	57	57	61	61
Adhesion to untreated nylon, kN/m				
Cure: 20 min / 150°C	0.4	1.3	1.6	1.6
Cure: 45 min / 150°C	0.8	14	15	13
Adhesion to RFL nylon				
Cure: 20 min / 150°C	17	17	17+	17+
Cure: 45 min / 150°C	16	13	16	13
Other ingredients: SMR-55; SBR1501-45; 65 m^2/g N_2SA Silica -30; N550-20; oil/resin-10; Sulfur-2.6				

2.27 FABRIC ADHESION: DYNAMIC TESTING

The disc fatigue procedure for dynamic evaluation of steel cord adhesion described above does not produce bond separation with flexible textile cord. The latter requires a special apparatus in which the cord is maintained under tension while undergoing cyclic strains in the 3 to 6 Hz range. This test has been called Tension Fatigue and is described in reference 14. Bond separation times of 6 to 10 replicates are plotted on Weibull distribution graphs to provide a characteristic fatigue life of 63% failures. Early failures (10%) are an important part of the characterization.

As in all adhesion testing, the problem of distinguishing compound from bond cohesion is present in the tension fatigue procedure, where most of the separated cords show rubber coverage of 50 to 90%. Only the early, bare cord failures represent true bond fatigue. Thus, tension fatigue life values contain a large component of compound tear fatigue.

In general, dynamic fatigue life data show little correlation with the commonly used static pull-out bond strengths of rubber-to-textile and rubber-to-metal cord composites. This lack of dynamic service predictability by static testing can be seen in Table 2.45 in a comparison of two activated polyester cord skim compounds. The precipitous drop in bond fatigue life of the silica–black compound is in sharp contrast to the barely significant difference between the two compounds in static pull-out values. Similar, although less extreme, results obtain with nylon and aramid cords.

Table 2.45 Comparison of Two Activated Polyester Cord Skim Compounds

60 m^2/g N_2SA Silica	60	-
150 m^2/g N_2SA Silica	-	35
GPF N660 Carbon Black	-	20
Durometer hardness: 23°C	62	59
100°C	59	58
Static pull-out adhesion, N/12mm	62	54
Tension Fatigue dynamic adhesion, 23°C, 3.5 Hz, 4.5Kg, 10 mm: Kilocycles to 63% separation failures	24	0.1
Other ingredients: SMR-70; SBR1502-30; resins-16; tall oil-2; ZnO-5; Stearic acid-2; R-F resin-2.5; HMMM-2; Sulfur-2.8; TBBS-2; ZMDC-0.1; ODPA-1		

2.28 HEAT RESISTANCE

In comparisons to carbon black, heat resistance is one of several properties in which precipitated silica provides distinct improvement. In some cases this is partly due to the higher original elongation characteristic of silica compounds. However, when the effective cure systems described in the accelerator sections are used to provide an equal hardness and elongation basis of comparison, improved heat resistance is still very much in evidence, as illustrated in Table 2.46.

In addition to the considerable margin in aged tensile and elongation, the silica compound has maintained its usual superiority in trouser tear strength. Low surface area, semi-reinforcing silicas are also noted for producing natural rubber compounds with superior heat resistance. Two such are formulary compound NR 5 and NR 8. Stress-strain properties of the 35 m^2/g N_2SA silica at 75 phr remain almost unchanged after 168 hours of aging at 100°C, and a 65 m^2/g N_2SA silica at 50 phr provides complete resistance to deterioration after aging 72 hours at 100°C.

Table 2.46 Heat Resistance: Silica and Black

	180 m^2/g N_2SA Silica	**N220 Carbon Black**
PEG 3350	1	--
TBBS	3	1
ODR cure rate, 150°C, T_{90} minutes	20	13
ODR MH-ML crosslinks, dN-m	75	73
Mooney viscosity, ML_4 100	58	48
Durometer hardness	64	64
Tensile, MPa: Original	28	29
500 hours, 85°C	15.0	6.1
Elongation, %: Original	660	540
500 hours, 85°C	430	140
MG trouser tear, kN/m	18.5	4.7
Other ingredients: SMR-100; Filler-40; ODPA-1; Stearic acid-2; ZnO-4; Sulfur-2.8		

The preceding accelerator sections illustrated the importance of effective cure systems and sulfur donors to improved heat resistance. A further silica–black comparison based on a sulfur donor cure system, in Table 2.47, also shows silica superiority at high aging temperatures. Superior heat resistance is here combined with reduced heat build-up, provided by the presence of mercaptosilane and TMTD.

Table 2.47 Heat Resistance: Sulfur Donor Cure

	150 m^2/g N_2SA Silica	**N330 Black**
TBBS	2	2
DTDM	2	2
TMTD	1	--
Mercaptosilane A189	0.8	--
ODR cure rate, 150°C, T_{90} minutes	18	31
Mooney scorch, 121°C, T_5 minutes	14	30+
Tensile, MPa: Original	29	30
Aged 72 hrs, 121°C	20	6.5
Aged 168 hrs, 121°C	8.6	3.5
Elongation, %: Original	520	600
Aged 72 hrs, 121°C	460	270
Aged 168 hrs, 121°C	310	80
Goodrich flexometer, 100c; 22.5%; 1 MPa:		
Permanent set, %	2.9	4.7
Heat build-up, ºC	9.5	17
Other ingredients: SMR-100; Filler-45; softeners-10; HPPD-1.5; DAPD-1.5; Zinc oxide-5; Stearic acid-1		

References

1. J.H.Bachmann, et al., "Fine Particle Reinforcing Silica and Silicates", Rubber Chem. Technol. 32, 1286 (1959)
2. Hewitt, N.L., "The Effect of Silica Structure on Resilience", Rubber World, May 1990
3.Hewitt N.L., "Processing Technology of Silica in SBR", Elastomerics, March 1981
4. Hewitt, N.L., "Tear Strength and Heat Build-Up", Rubber World, June 1982
5.Hewitt, N.L., "Use of Viscoelastic Series for Compound Design", Rubber World, November 1984
6. Hewitt, N.L., "Peroxide Curing with Precipitated Silica", Rubber World, April 1999
7.Hewitt, N.L., "The Effect of Silica Structure on Resilience", Rubber World, May 1990
8. Wagner,M.P. & Hewitt,N.L., "Dynamic Adhesion of Rubber to Tire Cord", Kautschuk und Gummi, October 1984
9. Wagner,M.P., "Silica Developments", Akron Rubber Group paper, December 1972
10. Hewitt,N.L., "Dynamic Aspects of Brass Adhesion", Rubber World, December 1991
11. Hewitt, N.L., "Mechanism of Brass Adhesion", Rubber World, September 1994
12. Wilson, M.W., "Adhesion by Disk Fatigue", Textile Res.J.,XXI,1 (1951)
13. Pieroth, M., et al., "Influence of Boric Acid Ester", Paper at ACS rubber Div. Louisville 1992
14. Hewitt, N.L., "Dynamic Testing of Adhesion", Rubber & Plastics News, Oct. 7, 1985

Natural Rubber Formulary

The silica surface areas indicated in the following compounds are N_2SA (BET) surface areas. A listing of commercially available precipitated silica products by surface area is provided in Appendix A. The common abbreviations used in these compounds are provided in Appendix E.

NR 1

Elastomer: NR Durometer: 40
Application: Heat resistance

SMR H5L	100	Stearic acid	2
150 m^2/g Silica	30	PEG 3350	1.5
ISAF N285	10	Zinc oxide	10
Tall oil	5	MDB	3
100ºC resin	8	TMTD	0.3
TMQ	2		
HPPD	3		
MC wax	1	Specific gravity	1.10

ODR cure rate, 146°C, T_{90} minutes	25
Mooney scorch, 130°C, T_5 minutes	9
Mooney viscosity, ML4100	50

30 minute cure, 146°C:	Original	Aged*	Aged**
Durometer	42	45	42
M300, MPa	3.6		3.7
Tensile, MPa	28	6.9	22
Elongation, %	780	530	730
Die B tear	130		110

Aged: *700 hours, 100°C; **2 hours, 150°C

Compression set, %:	
22 hours, 70°C	22
72 hours, 100°C	43

Goodrich flexometer: 100°C; 22.5%; 1MPa	
Static compression, %	31
Dynamic compression, %	20
Permanent set, %	5
Heat build-up, ºC	18

NR 2

Elastomer: NR Durometer: 40
Application: Air curing

SMR	100	Zinc oxide	5
35 m^2/g Silica	38	PEG 3350	1
Titanium dioxide	10	Sulfur	2.8
Naphthenic oil	5	MBS	0.6
Stearic acid	1.5		
ODPA	1	Specific gravity	1.10

ODR cure rate, 142°C, T_{90} minutes	31
Mooney scorch, 121°C, T_5 minutes	30
Mooney viscosity, ML_4100	53
Garvey extrusion, % swell	20
Edge/surface	9A

40 minute cure, 142°C:	Original		72 hrs, 100°C	
	Press	Air	Press	Air
Durometer	43	39	50	48
M300, MPa	3.2	2.8	4.5	5.1
Tensile, MPa	29	17	13	12
Elongation, %	700	700	570	500
Die B tear, kN/m	47	37		
Die C tear	39	28		

Grooved Trouser tear, kN/m	
20°C	9.8
70°C	11k

NR 3

Elastomer: NR Durometer: 40
Application: Hot air cure; Adhesion

SMR (3 min mill)	100	Zinc oxide	5
150 m^2/g Silica	25	Stearic acid	1.5
Whiting	25	Sulfur	0.7
TP90B	5	ZnMBT	1.5
Tall oil	3	TMTD	0.5
Pine tar	6	Telloy	0.3
Aminox	1	HMMM	2
R-F resin 1501	2.5		
		Specific gravity	1.09

ODR Cure rate, 142°C, T_{90} minutes	30
Mooney scorch, 121°C, T_5 minutes	1
Mooney viscosity, ML_4100	18

Strip adhesion to untreated nylon, kN/m
Hot air cure, 142°C

Fabric weight, oz.	1.5	10
30 minutes	2.3	8.2
60 minutes	2.8+ (tear)	9.7

60 minute cure:	Air, 142°C	Press, 150°C
M300, MPa	1.5	2.8
Tensile, MPa	9.0	19
Elongation, %	940	700

NR 4

Elastomer: NR Durometer: 44
Application: Elastics

SMR	100	Sulfur	0.7
150 m^2/g Silica	15	MDB	1.5
ODPA	1	MBTS	1.5
Stearic acid	1.5	DOTG	0.3
Zinc oxide	5		
PEG 3350	0.5	Specific gravity	1.02

ODR cure rate, 140°C, T_{90} minutes	29
Mooney scorch, 121°C, T_5 minutes	24
Mooney viscosity, ML_4100	47

40 minute cure, 140°C:

Durometer	44
M100, MPa	0.15
M300, MPa	2.0
M500, MPa	10
Tensile, MPa	27
Elongation, %	670

NR 5

Elastomer: NR Durometer: 47
Application: Heat resistance

SMR	100	PEG 3350	1
35 m^2/g Silica	75	Sulfur	2.5
Naphthenic oil	25	MBS	1.5
Tall oil	5		
Stearic acid	1		
ODPA	1	Specific gravity	1.16

ODR cure rate, 150°C, T_{90} minutes	15
Mooney scorch, 121°C, T_5 minutes	30
Mooney viscosity, ML_4100	33

15 minute cure, 150°C:	Original	168 hrs, 100°C
Durometer	47	55
M300, MPa	2.3	
Tensile, MPa	15	14
Elongation, %	700	600

Compression set, %, 22 hrs, 100°C 45

Water immersion, 100°C:	Durometer	Volume change, %
6 hours	49	2.5
24 hours	47	8.0
168 hours	41	23

NR 6

Elastomer: NR Durometer: 48
Application: Injection; Die C tear

SMR	100	Zinc oxide	5
150 m^2/g Silica	35	PEG 3350	2
Hard clay	30	Sulfur	2.5
Tall oil	5	TBBS	1.2
100ºC resin	10	DPG	0.3
Naphthenic oil	10		
ADPA	2		
Stearic acid	1	Specific gravity	1.17

ODR cure rate, 144°C, T_{90} minutes	30
Mooney scorch, 132°C, T_5 minutes	22
Mooney viscosity, ML_4100	40
30 minute cure, 150°C:	
Durometer	48
M300, MPa	2.7
Tensile, MPa	23
Elongation, %	750
Die C tear, kN/m	62

NR 7

Elastomer: NR Durometer: 49
Application: FDA seal; Tear strength

SMR	100	PEG 3350	1
150 m^2/g Silica	20	Sulfur	1
HAF N330	15	CBS	1
Pine tar	5	DPG	0.2
Stearic acid	1		
Zinc oxide	1		
		Specific gravity	1.08

ODR cure rate, 150°C, T_{90} minutes	10
Mooney scorch, 121°C, T_5 minutes	21
Mooney viscosity, $ML_4$100	52
12 minute cure, 150°C:	
Durometer	49
M300, MPa	3.5
Tensile, MPa	25
Elongation, %	700
Die C tear strength, kN/m	98
MG Trouser tear strength	30

NR 8

Elastomer: NR Durometer: 50
Application: Heat resistance, Low HBU

SMR	100	Sulfur	0.5
65 m^2/g Silica	50	TBBS	1.5
100ºC resin	5	DTDM	1.5
TMQ	1	TMTD	0.2
HPPD	1		
Stearic acid	2		
Zinc oxide	5	Specific gravity	1.15

ODR cure rate, 150°C, T_{90} minutes	23
Mooney scorch, 132°C, T_5 minutes	23
Mooney viscosity, ML_4100	74

45 minute cure, 150°C:	Original	72 hrs, 100°C
Durometer	50	51
M300, MPa	4.8	
Tensile, MPa	27	26
Elongation, %	640	600

Goodrich flexometer: 100°C; 22.5%; 1 MPa:		
Static compression, %	22	21
Dynamic compression	10	9
Drift	2	0
Set	2	3
Heat build-up, ºC	8	7

NR 9

Elastomer: IR Durometer: 50
Application: General; Colors

Natsyn 400	100	Zinc oxide	5
150 m^2/g Silica	50	MBS	1.5
Naphthenic oil	30	DPG	1.3
Stearic acid	1	Sulfur	2.8
ODPA	1		
PEG 3350	2.5	Specific gravity	1.12

ODR cure rate, 150°C, T_{90} minutes	18
Mooney scorch. 121°C, T_5 minutes	30+
Mooney viscosity, ML_4100	60

18 minute cure, 150°C:	Original	120 hrs , 100°C
Durometer	50	62
M300, MPa	2.1	
Tensile, MPa	24	13
Elongation, %	820	500
Die C tear, kN/m	59	37
Grooved trouser tear, kN/m	13k	3.5
NBS abrasion index	70	
Compression set, %:		
22 hours, 70°C	30	
72 hours, 100°C	80	

NR 10

Elastomer: NR Durometer: 50
Application: Traction; Tear strength

SMR CV60	100	Zinc oxide	3
220 m^2/g Silica	40	Sulfur	2.5
Naphthenic oil	15	TBBS	2.5
100C alkyl resin	10	PEG 3350	1
ODPA	1		
Stearic acid	2	Specific gravity	1.11

MDR cure rate, 150°C, T_{90} minutes	18
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, $ML_4$100	40

Durometer, 25 min/150°C, 23°C	50
100°C	48

	Original	700 hrs, 90°C
M300, MPa	2.4	
Tensile, MPa	22	3.9
Elongation, %	820	200

MG Trouser tear, kN/m, 23°C	39
100°C	39
Dynamic coefficient of friction, wet aluminum	1.50
PICO abrasion index	40

Goodrich flexometer: 100°C; 22.5%; 1 MPa:

Permanent set, %	32
Heat build-up. °C	51

Pendulum rebound (Z), %, 23°C	52
100°C	59

NR 11

Elastomer: NR/BR Durometer: 51
Application: Resilience; Low HBU

SMR CV60	80	Banbury 2	
BR 1220	20	Zinc oxide	5
Ciptane I	31	Sulfur	0.4
Paraffinic oil	8	Vultac 7	1.5
Stearic acid	2	TBBS	4.0
TMQ	2	OTOS (TCS)	0.5
HPPD	2		
PEG 3350	1	Specific gravity	1.06

MDR cure rate, 150°C, T_{90} minutes	13
Mooney scorch, 130°C, T_5 minutes	16
Mooney viscosity, ML_4 100	36

17 minute cure, 150°C:	Original	Aged, 100°C, days	
		14	28
Durometer	51	51	51
M300, MPa	4.8		
Tensile, MPa	29	12	9
Elongation, %	685	410	330

Pendulum rebound, (Z), %, 23°C	70
100°C	80
Goodrich flexometer: 100C; 17.5%; 1 MPa:	
Permanent set, %	1.4
Heat build-up	6ºC
Compression set, %, 72 hours, 100°C	33.6

DMA dynamic modulus: 1 Hz:

		E", MPa	E'	Tan delta
Original	30°C	0.50	3.3	0.151
	60°C	0.50	3.0	0.165
Aged 14 days, 100°C				
	30°C	0.45	3.3	0.136
	60°C	0.40	3.1	0.130

NR 12

Elastomer: NR/EPDM Durometer: 51
Application: White sidewall; Ozone

NR	60	Sulfur	0.8	
EPDM 2914	80	Vultac 710	1	
65 m^2/g Silica	55	TBBS	1	
Titanium dioxide	35	ZBDC	1	
Zinc oxide	5			
Stearic acid	2	Specific gravity		1.20

MDR cure rate, 160°C, T_{90} minutes	4.6
Mooney scorch, 121°C, T_5 minutes	17
Mooney viscosity, $ML_4$100	48
Garvey extrusion, % swell	25
Edge/surface rating	10A

10 minute cure, 160°C:	Original	500 hrs, 80°C
Durometer	51	56
M300, MPa	2.7	
Tensile, MPa	10	8.6
Elongation, %	700	670

Dynamic ozone cracking:	
60 days, 0.5 ppm	none
Strip adhesion to tread stock, kN/m	tear at 1%
MG Trouser tear, kN/m	14
PICO abrasion index	31
Pendulum rebound (Gdyr), %, 23°C	68
100°C	70
Monsanto fatigue, 100% strain:	
Aged 24 hours, 70°C	97 kc

NR 13

Elastomer: NR/SBR Durometer: 52

Application: Sundries

SMR	55	Zinc oxide	5
SBR1502	45	PEG 3350	0.5
65 m^2/g Silica	35	Sulfur	2.8
Whiting	65	MBTS	1
Tall oil	2	DPG	0.5
100ºC resin	5		
Naphthenic oil	5		
ODPA	1		
Stearic acid	2	Specific gravity	1.33

ODR cure rate, 150°C, T_{90} minutes	16
Mooney scorch, 121°C, T_5 minutes	22
Mooney viscosity, ML4100	45
Garvey extrusion: % swell	35
Edge/surface	9A

20 minute cure, 150°C:	Original	72 hrs, 70°C
Durometer	52	60
M300, MPa	3.2	
Tensile, MPa	14	11
Elongation, %	610	500

Trouser tear, grooved; kN/m	6.1
Compression set, %, 22 hours, 70°C	21
Resilience, Yerzley, %	73

NR 14

Elastomer: NR/SBR Durometer: 54
Application: Fabric adhesion

SMR	55	Banbury # 2	
SBR 1502	45	HMMM 963	3
65 m^2/g Silica	60	Sulfur	2.6
Tall oil	3	MBS	1.5
100ºC resin	8	TMTM	0.3
Aromatic oil	8		
Stearic acid	3		
Zinc oxide	5		
Resorcinol resin 1501	3	Specific gravity	1.12

ODR cure rate, 150°C, T$_{90}$ minutes	30
Mooney scorch, 132°C, T$_5$ minutes	30
Mooney viscosity, ML$_4$100	45

45 minute cure, 150°C:

Durometer	54
M300, MPa	3.8
Tensile, MPa	13
Elongation, %	600

Strip Adhesion to untreated fabrics, N/25mm:

Fabric	Press Cure	Original	72 hours, 70°C
Nylon	30 minutes, 150°C	250	
	60 minutes, 150°C	400+	
Rayon	30 minutes, 150°C	220	
	60 minutes, 150°C	200	
Activated polyester 790			
	30 minutes, 150°C	450	400
	60 minutes, 150°C	350	330
Cotton	30 minutes, 150°C	220+	180+
	60 minutes, 150°C	180+	180+

NR 15

Elastomer: NR/IR		Durometer: 55
Application: Racquet ball

SMR	50	PEG 3350	0.5
IR 2200	50	Sulfur	2.5
Silica	23	MBS	2
TMQ	0.5	TMTD	0.3
Stearic acid	1.5		
Zinc oxide	3	Specific gravity	1.05

	65 m^2/g Silica	150 m^2/g Silica
ODR cure rate, 150°C, T_{90} minutes	9	10
Mooney scorch, 121°C, T_5 minutes	17	29
Mooney viscosity, ML4100	39	42
Pendulum rebound (Goodyear), %	91.2	86.8

Cure:	12 minutes, 150°C	15 minutes, 150°C
Durometer	55	54
M100, Mpa	0.9	0.7
Tensile, Mpa	14	29
Elongation, %	460	680
Compression set, %, 24 hours, 70°C	12	14
Monsanto flex fatigue, 100%, kc	11	24

NR 16

Elastomer: NR/BR Durometer: 55
Application: Dynamic service

SMR CV60	80	Stearic acid	1
BR 1220	20	Zinc oxide	3
150 m^2/g Silica	25	Sulfur	2.5
Titanium dioxide	3	TBBS	2.5
100C resin	5		
ZMTI	1.5		
ODPA	1.5	Specific gravity	1.07

MDR cure rate, 150°C, T_{50} minutes	15
T_{90} minutes	17
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, ML_4 100	48

10/30 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer	56	59
M300, MPa	5.8	
Tensile, MPa	30	9.2
Elongation, %	620	275

MG trouser tear, kN/m	5.2
PICO abrasion index	63
Compression set, 70 hrs, 100°C, %	43

Pendulum rebound (Z), %	23°C	72
	100°C	80

Goodrich flexometer: 22.5%; 1 MPa	
Static compression, %	19
Dynamic compression	7.7
Drift	2.0
Set, %	3.7
Heat build-up	9ºC

DeMattia cut growth, aged 24 hrs, 70°C	
500% growth, kc	13

NR 17

Elastomer: IR/SBR Durometer: 55
Application: Translucent; (pale crepe) fast cure

IR SN600	50	PEG 4450	3
SBR 8107	50	Sulfur	2.2
150 m^2/g Silica	40	TBBS	0.8
65 m^2/g Silica	30	DOTG	0.6
Naphthenic oil	30	ZMDC*	0.6
ODPA	1	* omit to reduce scorch	
Stearic acid	2		
Zinc oxide	3	Specific gravity	1.16

ODR cure rate, 138°C, T_{90} minutes	7
Mooney scorch, 121°C, T_5 minutes	5.2
shelf aged 2 weeks, T_5 minutes	3.8
Mooney viscosity, ML_4100	35

Cure:	Press, 7 mins, 138°C	Air, 3 hrs,112°C
Durometer	55	50
M300, MPa	2.3	3.7
Tensile, MPa	9.3	6.8
Elongation, %	600	450

NBS abrasion index	65
PICO abrasion index	51

NR 18

Elastomer: NR Durometer: 56
Application: Sheeting; Tear strength

SMR H5L	100	Zinc oxide	5
65 m^2/g Silica	50	Stearic acid	2
Tall oil	2	Sulfur	2.5
Pine tar	3	CBS	0.5
MC wax	1	DPG	0.5
TMQ	0.5		
BLE25	0.5	Specific gravity	1.16

ODR cure rate, 154°C, T_{90} minutes	19
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, ML_4100	64
Garvey extrusion, % swell	30
Edge/surface	10A

	Original	72 hrs, 100°C
Durometer	56	52
M300, MPa	4.3	
Tensile, MPa	25	12
Elongation, %	680	540

Trouser tear, grooved, kN/m	18k
Compression set, %, 72 hrs, 100°C	58

NR 19

Elastomer: NR or IR Durometer: 55
Application: General, NR vs IR

NR or IR	100	PEG 3350	2.5
150 m^2/g Silica	50	Sulfur	2.6
Naphthenic oil	10	TBBS	1.5
Tall oil	5	DPG	0.6
Stearic acid	1.5		
ODPA	1		
Zinc oxide	5	Specific gravity	1.13

Elastomer	Natsyn® 400	SMR H5L
ODR cure rate, 150°C, T_{90} minutes	13	16
Mooney scorch, 121°C, T_5 minutes	27	30
Mooney viscosity, ML_4100	39	31

	minutes of cure, 150°C	
	15	18
Durometer	55	54
M300, MPa	2.1	3.3
Tensile, MPa	24	24
Elongation, %	680	680
Die C tear strength, kN/m		
Original	33	67
Aged 120 hrs, 100°C	40	53
Trouser tear, grooved, kN/m		
Original	17	18
Aged	2.6k	5.1k
Compression set, 72 hrs, 100°C, %		
22 hrs, 70°C	16	22
72 hrs,100°C	66	78

NR 20

Elastomer: NR Durometer: 57

Application: Dynamic; Heat; Low HBU

SMR	100	Banbury 2	
150 m^2/g Silica	50	Zinc oxide	4
Tall oil	1	Sulfur	0.5
Rosin ester resin	6	TBBS	2
100ºC resin	5	MDB	2
Stearic acid	2		
PEG 3350	2		
TMQ	2		
HPPD	2	Specific gravity	1.15

ODR cure rate, 138°C, T_{90} minutes	25
Mooney scorch, 130°C, T_5 minutes	10
Mooney viscosity, ML_4100	66

30 minute cure, 138°C:	Original	72 hrs, 121°C
Durometer	57	70
M300, MPa	3.9	
Tensile, MPa	29	12
Elongation, %	690	440

Trouser grooved tear, kN/m	43
PICO abrasion index	82
Compression set, %, 72 hrs, 100°C	53

Goodrich flexometer: 100°C; 22.5%; 1 MPa

Static compression, %	18
Dynamic compression, %	9
Permanent set, %	7
Heat build-up, ºC	17

DeMattia cut growth, kc to 500%	40

NR 21

Elastomer: NR/SBR Durometer: 57
Application: Fabric adhesion

SMR	55	Banbury 2	
SBR 1502	45	HMMM 963	0 or 2*
65 m^2/g Silica	30	Sulfur	2.6
FEF N550	20	TBBS	1.5
100ºC resin	5	TMTM	0.4
Aromatic oil	5		
Stearic acid	2.5		
TMQ	1		
HPPD	1		
Zinc oxide	5		
Resorcinol resin	0 or 2*	Specific gravity	1.11

Bonding system:		Silica	Direct (HRH*)
ODR cure rate, 150°C, T$_{90}$ minutes		19	14
Mooney scorch, 121°C, T$_5$ minutes		30+	30+
Mooney viscosity, ML$_4$ 100		15	17
Strip Adhesion, N/25mm:	Cure, 150°C		
Untreated nylon	20 minutes	9	44
	45 minutes	18	400
	Water, 48 hrs.20°C	10	240
RFL treated nylon	20 minutes	450	450
	45 minutes	400	400
	Water	310	380
Activated polyester 790	20 minutes	10	115
	45 minutes	21	115
	Water	44	115
	Aged 72 hrs, 100°C	155	220
RFL treated polyester (DD95)	20 minutes	135	160
	45 minutes	110	85
	Water	85	85
	Aged 72 hrs, 100°C	110	110
20 minute cure, 150°C:			
Durometer		57	61
M300, MPa		7.6	9.4
Tensile, MPa		15	15
Elongation, %		460	420

NR 22

Elastomer: NR/BR/IIR Durometer: 58
Application: White sidewall

SMR	50	Stearic acid	2
Bromobutyl X2	30	Phenolic A.O.	1
EPDM 502	20	Zinc oxide	3
35 m^2/g Silica	35	Sulfur, insoluble	1.3
150 m^2/g Silica	20	MDB	1.5
Titanium dioxide	25		
Naphthenic oil	5		
Tall oil	3	Specific gravity	1.20

ODR cure rate , 165°C, T_{90} minutes	12
Mooney scorch, 121°C, T_5 minutes	25
Mooney viscosity, ML_4 100	62

Garvey extrusion: % swell	35
Edge/surface	10A

15 minute cure, 160°C:	Original	168 hrs, 100°C
Durometer	58	67
M300, MPa	2.4	
Tensile, MPa	11	9.3
Elongation, %	700	610

Trouser tear, grooved, kN/m	12
DeMattia cut growth at 100kc	negligible

Dynamic ozone exposure, 50pphm, 40°C	
hours to initial cracking	24*

*commercial control 15 hours

NR 23

Elastomer: NR/SBR Durometer: 58
Application: Fabric adhesion

SMR	70	Zinc oxide	5
SBR 1502	30	Stearic acid	3
150 m^2/g Silica	55	PEG 3350	0.5
100ºC resin	15	Sulfur	2.5
Naphthenic oil	10	MBTS	1.5
MC wax	3	ZBDC	0.4
TMQ	0.5		
ODPA	1	Specific gravity	1.13

ODR cure rate, 150°C, T_{90} minutes	25
Mooney scorch, 130°C, T_5 minutes	30+
Mooney viscosity, ML_4100	31

Strip adhesion to RFL treated nylon fabric, N/25mm	
Cure: 40 minutes, 150°C	380+
80 minutes, 150°C	330+

30 minute cure, 150°C:	Original	168 hrs, 100°C
Durometer	58	65
M300, MPa	1.3	
Tensile, MPa	17	15
Elongation, %	820	620

MG Trouser tear, kN/m	
138°C Cure, 30 minutes	16
200 minutes	16

Yerzley resilience, %	
Original	44
350 hrs, 70°C	55

NR 24

Elastomer: NR/NBR Durometer: 59
Application: Hot tear strength

SMR CV60	70	PEG 3350	1
NBR 683B	30	Sulfur	2.5
220 m^2/g Silica	35	TBBS	3
Picco 6100	10	ZMDC	0.5
DOP	8		
Stearic acid	1		
Zinc oxide	3	Specific gravity	1.11

MDR cure rate, 165°C, T_{90} minutes	2.5
Mooney scorch, 121°C, T_5 minutes	>30
Mooney viscosity, ML_4100	39

10 minute cure, 165°C:	
Durometer, 23°C	59
100°C	56
MG trouser tear, kN/m, 23°C	9.3 k
100°C	18 k
Die C Tear, 23°C	68
100°C	47

5 minute cure,165°C:	Original	700 hrs, 90°C
Durometer	62	75
M300, MPa	3.8	
Tensile, Mpa	24	8.9
Elongation, %	700	205

Tension set, % (10 min, 300%)	10
Compression set, %, 70 hrs, 100°C	67
DIN abrasion loss, mg	228
Pendulum rebound (Z), %, 23°C	38
100°C	70

NR 25

Elastomer: NR/EPDM Durometer: 60
Application: Fabric adhesion; Ozone resistance

SMR CV60	60	Banbury 2	
EPDM 2914	80	HMMM 963	1.5
65 m^2/g Silica	60	Sulfur	0.8
150 m^2/g Silica	20	Vultac 710	1
100ºC resin	4	TBBS	3
R-F resin 1501	3		
ODPA	1		
Zinc oxide	8		
Stearic acid	3	Specific gravity	1.17

MDR cure rate, 150°C, T_{90} minutes	22
Mooney scorch, 121°C, T_5 minutes	18
Mooney viscosity, ML_4100	58
Garvey extrusion, % swell	35
Edge/Surface	7B
Strip adhesion to polyester hose fabric, 45 minutes, 150°C, N/25mm	215
Static ozone exposure, 100 pphm, 50°C (ASTM D518), 72 hours	no cracking

15 minute cure, 160°C:	Original	700 hrs, 100°C
Durometer	60	65
M300, MPa	5.5	
Tensile, MPa	12	9.6
Elongation, %	515	290

Compression set, %, 72 hrs, 100°C	49.6
PICO abrasion index	45
Pendulum rebound (Z), %, 23°C	53
100°C	62

NR 26

Elastomer: NR Durometer: 60
Application: Heat resistance

SMR CV60	100	PEG 3350	1
220 m^2/g Silica	40	Zinc oxide	3
100ºC CI resin	5	Sulfur	2.8
Stearic acid	1	TBBS	3
ODPA	1.5		
ZMTI	1.5	Specific gravity	1.10

MDR cure rate, 150°C, T_{90} minutes	3.6
Mooney scorch, 130°C, T_5 minutes	7.0
Mooney viscosity, ML_4100	77

5 minute cure, 150°C:	Original	700 hrs, 85°C	168 hrs , 100°C
Durometer	59	72	72
M300, MPa	6.8		
Tensile, MPa	36	29	23
Elongation, %	720	625	540

MG Trouser tear, kN/m	22
PICO abrasion index	90
Compression set, %, 70 hrs,100°C	84
Pendulum rebound (Z), %, 23°C	57
100°C	69

Goodrich flexometer: 100°C; 22.5%; 1MPa

Permanent set, %	17
Heat build-up, ºC	26

NR 27

Elastomer: NR Durometer: 60
Application: Aging, 90°C; ZnO addition

SMR CV60	100	Zinc oxide	4
160 m^2/g Silica	40	Sulfur	2.8
100ºC resin	5	MBTS	3
Stearic acid	2		
PEG 3350	1		
ODPA	1	Specific gravity	1.12

Zinc oxide addition, Banbury stage	1st	2nd
MDR cure rate, 150°C, T_{50} minutes	6.2	6.5
T_{90} minutes	22	21
Mooney scorch, 121°C T_5 minutes	26	20
Mooney viscosity, $ML_4$100	65	63
Durometer, 20 minutes, 150°C		
23°C	60	61
100°C	59	60
Stress/Strain, 15 minute cure, 150°C		
Original:		
M300, MPa	4.3	4.3
Tensile, MPa	32	34
Elongation, %	780	760
Aged 300 hours, 90°C:		
Durometer	74	70
Tensile, MPa	12	11
Elongation, %	780	760
Aged 700 hours, 90°C:		
Durometer	76	80
Tensile, MPa	4.4	2.8
Elongation, %	75	15
Compression set, %, 72 hours, 100°C	72	69

NR 28

Elastomer: NR Durometer: 60
Application: Plasticizing with Tall oil

SMR	100	Zinc oxide	5
150 m^2/g Silica	50	Sulfur	2.6/2.8
ODPA	1	MBS (MOR)	1.5
Stearic acid	1	DOTG	0.6/0.9
PEG 3350	2.5		

Plasticizer:	Tall oil	Naphthenic oil
phr	5	30
Specific gravity	1.11	1.16
ODR cure rate, 144°C, T_{90} minutes	20	25
Mooney scorch, 121°C, T_5 minutes	30+	30+
Mooney viscosity, ML_4100	42	41
30 minute cure, 144°C:		
Durometer	60	60
M300, MPa	4.1	3.2
Tensile, MPa	26	24
Elongation, %	650	740
Aged 120 hours, 100°C		
Durometer	65	65
Tensile, MPa	18	13
Elongation, %	520	510
Tear strength, kN/m		
Trouser, Original	100k	50k
Aged	30	18
Die C, Original	330	430
Aged	290	320
Compression set, %, 72 hours, 100°C	75	80

NR 29

Elastomer: NR/SBR Durometer: 61
Application: Hose wrap adhesion

SMR CV60	55	R-F resin B19s	3
SBR 1502	45	HMMM 963P	1.5
65 m^2/g Silica	70	Sulfur	2.5
Titanium dioxide	5	TBBS	1.5
100ºC resin	5	TMTM	0.5
Aromatic oil	5	Zinc oxide	3
Tall oil	3		
Stearic acid	3		
ODPA	1	Specific gravity	1.20

MDR cure rate, 150°C, T_{90} minutes	19
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, ML_4100	30
Garvey extrusion, 120°C	
Rating	9A
% swell	40%

30 minute cure, 150°C:	Original	700 hrs, 100°C
Durometer	61	75
M300, MPa	6.0	
Tensile	13	8.2
Elongation, %	565	125

Strip adhesion to polyester hose fabric	
Cured 45 minutes, 150°C, N/25mm	490
PICO abrasion index	57
Compression set, %, 72 hrs, 100°C	63
Pendulum rebound (Z), %, 23°C	46
100°C	62

NR 30

Elastomer: NR/BR Durometer: 61

Application: Low rolling resistance tread; Hot tear strength

Time, min	Banbury 1		Banbury 2	
0	SMR	60	Sulfur	1.3
0.5	SAF N110	40	DTDM	0.4
2	BR 1220	40	TBBS	1.3
	Ciptane(6% A189)	21		
	Naphthenic oil	10		
2.5	HPPD	2		
	Zinc oxide	3		
	Stearic acid	1		
3	Dump @ 140°C		Specific gravity	1.14

MDR cure rate, 150°C, T_{90} minutes	9
Mooney scorch, 130°C, T_5 minutes	12
Mooney viscosity, ML_4100	52
Sectional tire tread road wear (195/75 R14)	
Mils/1000 miles	6.535
Miles to wear bar	43,880
PICO abrasion index, 23°C	118
70°C	99

DMA dynamic modulus: 1 Hz; 15% strain

°C	E', MPa	E"	Tan delta
-15	18		
0	17	3.2	0.190
30	12		
60	8.8	1.6	0.171

Pendulum rebound (Z), %, 23°C	50
100°C	58
MG Trouser tear, kN/m, 23°C	9.2k
100°C	16.2k
Goodrich flexometer: 100°C; 22.5%; 1MPa	
Heat build-up, °C	33
15 minute cure, 150°C:	
Durometer	61
M300, MPa	9.2
Tensile, MPa	22
Elongation, %	605

NR 31

Elastomer: NR
Durometer: 62 (76)
Application: Tall oil

SMR	100	PEG 3350	1
220 m^2/g Silica	30	Zinc oxide	5
Ciptane 255 LD	20	Sulfur	3
100ºC resin	5	TBBS	3
Stearic acid	2		
ODPA	1	Specific gravity	1.16

Tall oil (Acintol D30):	4	0
MDR cure rate, 150°C, T_{90} minutes	11	10
MDR crosslinks, dN-m	18	34
Mooney scorch, 130°C, T_5 minutes	27	15
Mooney viscosity, ML_4100	37	82
Durometer (20 minutes, 150°C), 23°C	62	76
100°C	61	75
PICO abrasion index	73	74
MG trouser tear, kN/m	13k	16k

15 min cure, 150°C:	Original	Aged*	Original	Aged*
M20, MPa	0.9	1.8	1.3	1.9
M300, MPa	7.4		9.4	
Tensile, MPa	34	12	32	14
Elongation, %	690	280	655	260

*700 hrs, 85°C

Pendulum rebound (Z), 23°C	60	57
100°C	73	70
Goodrich flexometer: 100°C; 22.5%; 1 MPa		
Dynamic compression, %	8.1	3.7
Drift, %	7.9	8.0
Permanent set, %	11	9.1
Heat build-up, ºC	19	19

NR 32

Elastomer: NR/SBR Durometer: 63
Application: Fabric adhesion, skim/friction

SMR	75	Zinc oxide	5
SBR 1500	25	Stearic acid	2
150 m^2/g Silica	15	Sulfur	2.8
65 m^2/g Silica	15	MBS (MOR)	1.4
FEF N550	20	ZBDC	0.3
Aromatic oil	6		
100ºC resin	10		
TMQ	1	Specific gravity	1.10

ODR cure rate, 150°C, T_{90} minutes	19
Mooney scorch, 130°C, T_5 minutes	22
Mooney viscosity, ML_4100	34

Strip adhesion to RFL treated nylon fabric, N/24mm

23°C	310
100°C	285

30 minute cure, 150°C:	Original	120 hrs, 100°C
Durometer	63	65
M300, MPa	4.8	
Tensile, MPa	18	11
Elongation, %	580	350

NR 33

Elastomer: NR Durometer: 64

Application: Coated fabric

SMR	100	Sulfur	2.6
150 m^2/g Silica	35	MBS (MOR)	1.2
ODPA	1	DPG	0.4
Stearic acid	1.5		
Zinc oxide	5		
Triethanolamine	1.5	Specific gravity	1.12

ODR cure rate, 150°C, T_{90} minutes		11
Mooney scorch, 130°C, T_5 minutes		
	Original	8
	Remilled, 7 days	9
Mooney viscosity, ML_4100		
	Original	65
	Remilled, 7 days	48

15 minute cure, 150°C:	Original	96 hrs, 100°C
Durometer	64	67
M300, MPa	50	
Tensile, MPa	28	14
Elongation, %	640	400
Die C tear, kN/m	73	53

Trouser tear, grooved, kN/m	10 k

NR 34

Elastomer: NR Durometer: 64
Application: Low HBU, tan delta

SMR	100	PEG 3350	1
160 m^2/g Silica	40	Sulfur	2.8
100ºC resin	5	TBBS	3
ODPA	1		
Stearic acid	2		
Zinc oxide	4	Specific gravity	1.11

ODR cure rate, 150°C, T_{90} minutes	20
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, ML_4100	58

30 minute cure, 150°C:	Original	700 hrs, 85°C
Durometer	64	72
M300, MPa	5.8	
Tensile, MPa	28	15
Elongation, %	660	430

MG Trouser tear, kN/m	18

Pendulum rebound , %	Zwick	Goodyear-Healy
23°C	63.1	78.1
100°C	78.8	84.7

DMA dynamic modulus: 1 Hz; 30°C

E"	0.38 MPa
E'	7.0
Tan delta	0.055

Goodrich flexometer: 100°C; 22.5%; 1 MPa

Permanent set, %	5.1
Heat build-up	15ºC
Compression set, 72 hrs, 100°C, %	56
PICO abrasion index	90
DeMattia cut growth, kc to 500%	15
Monsanto flex fatigue, 100%, kc	15

NR 35

Elastomer: NR/EPDM Durometer: 65/70
Application: Ozone resistance

SMR	70	Banbury 2	
EPDM 2914	60	Zinc oxide	5
150 m^2/g Silica	25	Sulfur	1
Clay or silica	75	DTDM	1
Titanium dioxide	5	TBBS	3
100ºC resin	10		
Stearic acid	3		
ODPA	1		

Filler:	Hard Clay	65 m^2/g Silica
Specific gravity	1.26	1.20
MDR cure rate, 150°C, T_{90} minutes	23	19
Mooney scorch, 121°C, T_5 minutes	30+	30+'
Mooney viscosity, ML4100	62	130
Garvey die extrusion, edge/surface, 120°C		10A

30 min cure, 150°C:	Original	Aged*	Original	Aged*
Durometer	65	71	71	76
M300, MPa	5.4		6.5	
Tensile, MPa	9.7	7.9	10.3	8.2
Elongation, %	555	425	525	380

*700 hrs, 70°C

Ozone Exposure: 50 pphm; 40°C; 550 hours

Cracking, static	none	none
Cracking, dynamic	none	none
MG Trouser tear, kN/m	12.2	13.4
PICO abrasion index	56	56
Compression set, %, 72 hours, 100°C	79	69

NR 36

Elastomer: NR Durometer: 65
Application : Calendering; Footwear

SMR	100	Sulfur	2.8
150 m^2/g Silica	30	TBBS	1.5
35 m^2/g Silica	45	DPG	0.3
Staybelite resin	5	PEG 3350	2
Naphthenic oil	5	Zinc oxide	5
Stearic acid	3		
MC wax	2		
ODPA	1	Specific gravity	1.20

Processing	Original	Remilled
ODR cure rate, 144°C, T_{90} minutes	20	21
Mooney scorch, 135°C, T_5 minutes	12	14
Mooney viscosity, ML_4100	41	30

Stress/Strain, cure

20 minute cure, 144°C:	Original	Aged 72 hrs,100°C
Durometer	65	76
M300, MPa	5.0	
Tensile, MPa	18	16
Elongation, %	600	490

NBS abrasion index	68
Trouser tear, grooved kN/m	14
DeMattia cut growth, 500%, kc	
23°C	40
100°C	20
Compression set, %, 70 hours, 100°C	71
Goodrich flexometer: 100°C; 22.5%; 1 MPa	
Static compression, %	22
Permanent set	13
Heat build-up, ºC	29

NR 37

Elastomer: NR Durometer: 65
Application: Extrusions; surface gloss

SMR	100	PEG 3350	1.5
35 m^2/g Silica	90	Sulfur	2.6
Tall oil	5	MBS	2
Naphthenic oil	5	DPG	0.3
Stearic acid	1.5		
ODPA	1		
Zinc oxide	5	Specific gravity	1.23

ODR cure rate, 150°C, T_{90} minutes	8
Mooney scorch, 121°C, T_5 minutes	22
Mooney viscosity, ML_4100	62

Garvey extrusion, 120°C	
% swell	3
Edge/surface rating	10A
Surface	glossy

9 minute cure, 150°C:	Stress/Strain, Original	120 hrs, 100°C
Durometer	65	71
M300, MPa	6.2	
Tensile, MPa	14	10
Elongation, %	530	380

Die C Tear. kN/m	35
Abrasion indices :	
PICO	63
NBS	54
Yerzley Resilience	80%

Water immersion, 70°C, % volume change	
24 hours	6
72 hours	12
330 hours	24

NR 38

Elastomer: NR Durometer: 65
Application: Surface area

SMR CV60	100	Zinc oxide	5
Silica	40	Sulfur	3
100ºC aromatic resin	5	TBBS	3
Stearic acid	2		
ODPA	1		
PEG 3350	1	Specific gravity	1.13

Silica surface area, N$_2$SA m$_2$/g	150	190	220	250
MDR cure rate, 150°C, T$_{90}$ minutes	15	12	11	10
MDR crosslinks, dN-m	26	29	30	35
Mooney scorch, 130°C, T$_5$ minutes	30	27	24	15
Mooney viscosity, ML$_4$100	36	63	69	102
Durometer, 23°C	64	64	66	73
100°C	64	64	65	73
15 minute cure, 150°C (#1 - 20')				
M20, MPa	1.0	0.9	1.0	1.1
M300, MPa	7.0	6.0	5.9	5.6
Tensile, MPa	32	33	36	35
Elongation, %	655	700	720	745
Aged 700 hours, 85°C				
M20, MPa	1.7	1.5	1.6	1.8
Tensile, MPa	6.8	12	11	12
Elongation, %	140	250	235	260
MG Trouser tear, kN/m	5.5k	12k	6k	25k
PICO abrasion index	74	65	68	70
Goodrich flexometer: 100°C; 22.5%; 1 MPa				
Dynamic compression, %	17	18	17	14
Permanent set	7.9	8.1	8.8	16
Heat build-up, ºC	16	15	17	25
Pendulum rebound (Z), %, 23°C	67	64	62	58
100°C	77	75	74	70

NR 39

Elastomer: NR Durometer: 66
Application: General; Tear strength

SMR CV60	100	Sulfur	2.6
150 m^2/g Silica	50	MBS (MOR)	2
Tall oil	5	DPG	0.6
Stearic acid	1	PEG 3350	2.5
Zinc oxide	5		
ODPA	1	Specific gravity	1.17

ODR cure rate, 150°C, T_{90} minutes	21
Mooney scorch, 121°C, T_5 minutes	30
Mooney viscosity, ML $_4$100	52

21 minute cure, 150°C	Original	Aged*	Aged**
Durometer	66	71	72
M300, MPa	5.9		
Tensile, MPa	25	24	18
Elongation, %	350	330	300

*170 hrs, 70°C; **120 hrs, 100°C

Trouser tear, Grooved, kN/m	42
Compression set, %	
22 hours, 70°C	25
70 hours, 100°C	70

NR 40

Elastomer: NR/BR Durometer: 66
Application: Truck drive tread

SMR	65	MC wax	1
BR 1221	35	Zinc oxide	4
150 m^2/g Silica	35	PEG 3350	1.5
HAF N330	20	Sulfur	0.3
Staybelite resin	6	TBBS	2
100ºC resin	5	MDB	2
Tall oil	1	TBTD	0.3
Stearic acid	2		
TMQ	1		
HPPD	2	Specific gravity	1.17

ODR cure rate, 138°C, T_{90} minutes	40
Mooney scorch, 121°C, T_5 minutes	27
Mooney viscosity, ML_4100	59

45 minute cure, 138°C:	Original	72 hrs, 121°C
Durometer	66	73
M300, MPa	6.2	
Tensile, MPa	22	14
Elongation, %	620	400

Trouser tear, grooved, kN/m	17
PICO abrasion index	110
Pendulum rebound (G-H), %, 23°C	59
100°C	71

Goodrich flexometer: 100°C	22.5%; 1MPa	25%; 1.6MPa
Static compression, %	14	28
Dynamic compression	5	17
Permanent set	6	18
Heat build-up, ºC	30	67

DeMattia cut growth, kc to 500% 30

NR 41

Elastomer: NR Durometer: 66
Application: Sundries; Footwear

SMR	100	Zinc oxide	5
65 m^2/g Silica	60	Stearic acid	1.5
Whiting	30	Sulfur	2.5
Hard clay	20	TBBS	1.2
100ºC resin	9	DOTG	1.2
Tall oil	3		
Naphthenic oil	5		
Phenolic A.O.	1	Specific gravity	1.30

ODR cure rate, 154°C, T_{90} minutes	15
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, ML_4100	40
Garvey extrusion, ASTM rating	16
15 minute cure, 154°C:	
Durometer	66
M300, MPa	6.9
Tensile, Mpa	13
Elongation, %	500
Die C tear, kN/m	53
NBS abrasion index	80

NR 42

Elastomer: NR Durometer: 66
Application: Brass adhesion

SMR	100	Zinc oxide	6
Naphthenic oil	5	Sulfur	4
R-F resin 1501	3	HMMM 963P	1.5
HPPD	2		
Stearic acid	2	Specific gravity	1.12

	Silica	Black control
HAF N330	50	60
150 m^2/g Silica	15	-
Cobalt CP216	-	2
TBBS	1.2	0.7
ODR cure rate, 160°C, T_{90} minutes	6.0	6.3
ODR crosslinks, dN-m	70	66
Mooney scorch, 130°C, T_5 minutes	9.5	10
Mooney viscosity, ML_4100	52	59
Durometer (11 min, 160°C)	66	73
M300, MPa	14	15
Tensile, MPa	24	25
Elongation, %	505	505
Static adhesion to brassed wire (6+3), N/13 mm (% cover)		
Original	510 (90)	550 (90)
Green aged 70 hrs, 50°C	520 (10)	270 (40)
Humid aged 120 hrs, 90°C	380 (60)	360 (30)
Disc fatigue dynamic adhesion, 70°C; 4 hrs; 30 Hz		
Green aged, 100% relative humidity		
Separation failures	0	2
Avg. pull-out, N	550	330
Humid aged 120 hrs, 90°C		
Separation failures	0	6
Avg. pull-out, N	490	210
Tension fatigue dynamic adhesion: 5 Hz; 70°C; 55N stress		
Green aged, cycles to separation failure		
63% fail	200 (100)	30 (40)
10% fail	6	0.3

NR 43

Elastomer: NR Durometer: 66
Application: Tear; Tensile; Low HBU

SMR	100	Zinc oxide	5
150 m^2/g Silica	20	PEG 3350	0.5
HAF N339	35	Sulfur	2
Aromatic oil	6	MBS (MOR)	2
Stearic acid	2	DPG	0.4
HPPD	2		
TMQ	2	Specific gravity	1.16

ODR cure rate, 144°C, T_{90} minutes	15
Mooney scorch, 121°C, T_5 minutes	19
Mooney viscosity, ML_4100	52
21 minute cure, 144°C:	
Durometer	66
M300, MPa	13
Tensile, Mpa	29
Elongation, %	550
MG Trouser tear, kN/m	
20 min, 144°C	13
120 min, 144°C	11
Pendulum rebound (Z), %, 23°C	62
100°C	75.2
Goodrich flexometer: 100°C; 22.5%; 1 MPa	
Static compression, %	15
Permanent set, %	6.1
Heat build-up, ºC	24
DMA Dynamic modulus, 1Hz; MPa	
E", 80°C	0.82
E', 80°C	6.3
E', 30°C	12.2
Tangent delta, 80°C	0.131
DeMattia cut growth, kc to 500%	35
PICO abrasion index	73

NR 44

Elastomer: NR Durometer: 67
Application: Fabric adhesion; heat resistance

SMR	100	PEG 3350	1
220 m^2/g Silica	45	Sulfur	2.8
100ºC resin	10	TBBS	var.
HPPD	2		
Stearic acid	2		
Zinc oxide	3	Specific gravity	1.13

Mercaptosilane A189	0	1.5
TBBS	3	2
MDR cure rate, 155°C, T$_{50}$ minutes	9.2	5.3
MDR Reversion, dN-m	9	4
Mooney scorch, 121°C, T$_5$ minutes	30+	27
Mooney viscosity, ML$_4$100	74	53
Strip adhesion to RFL treated fabric, N/25mm	700	250

20 minute cure, 155°C	Original	Aged*	Original	Aged*
Durometer, 23°C	67	75	67	80
100°C	64		63	
M300, MPa	5.9		7.8	
Tensile, MPa	35	10	34	11
Elongation, %	760	225	745	220

* 700 hours, 90°C

MG Trouser tear, kN/m	16k	13k
PICO abrasion index, 23°C	74	71
70°C	56	53
DIN abrasion loss, ml	176	154
Pendulum rebound (Z), %, 23°C	54	54
100°C	70	71
DMA dynamic modulus: 1 Hz; 60°C		
E', MPa	8.8	8.4
Tangent delta	0.068	0.078
Goodrich flexometer: 100°C; 22.5%; 1MPa		
Permanent set, %	13	8.6
Heat build-up, ºC	17	13
DeMattia cut growth, kc to 500%	9	15

NR 45

Elastomer: NR/BR Durometer: 67
Application: Heat resistance; Low HBU; tear

SMR	80	Banbury 2	
BR 1220	20	Zinc oxide	8
150 m^2/g Silica	50	Sulfur	0.4
100ºC resin	5	Vultac 710	1.5
TMQ	4	TBBS	4
HPPD	2	OTOS	0.6
Stearic acid	2	Specific gravity	1.15

ODR cure rate, 150°C, T_{90} minutes	17
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, ML_4100	86

35 minute cure, 150°C:	Original	700 hrs,100°C	168 hrs, 120°C
Durometer	67	72	73
M300, MPa	4.4		
Tensile, MPa	21	12	7
Elongation, %	660	405	305

MG Trouser tear, kN/m	17
Pendulum rebound (Z), 23°C	52
100°C	66

Goodrich flexometer: 93°C; 25%;1.6MPa	
Permanent set, %	19
Heat build-up, ºC	51
DMA Dynamic modulus: 1 Hz; 30°C	
E" MPa	2.2
E'	16.4
Tan delta:	0.137
DeMattia cut growth, kc to 500%	100+
Compression set, %, 72 hours, 100°C	59

NR 46

Elastomer: NR/SBR		Durometer: 67	
Application: Low HBU			

SMR	70	Banbury 2	
SBR 1502	30	Zinc oxide	3
150 m^2/g Silica	50	PEG 3350	1.5
Mercaptosilane	0.8	Sulfur	2.8
Titanium dioxide	5	MBS	2
100ºC resin	10		
Stearic acid	2		
MC wax	2		
ODPA	1	Specific gravity	1.17

ODR cure rate, 150°C, T_{90} minutes	14	
Mooney scorch, 130°C, T_5 minutes	20	
Mooney viscosity, ML_4100	60	
Goodrich flexometer: 100°C, 22.5%:	MPa	Heat build-up ºC
	0.7	17
	1.0	21
	1.3	27
	1.6	33
Pendulum rebound (Z), %	23°C	100°C
	56	73
Yerzley resilience, %	57	61
MG Trouser tear, kN/m Cure:	20 min, 150°C	200 min, 138°C
23°C	20	12
100°C	19	6
PICO abrasion index	85	
DeMattia cut growth, kc to 500%	40	
Monsanto flex fatigue, 100% strain, kc	57	
Stanley London Skid index wet textured glass	61	

NR 47

Elastomer: NR Durometer: 67
Application: Non-marking, Solid tire

SMR, milled 1 min	100	Zinc oxide	3
Ciptane TM (1.2%)	45	PEG 3350	1
100ºC aromatic resin	5	Sulfur	2.8
Stearic acid	1	TBBS	3
MC wax	1		
ZMTI	1.5		
ODPA	1.5	Specific gravity	1.13

MDR cure rate, 140°C, T_{50} minutes	11
T_{90} minutes	17
reversion, 60 minutes, dN-m	2.8
Mooney scorch, 121°C, T_5 minutes	30
Mooney viscosity, $ML_4 100$	46

Stress/Strain	Original	Aged*	Aged**
Durometer, 23°C	67	75	77
100°C	64		
M300, MPa	6.7		
Tensile, MPa	28	20	12
Elongation, %	655	460	295

*90°C, 300 hrs **90°C, 700 hrs

MG Trouser tear, kN/m	11
PICO abrasion index	83
Pendulum rebound (Z), %, 23°C	62
100°C	71
Goodrich flexometer: 100°C; 22.5%; 1 MPa	
Permanent set, %	9.0
Heat build-up, ºC	16
DMA dynamic modulus: 1 Hz; 15% strain	
E', MPa, 0°C	17.0
60°C	10.2
E", 0°C	1.45
60°C	1.33
Tangent delta, 60°C	0.130

NR 48

Elastomer: NR Durometer: 68
Application: TBzTD; Non-nitrosoamine

SMR	100	Zinc oxide	3
150 m^2/g Silica	25	PEG 3350	0.8
ISAF N231	40	Sulfur	1
100ºC Aromatic resin	12	TBBS	2
Aromatic oil	7	MDB	1
MC wax	2	TBzTD	0.4
Stearic acid	2		
HPPD	2		
TMQ	1	Specific gravity	1.15

MDR cure rate, 138°C, T$_{90}$ minutes	18
Mooney scorch, 130°C, T$_5$ minutes	22
Mooney viscosity, ML$_4$100	39

60 min cure, 138°C:	Original	500 hrs, 90°C
Durometer	68	76
M300, MPa	8.1	
Tensile, MPa	22	19
Elongation, %	580	485

MG Trouser tear, 23°C, kN/m, 138°C cure

60 min	15.2
200 min	17.0
PICO abrasion index	86
Pendulum rebound (Z), %, 23°C	40
100°C	49

Goodrich flexometer, 100°C:	22.5%; 1MPa	25%; 1.6 MPa
Static compression, %	27	35
Dynamic compression, %	20	23
Drift	4.8	
Permanent set, %	4.9	19
Heat build-up, ºC	19	55

DMA dynamic modulus: 1 Hz; 30°C

E', MPa	33
E"	7.3
Tangent delta	0.222

NR 48A

Elastomer: NR Durometer: 68
Application: Brass adhesion; Tire belt skim

SMR	100	Zinc oxide	1
150 m^2/g Silica	8	HMMM 963	3
HAF N330	42	Sulfur	4
TMQ	1	TBBS	1
Stearic acid	2		
Resorcinol resin B19s	3		

MDR cure rate, 160°C, T_{90} minutes	5.4
Mooney scorch, 130°C, T_5 minutes	14
Mooney viscosity, ML_4100	58

12 minute cure, 160°C:	
Durometer, 23°C	68
100°C	65

Stress/Strain	Original	70 hrs, 90°C
Durometer	68	74
M300, MPa	14	
Tensile, MPa	28	13
Elongation, %	510	260

Pendulum rebound (Z), %, 23°C	52
100°C	64

Disc Fatigue dynamic wire adhesion: flexed 6 hours at 80°C;
Separation failures per 12 replicates:

Original	0
Humid aged 70 hrs, 90°C	0
Green humid aged 70 hrs, 50°C	0

NR 49

Elastomer: NR Durometer: 68
Application: Tear strength

SMR	100	Zinc oxide	3
150 m^2/g Silica	55	Sulfur	3
Staybelite resin	5	MBS	1.2
100ºC resin	10	TMTM	0.3
ODPA	1.5		
Stearic acid	2		
PEG 3350	3	Specific gravity	1.17

ODR cure rate, 144°C, T_{90} minutes	15
Mooney scorch, 121°C, T_5 minutes	24
Mooney viscosity, ML $_4$100	75
Trouser tear, grooved, kN/m	28

20 minute cure, 144°C:	Original	700 hrs, 80°C
Durometer	68	75
M300, MPa	3.7	
Tensile, MPa	23	9
Elongation, %	680	310

Goodrich Flexometer: 100°C; 22.5%; 1 MPa

Static compression, %	13
Dynamic compression	3
Permanent set	20
Heat build-up, ºC	31

Compression set, %, 72 hours, 100°C 72

NR 50

Elastomer: NR/SBR Durometer: 69
Application: Silanes; TBzTD

SMR CV60	80	Zinc oxide	3
SBR 1500	20	PEG 3350	0.8
Silica (below)	30	Sulfur	1
N231	30	MDB (Morfax)	1.5
100ºC resin	10	TBBS	2
Aromatic oil	5	TBzTD (below)	0 / 0.2
TMQ	1	Silane SI69 (below)	0 / 1
HPPD	2		
MC wax	1		
Stearic acid	2	Specific gravity	1.15

Silica surface area, m2/g	150	150	220	220
Silane A189	-	1	-	1
TBzTD	0.2	-	0.2	-
MDR cure rate 138°C, T_{90} minutes	27	32	27	34
Mooney scorch 130°C, T_5 minutes	22	20	23	23
Mooney viscosity $ML_4$100	38	38	48	43
Durometer, 23°C	66	69	63	68
100°C	59	61	58	60
MG trouser tear, kN/m				
60 minute cure, 138°C	14	12	15	15
200 minute cure, 138°C	9.3	8.6	10	11
Goodrich flexometer: 22.5%; 1 MPa				
Heat build-up, ºC	24	25	31	28
DMA dynamic modulus: 30°C; 1 Hz, MPa				
Elastic modulus E'	6.9	6.3	7.2	7.4
Loss modulus E"	1.56	1.42	1.52	1.66
Tangent delta	0.226	0.226	0.212	0.225
Abrasion: PICO index	73	81	74	81
DIN loss, ml	156	141	145	137
Compression set, %: 70 hrs, 100°C	56	63	57	65

NR 50, continued

Silica surface area, m2/g	150	150	220	220
Silane	-	1	-	1
TBzTD	0.2	-	0.2	-
Stress/Strain, 138°C				
Durometer				
60 min cure	71	71	69	70
200 min cure	70	73	70	68
M300, MPa,				
60 min cure	8.4	11	7.4	9.7
200 min cure	7.7	11	6.7	9.7
Tensile, MPa,				
60 min.	27	28	28	28
200 min cure	26	27	26	27
Elongation, %				
60 min cure	625	645	685	660
200 min cure	640	510	680	640

NR 51

Elastomer: NR Durometer: 69

Application: Tear strength

SMR	100	Zinc oxide	5
150 m^2/g Silica	20	PEG 3350	0.5
ISAF N285	35	Sulfur	2.5
Tall oil	3	TBBS	2
100ºC resin	3	DPG	0.4
Stearic acid	2		
MC wax	1		
TMQ	2		
HPPD	2	Specific gravity	1.15

ODR cure rate, 144°C, T_{90} minutes	9.5
Mooney scorch, 138°C, T_5 minutes	5
Mooney viscosity, ML_4100	62
PICO abrasion index	106

Trouser tear, grooved, kN/m:

Cure, 144°C	20°C	70°C
15 min	12k	11k
25 min	17k	11k
40 min	28k	22k

20 minute cure, 144°C:	Original	120 hrs, 100°C
Durometer	69	77
M300, MPa	12	
Tensile, Mpa	23	17
Elongation, %	500	290
Die C tear, kN/m	7.9	4.9

NR 52

Elastomer: Polyisoprene Durometer: 69
Application: OTR tread; Compression-deflection

IR SN600	100	Zinc oxide	5		
150 m^2/g Silica	25	PEG 3350	0.5		
ISAF N220	35	Sulfur	2.5		
Phenolic 12687	6	TBBS	1.8		
Tall oil	3	DPG	0.5		
100ºC resin	7				
HPPD	2	Specific gravity			1.16

ODR cure rate, 144°C, T_{90} minutes	16
Mooney scorch, 138°C, T_5 minutes	6.4
Mooney viscosity, ML_4100	66

20 minute cure, 144°C:	Original	100 hrs, 100°C
Durometer	69	77
M300, MPa	6.1	
Tensile, MPa	22	14
Elongation, %	620	340

Trouser tear, grooved, kN/m, 23°C	25
70°C	31k
PICO abrasion index	109

Compression - Deflection, Mpa:

% deflection	1st cycle	10th cycle
5	0.6	0.4
10	0.9	0.8
20	1.7	1.5
25	2.1	2.0

Compression set, %72 hours, 100°C	68
Goodrich Flexometer: 38°C; 17.5%; 1 MPA	
Permanent set, %	6
Heat build-up, ºC	39

NR 53

Elastomer: NR/BR Durometer: 70
Application: Truck tread

SMR	60	Zinc oxide	4		
BR 1203*	40	PEG 3350	1.5		
150 m^2/g Silica*	27	Sulfur	0.3		
HAF N330	30	MBS (MOR)	2		
Staybelite resin*	5	MDB	1		
100ºC resin*	7	TBTD	1		
Stearic acid	1				
TMQ	1				
HPPD	2	Specific gravity			1.15

* Blend first in Banbury for optimum tear strength.

ODR cure rate, 138°C, T_{90} minutes	30
Mooney scorch, 130°C, T_5 minutes	17
Mooney viscosity, ML_4100	67
Garvey Die extrusion: % swell	19
Edge/ surface	8A

138°C cure:	40 minutes	200 minutes
Durometer	70	69
M300, MPa	8.0	8.1
Tensile, MPa	22	20
Elongation, %	560	530
MG Trouser tear, kN/m	10.7	10.7

PICO abrasion index	98
DeMattia cut growth, kc to 500%	35
Stanley - London skid index	50

Goodrich Flexometer: 200 minute cure, 138°C:

	22.5%, 1 MPa	25%, 1.6 MPa
Permanent set, %	2.1	7.6
Heat build-up, ºC	34	56

NR 54

Elastomer: NR Durometer: 70
Application: OTR tread

SMR CV60	100	<u>Banbury 2</u>	
150 m^2/g Silica	25	Sulfur	1
ISAF N231	25	MDB (Morfax)	1
100ºC aromatic resin	8	TBBS	2
Stearic acid	2	TBTD	0.2
Zinc oxide	3	PEG 3350	1
TMQ	1		
HPPD	2	Specific gravity	1.16

MDR cure rate, 138°C, T_{90} minutes	24
Mooney scorch, 130°C, T_5 minutes	20
Mooney viscosity, $ML_4$100	57

138°C cure:	<u>40 minutes</u>	<u>200 minutes</u>
Durometer	67	71
M20, MPa	1.1	1.2
M300, MPa	9.3	8.3
Tensile, MPa	28	29
Elongation, %	590	625
MG Trouser tear, kN/m	13.2	19.4

PICO abrasion index	75
Pendulum rebound (G-H), %, 23°C	58
100°C	70

Goodrich Flexometer: 93°C; 25%; 1.6 MPa (blow-out conditions)

Static compression, %	28
Permanent set	15
Heat build-up	59ºC

DeMattia cut growth, kc to 500%	7

NR 55

Elastomer: NR Durometer: 70
Application: Solid tire; non-marking

SMR	100	Zinc oxide	3
220 m^2/g Silica	45	PEG 3350	0.5
Mercaptosilane A189	0.5	Sulfur	3.3
100ºC resin	7	TBBS	3
Stearic acid	1		
ZDMA 634	3		
ZMTI	1		
ODPA	1	Specific gravity	1.12

MDR cure rate, 140°C, T_{50} minutes	17
Mooney scorch, 121°C, T_5 minutes	30+
Mooney viscosity, ML$_4$100	41

Cure:	35 min, 140°C	200 min, 130°C
Durometer, 23°C	69	71
100°C	67	67
MG Trouser tear, 23°C	13k	25
70°C	44k	14k
Goodrich flexometer: 100°C; 22.5%; 1 MPa		
Heat build-up, 120 min, ºC	15	
DMA dynamic modulus: 1Hz; 60°C		
E'', MPa	0.61	
E'	6.20	
Tangent delta	0.098	
PICO abrasion index, 23°C	59	60
100°C	46	
DIN abrasion loss, mg	155	
Pendulum rebound (Z), 23°C	57	53
100°C	66	67

35 minute cure, 140°C:	Original	700 hours, 80°C
Durometer	71	77
M300, MPa	8.2	
Tensile	33	24
Elongation, %	725	545

NR 56

Elastomer: NR/SBR Durometer: 71
Application: Tear, heat resistance; Solid tread

SMR	70	Zinc oxide	3
SBR 1502	30	PEG 3350	2
150 m^2/g Silica	50	Sulfur	0.4
65 m^2/g Silica	25	MBS (MOR)	2
Titanium dioxide	5	MDB (Morfax)	1
100ºC resin	10	TBTD	1
Stearic acid	2		
MC wax	2		
ODPA	1	Specific gravity	1.20

ODR cure rate, 150°C, T_{90} minutes	10
Mooney scorch, 130°C, T_5 minutes	16
Mooney viscosity, $ML_4$100	65

15 minute cure, 150°C	Original	72 hrs, 100°C
Durometer	71	71
M300, MPa	5.1	
Tensile, MPa	16	15
Elongation, %	570	530

MG Trouser tear, 200 minute cure, 138°C, kN/m	
23°C	17
100°C	10

Goodrich Flexometer, 100°C, 22.5%:	MPa	Heat build-up,ºC
	0.7	26
	1.0	42
	1.3	50
	1.6	58

DeMattia cut growth, kc to 500%	20
Monsanto flex fatigue, 100%	9 kc
Pendulum rebound (G-H), %, 23°C	53
100°C	63
Stanley London skid index,	
wet textured glass	61
dry textured glass	138

NR 57

Elastomer: NR Durometer: 70
Application: Heat resistance

SMR CV60	100	Zinc oxide	5
220 m^2/g Silica	30	PEG3350	1.5
Ciptane I	20	Sulfur	2.5
100ºC resin	10	TBBS	varied
ZMTI	1	TMTM	varied
TMQ	1		
Stearic acid	2	Specific gravity	1.13

Performance:	Low HBU	Fast cure
TBBS	3	2
TMTM	-	0.3
MDR cure rate, T_{90} minutes	9.8	4.2
Mooney scorch, 121°C, T_5 minutes	30+	20
Mooney viscosity, ML_4100	44	45

Stress/Strain		Original	Aged*	Original	Aged*
Durometer,	23°C	71	67	67	72
	100°C	65	62		
M300, MPa		8.0		7.2	
Tensile, Mpa		30	27	29	21
Elongation, %		650	615	665	515

*aged 700 hours at 90°C

	Low HBU	Fast cure
MG Trouser tear, kN/m	20	22
PICO abrasion index	93	87
Goodrich flexometer: 100°C; 22.5%; 1 MPa		
Permanent set, %	16	19
Heat build-up, ºC	21	29
DMA dynamic modulus: 1 Hz; 17%; 60°C		
E", MPa	0.82	0.84
E'	6.4	7.4
Tangent delta	0.129	0.112
Pendulum rebound (Z), %, 23°C	48	47
100°C	62	62
Compression set: 72 hours, 100°C, %	80	71

NR 58

Elastomer: Epoxy NR Durometer: 70
Application: Low HBU

ENR 25	100	PEG3350	1
Silica or Ciptane	48	Sulfur	1
MS40	3	MOR	2
HPPD	2	MDB	1
TMQ	1	TBTD	0.3
Zinc oxide	4		
Stearic acid	2	Specific gravity	1.17

Silica:	150 m^2/g Silica	Ciptane I
ODR cure rate, 138°C, T_{90} minutes	28	14
Mooney scorch, 121°C, T_5 minutes	25	9.0
Mooney viscosity, ML $_4$100	70	66

Stress/Strain	Original	Aged*	Original	Aged*
Durometer	71	83	69	81
M300, MPa	13		14	
Tensile, MPa	31	9.0	14	11
Elongation, %	535	95	545	125

*aged 170 hours, 100°C

MG Trouser tear, kN/m	4.8	4.0
PICO abrasion index	96	104
Goodrich flexometer: 100°C; 25%; 1.6 MPa		
Heat build-up, ºC	42	29
DMA dynamic modulus: 1 Hz; 15%		
Tangent delta, 80°C	0.076	0.080
0°C	0.290	0.510
E", MPa, 0°C	5.9	15.7
Pendulum rebound (Z), %, 23°C	57.4	57.4
100°C	78.7	79.9

NR 59

Elastomer: NR Durometer: 70
Application: Silica vs. HAF

SMR	100	Sulfur	1
Silica/N339	70	MDB	1
Aromatic oil	15	MBS	2
Stearic acid	2	TBTD	0.1
HPPD	2	PEG 3350	0.8
TMQ	2		
MC wax	1		
Zinc oxide	5	Specific gravity	1.16

150 m^2/g Silica	20		-	
HAF N 339	50		70	
ODR cure rate, 144°C, T_{90} minutes	15		12	
Mooney scorch, 121°C, T_5 minutes	22		14	
T_{35} minutes	26		16	
Mooney viscosity, $ML_4$100	52		54	
DMA dynamic modulus: 1 Hz; 15% strain, MPa				
Cure at 144°C	30 min	120 min	30 min	120 min
E", 0°C	7.4	7.8	10.0	9.8
E", 60°C	0.234	0.239	0.304	0.282
E', 30°C	20	21	25	24
E', 80°C	7.6	7.4	9.3	9.2
Tangent delta at 80°C	0.199	0.211	0.277	0.262
MG Trouser tear, kN/m	75k	55	55k	50
Goodrich flexometer: 100°C; 22.5%; 1 Mpa				
Static compression, %	16		15	
Permanent set	6.6		5.8	
Heat build-up, ºC	32		35	
Pendulum rebound (G-H), %, 23°C	52.0		45.5	
100°C	71.2		65.2	
DeMattia cut growth, kc to 500%	100+		100+	
PICO abrasion index	74		91	
Stress/Strain, 20 minute cure, 144°C				
Durometer	68		72	
M300, MPa	15.5		18	
Tensile, MPa	28		26	
Elongation, %	570		460	

NR 60

Elastomer: NR/BR Durometer: 70
Application: Tennis ball

SMR CV60	90	Zinc oxide	3
BR 1220	10	PEG 3350	1
150 m^2/g Silica	50	Sulfur	variable
Ground silica	20	TBBS	variable
100ºC resin	10	DCP	variable
Stearic acid	2		
ODPA	1	Specific gravity	1.15

Sulfur	2.8	-
TBBS	3	-
Dicumyl peroxide	-	2.4
MDR 150°C, T_{50} minutes	11	12
T_{90} minutes	15	38
MDR xlinks, dN-m, T_{90} minutes	36	34
Mooney scorch 121°C	30+	8
Mooney viscosity ML_4100	58	74
Cure, 150°C	20 minutes	40 minutes
Durometer	70	65
M20, MPa	1.4	1.2
M300, MPa	6.3	5.5
Tensile, MPa	24	20
Elongation, %	595	540
Aged 480 hours, 90°C:		
Durometer	75	76
Tensile, MPa	11	1.0
Elongation, %	260	10
Stress relaxation from M300, %	13.2	24.4
Pendulum rebound (Z), 23°C	55	53
100°C	66	51
Compression set: 70 hrs, 100°C, %	78	58
Tension set from 300%, %	19.6	18.5
MG Trouser tear, kN/m	15.0	14.6

NR 61

Elastomer: NR Durometer: 71
Application: Air cure

Pale crepe	100	PEG3350	2.5
150 m^2/g Silica	50	Sulfur	2.5
Mercaptosilane 189	1	MBS	1.5
Titanium dioxide	20		
Non-discolor Antiox.	1		
Zinc oxide	5		
10ºC CI resin	5	Specific gravity	1.22

ODR cure rate, 138°C, T_{90} minutes	8.0
Mooney scorch 121°C, T_5 minutes	10
Mooney viscosity, ML_4100	85
Air cure discoloration, 60 min, 138°C	none
15 minute press cure, 138°C:	
Durometer	71
M300, MPa	13
Tensile	27
Elongation, %	510
PICO abrasion index	87

NR 62

Elastomer: NR/BR Durometer: 73
Application: Zinc-free; hot tear; abrasion

SMR CV60	50	Sulfur	2	
BR1220	50	MBS (MOR)	2	
220 m^2/g Silica	30	HMT	2	
SAF N121	33	Zinc oxide	5	
Wingstay300	3			
Aromatic oil	9	Specific gravity		1.17

MDR cure rate, 150°C, T_{90} minutes	14
Mooney scorch, 121°C, T_5 minutes	27
Mooney viscosity, ML_4100	72
Durometer, 23°C	73
100°C	68
PICO abrasion index, 23°C	173
100°C	118
DIN abrasion loss, ml	118
MG trouser tear, kN/m, 23°C	17
100°C	22

Goodrich flexometer: 100°C; 22.5%; 1 MPa

Set, %	25
Heat build-up	44ºC

30 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer	73	89
M300, MPa	7.5	
Tensile, MPa	21	13
Elongation, %	645	165

Compression set, %, 70 hrs, 100°C	76

NR 63

Elastomer: NR Durometer: 74
Application: OTR tread; Tear; low HBU

SMR	100	PEG 3350	1
150 m^2/g Silica	30	Sulfur	2
ISAF N231	30	MDB	1
100ºC aromatic resin	9	MBS	2
Aromatic oil	3	TBTD	0.2
Stearic acid	2		
TMQ	1		
HPPD	2		
Zinc oxide	4	Specific gravity	1.13

ODR cure rate, 138°C, T_{90} minutes	22
Mooney scorch, 130°C, T_5 minutes	20
Mooney viscosity, $ML_4$100	59

MG Trouser tear, 200 minute cure, 138°C, kN/m	
23°C	19
100°C	15
Goodrich flexometer: 93°C; 25%; 1.6 MPa (blow-out conditions)	
Static compression, %	24
Permanent set, %	16
Heat build-up, ºC	60
200 minute cure, 138°C:	
Durometer	74
M300, MPa	7.6
Tensile, MPa	23
Elongation, %	570
Pendulum rebound (G-H), %	
23°C	52.8
70°C	55.9
100°C	56.9

NR 64

Elastomer: IR Durometer: 74
Application: Low ML_4100, tan D; Bushing

IR 2200	100	Zinc oxide	3
Ciptane I	55	PEG 3350	1
Tall oil D30	3	Sulfur	3
Naphthenic oil	3	TBBS	3
Titanium dioxide	3	TMTM	0.3
ZMTI	1		
ODPA	1		
Stearic acid	2	Specific gravity	1.14

MDR cure rate, 155°C, T_{50} minutes	2.9
Mooney scorch, 121°C, T_5 minutes	21
Mooney viscosity, ML_4100	40

Stress/Strain	Original	700 hrs, 80°C
Durometer, 23°C	74	84
100°C	71	
M300, MPa	11	
Tensile, MPa	27	14
Elongation, %	555	270

MG Trouser tear, kN/m	8.6
PICO abrasion index	88
Compression set, 72 hours, 100°C, %	62
DMA dynamic modulus: 30°C; 1 Hz; 18 %	
E", MPa	1.7
E'	21
Tangent delta	0.082
Goodrich flexometer: 100°C, 22.5%; 1MPa	
Permanent set, %	7.0
Heat build-up, °C	19

Pendulum rebound (Z), %, 23°C	52
100°C	63
DeMattia cut growth, kc to 500%	9

NR 65

Elastomer: IR		Durometer: 76	
Application: Soling; Crepe color			

IR 2200	80	PEG 3350	2
SMR	20	Sulfur	2.5
HSR SS260	25	TMTD	1
150 m^2/g Silica	60	CBS	1.5
Naphthenic oil	30		
Stearic acid	1		
Phenolic A.O.	0.5		
Zinc oxide	3	Specific gravity	1.12

ODR cure rate, 146°C, T_{90} minutes	8
Mooney scorch, 121°C, T_5 minutes	10
Mooney viscosity, ML_4100	91
10 minute cure, 144°C:	
Durometer	76
M300, Mpa	3.9
Tensile, MPa	20
Elongation, %	670
NBS abrasion index	60

NR 66

Elastomer: NR		Durometer: 77	
Application: General purpose			

SMR CV60	100	Zinc oxide	5
150 m^2/g Silica	50	Sulfur	3
100ºC resin	5	TBBS	3
ODPA	1		
Stearic acid	2		
PEG 3350	1	Specific gravity	1.16

MDR cure rate, 150°C, T_{90} minutes	14
Mooney scorch, 130°C, T_5 minutes	30+
Mooney viscosity, ML_4100	80

Stress/Strain, 20 minute cure, 150°C:	Original	Aged*	Aged**
Durometer	77	82	80
M20, MPa	1.3	1.8	1.8
M300, MPa	7.1		
Tensile, MPa	27	19	10
Elongation, %	660	410	230

*aged 700 hrs, 85°C; **aged 170 hrs, 100°C

MG Trouser tear, kN/m	11
PICO abrasion index	74
Compression set, 70 hrs, 100°C, %	78
Pendulum rebound (Z), %, 23°C	56
100°C	66
Goodrich flexometer:100°C; 22.5%; 1 MPa	
Permanent set, %	14
Heat build-up, ºC	30
DMA dynamic modulus: 60°C; 1 Hz; 20% strain	
E", MPa	1.5
E'	21
Tangent delta	0.070
DeMattia cut growth, kc to 500%	9

NR 67

Elastomer: NR Durometer: 77
Application: Zinc-free, Tear; Hardness

SMR CV60	100	Zinc oxide	2	
220 m^2/g Silica	45	Sulfur	2.8	
100ºC resin	5	TBBS	3	
ODPA	1.5	HMT	2	
ZMTI	1.5	Specific gravity		1.13

MDR cure rate, 138°C, T_{50} minutes	6.4	
T_{90} minutes	18	
Mooney scorch, 121°C, T_5 minutes	15	
Mooney viscosity, $ML_4$100	57	
25 minute cure, 138°C:		
Durometer, 23°C	77	
100°C	72	
MG Trouser tear, kN/m, 23°C	29k	
70°C	52	
15 minute cure, 138°C:	Original	700 hrs, 90°C
Durometer	78	87
M300, MPa	7.2	
Tensile, MPa	32	7.8
Elongation, %	715	125
PICO abrasion index		81
DIN abrasion loss, ml		180
Pendulum rebound (Z), %, 23°C	59	
100°C	70	
Goodrich flexometer: 100°C; 22.5%; 1 MPa		
Permanent set, %	20	
Heat build-up, ºC	23	
DMA Dynamic modulus: 1 Hz	0°C	60°C
E", Mpa	1.42	0.88
E'	18.5	13.2
Tangent delta	0.077	0.067
Compression set, %, 72 hrs, 100°C	87	

NR 68

Elastomer: IR Durometer: 79
Application: Dynamic; mold flow; Bushing

IR 2200	100	Zinc oxide	3
150 m^2/g Silica	65	Stearic acid	2
Silane TESPT	5	PEG 3350	1
Tall oil D30	3	Sulfur	3
Naphthenic oil	3	TBBS	3
Titanium dioxide	3	TMTM	0.3
ZMTI	1		
ODPA	1	Specific gravity	1.15

MDR cure rate, 155°C, T_{50} minutes	4.3
T_{90} minutes	17
Mooney scorch, 121°C, T_5 minutes	28
Mooney viscosity, ML_4100	44

10 minute cure, 155°C:	Original	700 hrs, 80°C
Durometer, 23°C	79	90
100°C	77	
M300, MPa	14	
Tensile, MPa	26	10
Elongation, %	560	110

Pendulum rebound (Z), %, 23°C	53
100°C	69
Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent set, %	4.6
Heat build-up, °C	16
DMA Dynamic modulus: 1 Hz; 18%; 30°C	
E', MPa	34
E"	3.4
Tangent delta	0.100
PICO abrasion index	95
MG Trouser tear, kN/m	12
Compression set: 72 hrs. @ 100°C, %	70
DeMattia cut growth, kc to 500%	8

NR 69

Elastomer: NR/BR Durometer: 79
Application: Zinc-free; Fast cure; Soling; Tear

SMR	50	Zinc oxide	1
BR 1220	35	Sulfur	2
SBR 1205	15	MBTS	2
160 m^2/g Silica	55	HMT	2
Naphthenic oil	3		
MC wax	1		
Phenolic A.O.	0.3	Specific gravity	1.14

MDR cure rate, 155°C, T_{S2}	2.0
T_{90}	3.0
Reversion, 20 min	none
Mooney scorch, 121°C, T_5 minutes	12
Remilled, T_5 minutes	14
Mooney viscosity, ML_4100	125

12 minute cure, 155°	Original	170 hrs, 110°C
Durometer	79	
M300, MPa	5.4	
Tensile, MPa	21	5.7
Elongation, %	725	90

MG Trouser tear, kN/m	22
PICO abrasion index	87
DeMattia cut growth, kc to 500%	8
Compression set, %, 72 hrs, 100°C	89
Pendulum rebound (Z), %, 23°C	52
100°C	60

DMA Dynamic modulus: 1Hz; 15%:	0ºC	30ºC	60ºC
E' MPa	42	32	24
E"	4.8	4.5	3.1
Tangent delta	0.114	0.142	0.132

Goodrich Flexometer: 100°C; 22.5%; 1 MPa

Permanent set, %	23
Heat build-up, ºC	39

NR 70

Elastomer: NR Durometer: 79
Application: General; clay; Reversion resistant

SMR	100	Banbury 2	
150 m^2/g Silica	50	Sulfur	0.5
Hard clay	50	TBBS	2
100ºC resin	10	TBTD	2
Staybelite resin	5	PEG 3350	2
Stearic acid	2	Zinc oxide	5
ODPA	1		
		Specific gravity	1.23

	Original	Remilled*
ODR cure rate, 158°C, T_{S2} minutes	6.3	5.0
T_{90} minutes	11	9

* remilled after 14 days' shelf aging

ODR cure rate, 138°C T_{90} minutes	33
Mooney scorch, 121°C, T_5 minutes	25
Mooney viscosity, ML_4100	60

20 minute cure, 158°C:	
Durometer	78
M300, MPa	8.0
Tensile	18
Elongation, %	480

NR 71

Elastomer: IR/EPDM Durometer: 79
Application: Ozone resistance; Hose

IR 2200	75	Stearic acid	1
Nordel 1700	22	PEG 3350	1.5
BR 1203	3	Sulfur	2.5
150 m^2/g Silica	40	TBBS	1.2
Hard clay	75	DPG	0.6
Titanium dioxide	4	TMTM	0.3
100°C resin	10		
Tall oil	5		
Phenolic A.O.	1	Specific gravity	1.32

ODR cure rate, 150°C, T_{90} minutes	7
Mooney scorch, 121°C, T_5 minutes	16
Mooney viscosity, ML_4100	72
Garvey extrusion: Edge/surface	9A
% swell	24
Ozone exposure: 50 pphm; 38°C	
First cracking, hours, Static	188*
Dynamic	15*

*non-EPDM control 3 hours

12 minute cure, 150°C:	Stress/Strain, Original	96 hrs, 100°C
Durometer	79	81
M300, MPa	5.9	
Tensile, MPa	15	12
Elongation, %	580	430

Trouser tear, grooved, kN/m	22
PICO abrasion index	55
DeMattia cut growth, uncut,100°C cracked through at	50 kc

NR 72

Elastomer: NR Durometer: 81
Application: General purpose; Solid tire; Low HBU

SMR60CV	93	PEG3350	1
SBR 1904	15	Zinc oxide	5
Ciptane 255	50	Sulfur	3
100ºC resin	5	TBBS	3
Stearic acid	2		
ODPA	1	Specific gravity	1.16

MDR cure rate, 150°C, T_{90} minutes	9.7
Mooney scorch, 130°C, T_5 minutes	22
Mooney viscosity, ML_4100	59

15 minute cure, 150°C:	Original	Aged*	Aged**
Durometer, 23°C	81	85	84
100°C	69		
M20, MPa	1.6	2.2	2.0
M300, MPa	12		
Tensile, MPa	30	15	11
Elongation, %	615	265	200

*aged 700 hrs, 85°C; ** 170 hrs, 100°C

MG Trouser tear, kN/m	9.0
PICO abrasion index	95
Compression set, 70 hrs, 100°C	71%
Pendulum rebound (Z), %, 23°C	55
100°C	59

DMA dynamic modulus: 60°C; 1 Hz; 20% strain

E", MPa	2.3
E'	18
Tangent delta	0.125

Goodrich flexometer: 100°C; 22.5%; 1 MPa

Permanent set, %	5.6
Heat build-up	15ºC
DeMattia cut growth, kc to 500%	4

NR 73

Elastomer: IR Durometer: 80
Application: Bushing

IR 2200	100	Zinc oxide	3
150 m^2/g Silica	65	PEG 3350	1
Silane TESPT	5	Sulfur	3
Naphthenic oil	3	TBBS	3
Stearic acid	1	TMTM	0.3
ZMTI	1		
ODPA	1		
Titanium dioxide	3	Specific gravity	1.15

Tall oil (Acintol D30), phr	0	3
MDR cure rate, 155°C, T_{50} minutes	2.9	4.3
T_{90} minutes	19	17
Mooney scorch 121°C, T_5 minutes	14	28
Mooney viscosity, $ML_4$100	52	44
Durometer (20 min/155°C), 23°C	80	79
100°C	77	77
Spider Mold flow, mm	18	38

10 minute cure, 155°C:	Original	Aged*	Original	Aged*
M300, MPa	14		13	
Tensile, MPa	29	7.8	26	10
Elongation, %	535	105	560	110

*aged 700 hours, 80°C

MG trouser tear, kN/m	8.1	12
PICO abrasion index	114	95
Pendulum rebound (Z), %, 23°C	52	53
100°C	65	69
DMA dynamic modulus, 30°C		
E", MPa	3.0	3.4
Tangent delta	0.086	0.100
Goodrich flexometer: 100°C; 22.5%; 1 MPa		
Permanent set, %	5.4	4.6
Heat build-up, ºC	19	16
DeMattia cut growth, kc to 500 %	35	8

NR 74

Elastomer: NR/SBR Durometer: 85
Application: Heavy duty tread

SMR	80	Zinc oxide	4
SBR 1500	10	PEG 3350	1
SBR 1900	10	Sulfur	1
150 m^2/g Silica	30	MDB	1
65 m^2/g Silica	20	MBS (MOR)	2
ISAF N231	30	TBTD	0.3
100ºC aromatic resin	8		
Struktol MS40	3		
Stearic acid	2		
TMQ	1		
HPPD	2	Specific gravity	1.19

ODR cure rate, 138°C, T_{90} minutes	48
Mooney scorch, 130°C, T_5 minutes	30+
Mooney viscosity, ML_4100	64
200 minute cure, 138°C:	
MG Trouser tear, kN/m, 23°C	24
100°C	18
Goodrich flexometer: 93°C; 25%; 1.6MPa (blow-out conditions)	
Heat build-up, ºC	2
PICO abrasion index	124
Stress/Strain	
Durometer	85
M300, MPa	9.2
Tensile, MPa	18
Elongation, %	540
DeMattia cut growth, kc to 500%	100+
Skid index (Stanley London) on glass	
Wet textured	52
Dry smooth	103

NR 75

Elastomer: NR Durometer: 93
Application: Low HBU; rolls

SMR 5	70	Banbury 2	
HSR 1900	40	Zinc oxide	3
SBR 1502	10	Insoluble sulfur 80	13
150 m^2/g Silica	80	TBBS	4
100ºC resin	10		
Zinc methacrylate	2		
Stearic acid	2		
ZMTI	2		
PEG 3350	2	Specific gravity	1.24

MDR cure rate, 160°C, T_{90} minutes	7
Mooney scorch, 121°C, T_5 minutes	13
Mooney viscosity, ML_4100	64
Garvey extrusion rating, edge/surface	10A
15 minute cure, 160°C:	
Durometer, 23°C	93
100°C	85
M20, MPa	5.4
M100, MPa	12
Tensile, MPa	13
Elongation, %	120
Goodrich Flexometer: 100°C; 17.5%; 1 MPa	
Static compression, %	12
Dynamic compression	2.4
Drift	2.4
Set	0.0
Heat build-up	24ºC

CHAPTER 3

COMPOUNDING PRECIPITATED SILICA IN EMULSION SBR

3.1 INTRODUCTION

Among early applications of precipitated silica, those based on emulsion SBR were most important in developing general principles for compounding the new fine particle silica. During the early forties, calcium silicate had already established a significant position as a semi-reinforcing filler in non-black SBR compounds, principally those defined as “nuclear” soling. The introduction of precipitated silicas such as Hi-Sil®, Ultrasil®, and Vulcasil® produced a dramatic improvement in the wear resistance of these compounds. The formulas, based on a combination of SBR, silica, and high styrene resin, provided hitherto unavailable levels of abrasion and tear resistance. These benefits , together with the elimination of the floor marking deficiency of black soles, led to the gradual replacement of carbon black and clay in both hard and soft soling. The translucent nature of silica also made it possible to replace natural rubber crepe soling with similar appearing compounds based on SBR. Beyond the soling and footwear markets, silica’s adaptability to compounding in color made it a valuable new resource in belting, hose, and other mechanical goods products.

3.2 SILICA AND CARBON BLACK

In view of carbon black's position as the pre-eminent filler in the rubber industry, a compounding discussion of precipitated silica or any reinforcing filler is greatly facilitated by comparison with a comparable grade of black. Selection of an equitable basis of comparison is a complex matter. Should the choice of filler grades be based on filler particle size (surface area) or on a property of the cured compound? This chapter provides examples of both approaches.

Since the primary particle size of precipitated silicas is generally smaller than that of blacks, it is necessary to select one of the finest black grades, N121, to make an equal size comparison to a medium reinforcing (150 m^2/g $N_2SA/130$ m^2/g CTAB) silica. Particle size is indicated by CTAB surface area measurements in Table 3.1. In this comparison of comparable surface area silica and black, the usual silica feature of enhanced tear resistance is not apparent. However, heat resistance, in terms of aged elongation, is still improved. The relationship of silica to black in terms of the major black superiority in abrasion resistance, 300% modulus and low flexometer set is typical. These properties can all be related to stronger filler-polymer bonding with carbon black. As it happens, these data can also serve as an equal compound hardness example.

Table 3.1 Silica and Black; Equal Surface Area Comparison in SBR

	Silica	**SAF Black**
CTAB surface area, m^2/g	130	121
ODR cure rate, 150^oC, T_{90} minutes	13	29*
Mooney Viscosity, ML_4100	123	68
Durometer hardness	73	74
M300 modulus, MPa	3.3	12
Elongation, %	650	500
Aged elongation, 340 hrs, 100°C, %	330	150
MG trouser tear, kN/m	18	16
PICO abrasion index	60	145
Goodrich Flexometer set, %	7.7	3.1
Other ingredients: SBR 1502-100; filler-50; resin-10; HPPD-2; Stearic acid.-2; Zinc Oxide-3; Oil-3; Sulfur-2; MBS-1.5; TMTM-0.6; PEG-1.5		
* to maintain adequate scorch safety TMTM omitted		

A comparison based on equal set properties presents a somewhat altered picture in Table 3.2.

Table 3.2 Silica and Black; Equal Set and Hardness Comparison

	130 m^2/g CTAB Silica	**ISAF N220 Black**
Filler Content, phr	50	45
PEG 3350	2	0
TBBS	2	1
TCS (Curite 18)	0.7	0
Compression set, 70 hrs, 100°C, %	52	57
Durometer hardness	69	67
MDR cure rate, 150°C, T_{90} minutes	15	27
MG trouser tear, kN/m	12	17
M300 modulus, MPa	4.2	8.9
Elongation, %	680	690
Aged elongation, %	120	45
Pendulum rebound, 100°C, %	61	59
DMA dynamic modulus: 30°C; 1 Hz		
Storage modulus, E', MPa	18.2	11.4
Tangent delta	0.141	0.172
Other ingredients: SBR 1502-100; resin-10; Stearic acid-2; ZnO-3; ZMTI-2; Sulfur-2		

The acceleration in the silica compound was selected to attain a match to the compression set of the black control. Compression set is considered to be a representation of sulfur crosslink distribution in terms of mono-, di- and polysulfide bonds. Many silica acceleration systems produce a majority of polysulfide crosslinks and, thereby, high set values. However, achieving the low set objective here was accompanied by a significant loss in trouser tear strength. Fortunately, superior heat resistance is retained in the silica compound. Reduced tangent delta and a slight margin in hot rebound, despite higher dynamic modulus, foretells the eventual use of silica in achieving lower rolling resistance in passenger tire treads. It should be noted that no silane coupling agent is present in the silica compound.

Comparisons between low surface area silicas (35 m^2/g N_2SA) and thermal black also show advantages in processing, heat resistance and tear strength in mechanical goods formulas where thermal black has been replaced by these silicas. An equal hardness comparison at 60 phr filler in a blend of SBRs 1500 and 1608 includes the significant property variations seen in Table 3.3.

Table 3.3 Silica and Black; Low Surface Area Grades

		35 m^2/g Silica	**MT Black**
Garvey die extrusion:	Rate, m/min	1.5	1.1
	Swell, %	0.09	0.13
	Mill shrinkage, %	35	50
Elongation, %:	Original	600	500
	Aged, 96 hrs, 100°C	400	250
Trouser tear, kN/m:	Original	10.4	4.9
	Aged, 96 hrs, 100°C	4.9	2.2

None of the silica compounds in these and related discussions provide abrasion indices which approach those of the black controls. Abrasion parity can be attained only with mercapto silane coupling or zinc-free curing systems in solution polymers. The use of silica to improve tear strength in an agricultural tire tread is illustrated in Formulary compound SBR 22.

3.3 CURE SYSTEMS: ACTIVATION WITH GLYCOLS

Cure systems for emulsion SBR compounds are particularly influenced by the silica-zinc reaction which removes soluble zinc from its normal accelerator activating function and produces compounds of inadequate crosslink density. The conventional remedy for this problem is to buffer the silica surface with glycols or amine derivatives. These materials include polyethylene glycol (PEG 3350), diethylene glycol, and triethanolamine. Amine antioxidants and antiozonants inadvertently perform a similar function. A summary of the major glycol effects appears in the graphs of Figure 3.1a through 3.1d.

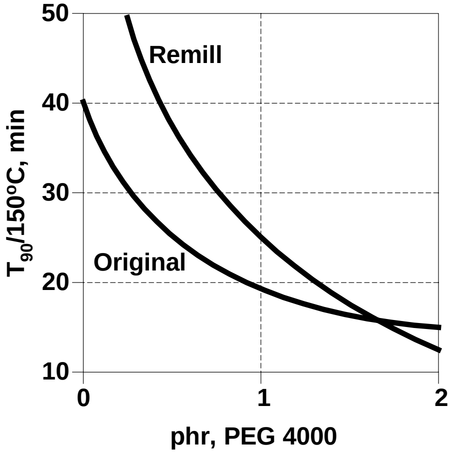


Figure 3.1a. ODR 90% Cure at 150^{o}C

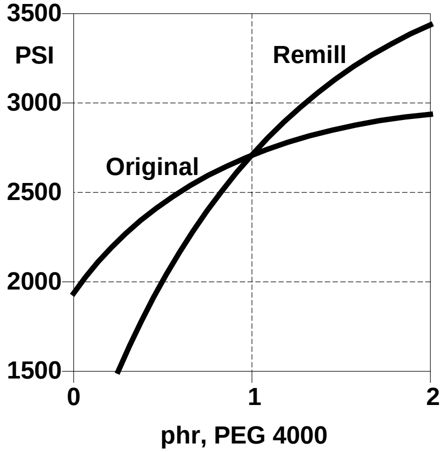


Figure 3.1b. Tensile Strength

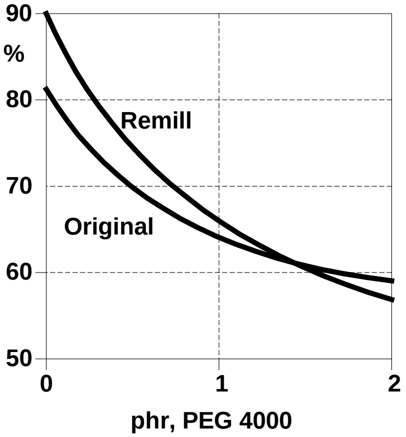


Figure 3.1c. Compression Set 70 Hours at 100°C

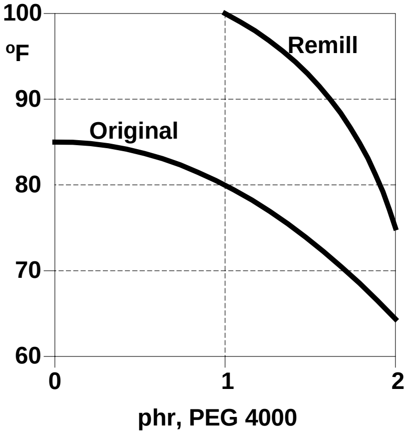


Figure 3.1d Flexometer Heat Build-Up

Cure rate and vulcanizate properties for compounds which contain 0, 1, or 2 phr of polyethylene glycol are noted for both original and remilled stocks. The wide divergence between freshly mixed and remilled non-glycol batches illustrates the importance of a buffer such as PEG in factory operations where variability in cure rate and other properties cannot be tolerated. In many cases, lack of a glycol buffer will prevent a shelf aged stock from ever attaining adequate cured properties, This divergence in crosslinking behavior is due to a loss in silica free water content and its buffering ability after remilling. The influence of water in silica reinforced SBR and other elastomers was discussed at length in Chapter 1.

For both original and remilled compounds the addition of 1 and 2 phr PEG produces large increases in cure rate and tensile strength as well as substantial and desirable reductions in set and heat build-up. Abrasion resistance and hardness show little or no change.

Significant differences between the action of DEG and PEG (2 phr) in a blend of emulsion and solution SBRs reinforced with 50 phr 160 m^2/g N_2SA silica are summarized in Table 3.4. Polyethylene glycol is obviously superior in producing more effective crosslinking; diethylene glycol, because of its smaller size, is a better barrier to silica-silica structure formation. and thus a superior viscosity reducer. Triethanolamine (TEA) reacts much the same as PEG but, like DEG, is more volatile and subject to slow cure rates after remilling.

Table 3.4 Cure Activation by Glycols; DEG and PEG

	DEG	**PEG**
MDR cure rate, 150°C, T_{50} minutes	6.6	5.2
MDR crosslinks, dN-m	26	28
Mooney viscosity, ML_4100	68	84
Durometer hardness	59	67
M300 modulus, MPa	3.2	4.4
Pendulum rebound, 100°C, %	58	63
Color	lt red	tan
Abrasion and tear resistance	no change	

3.4 CURE SYSTEM: ZINC OXIDE ACTIVATION

The majority of commercial silica reinforced elastomer compounds contain 3 to 5 phr zinc oxide for accelerator activation. There are, however, certain advantages to be realized at concentrations below 3 phr. In Table 3.5, significant property effects are noted over the zinc oxide range of 0.5 to 5 phr. The property changes noted in Table 3.5 are, as in most compounding studies, based on both crosslinking and silica-polymer bonds. The increase in cure rate and MDR delta torque at higher zinc concentrations correlates well with reductions in set, elongation and trouser tear, and rising 300% modulus, changes which reflect not only more crosslinks but also fewer polysulfide species. A zinc oxide concentration of 10 phr (not shown) produces the expected improvement in heat resistance in the form of an additional 100 to 200% aged elongation. No other significant processing or vulcanizate changes occur.

Silica-polymer bonding is influenced by increased amounts of soluble zinc attached to the silica surface. The result of this bond interference is reduced abrasion resistance (PICO values are more revealing than DIN here). A similar interference with silica-silica structure produces lower viscosities at higher zinc oxide levels.

Table 3.5 Cure Systems: Zinc Oxide Activation

Zinc oxide (Banbury 1)	0.5	0.8	1.3	2.0	3.0	5.0
MDR cure rate, 150°C						
T_{50} minutes	12	8.1	7.8	7.9	7.9	8.0
T_{90} minutes	27	12	10	11	11	11
MDR crosslinks, dN-m	20	19	22	25	27	27
Reversion, dN-m, 60 min	(+)	0.5	1	1	1	0.6
Compression set, 70/100°C, %	88	78	64	53	47	50
Mooney viscosity, MS121°C	46	41	35	26	23	23
Durometer: 23°C	65	67	68	68	68	68
100°C	55	58	60	63	63	64
M300 modulus, MPa	3.0	3.0	3.7	4.2	3.9	4.3
Elongation, %	890	895	810	735	700	665
Aged* elongation, %	285	400	400	400	375	350
MG trouser tear, kN/m	33	25	14	10	11	9.2
PICO abrasion index	62	61	57	58	51	49
Pendulum rebound,100°C,%	49	52	55	58	61	61

*700 hours, 90°C

Other ingredients: SBR1502-100; Hi-Sil 210-50; Resin-10; oil-5; ODPA-1; Stearic acid-2; PEG-1.5; Sulfur-2; MOR 1.5; TMTM-0.6

Compounds in this study were also tested for "pilling", the appearance of particles clinging to abraded surfaces. Zinc oxide concentrations below 2 phr show considerable occurrence of this phenomenon. This may be taken as a typical example of flow in a viscoelastic material.

Light transmission of translucent compounds is another property for which it is useful, beyond its commercial application in footwear, to follow the reactions of zinc oxide in silica reinforced SBR. Generally, the bonding of soluble zinc to silica silanols increases light transmission, sometimes to the point of transparency. In the Figure 3.2 plot of transmission versus zinc oxide content a point of maximum transmission appears at 2 phr. The transmission loss above this point is evidently due to the presence of more unsolubilized and unreacted zinc, a significant contributor to opacity.

Lower transmission at low concentrations indicates that there is insufficient soluble zinc to react fully with sulfur and accelerators.

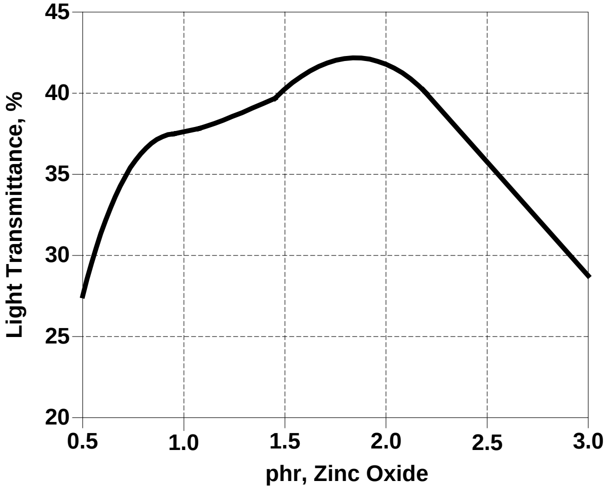


Figure 3.2. Effect of ZnO on Light Transmittance

What is the result of a complete omission of zinc oxide? In one of the early processing studies of zinc concentration, a comparison of zinc oxide at 0 and 3 phr, in Table 3.6, provided an interesting prelude to later studies of zinc-free curing systems . Elimination of zinc oxide from emulsion SBR is possible only through use of accelerators which act somewhat independently of soluble zinc complexing. In this case, the cure, based on MBTS and DOTG, is adequate to perceive the enhanced reinforcement gained from zinc elimination. Without zinc interference with silica-SBR bonding, both modulus and tensile are significantly improved. This approach to improved silica reinforcement is discussed at length in the chapters devoted to solution polymers.

The obvious importance of concentration in respect to soluble zinc might lead to a prediction that zinc oxide mixing order would also be a significant source of property variation. The comparison in Table 3.7 of first versus second stage Banbury addition in the formula noted in Table 3.6 confirms the importance of mixing procedures. Variation in rubber compound properties can best be explained in terms of their relation to crosslinking or filler-polymer bonding or filler-filler structure. In this case, all three mechanisms are involved.

Table 3.6 Effect of Omission of Zinc Oxide

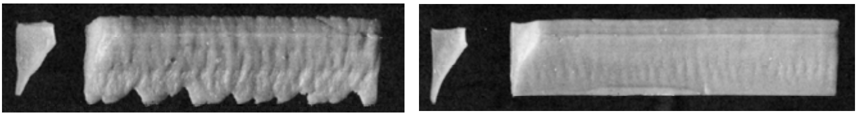
Zinc oxide, phr	3	0
Mooney viscosity, ML_4100	88	99
Mooney scorch, 138C, T_5 minutes	10	6.8
Shrinkage after milling, %	33	27
Durometer	65	64
M300 modulus, MPa:		
20 min/140°C	3.1	4.2
40 min/140°C	3.7	4.5
60 min/140°C	3.7	4.5
Tensile	16	23
Elongation, %	600	630
Other ingredients: SBR 1502-100; Hi-Sil 210-40; oil-5; ODPA-1; PEG-1.5; Sulfur-2.0; MBTS-0.8; DOTG-1.2		

Table 3.7 Zinc Oxide: First or Second Stage Addition

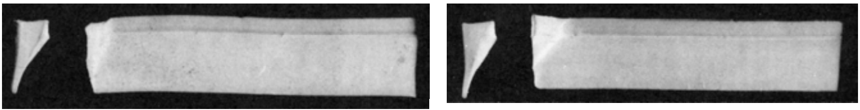
	A	**B**
Zinc oxide, 2 phr: Banbury stage	1	2
MDR cure rate, 150°C		
T_{50} minutes	8.0	10.3
T_{90} minutes	11	14
MDR crosslinks, dN-m	21.3	19.3
Mooney viscosity, ML_4100	51	98
Compression set, 70 hrs, 100°C, %	64.7	60.1
Durometer hardness	65	68
M300 modulus, MPa	2.2	3.1
MG trouser tear, kN/m	25	23
PICO abrasion index	52	56
Goodrich flexometer blow-out	8'	12'
Pendulum rebound (Z), %, 23°C	34	38
100°C	50	51

Addition of zinc oxide in Banbury 2 involves a shorter period of reaction with stearic acid and silica, and a lower temperature (110°C in Banbury 2 versus 130°C in Banbury 1). As a result there is less zinc modified silica in second stage addtion and thus stronger silica-polymer bonding. Evidence for this includes increased durometer, modulus and rebound resilience as well as improved resistance to abrasion and flexometer blow-out. Actually the major change arising from second stage addition is a 100% viscosity increase. High compound viscosity is characteristic of silica not reacted with zinc or other surface modifier. This silica structure effect varies with polymer type, and is discussed in each chapter.

Since there is a balance between the amounts of zinc on silica and zinc available for accelerator complexing, second stage addition provides more zinc for improved crosslinking, in terms of speed and density. This improvement produces increased modulus, lower compression set (fewer polysulfide crosslinks), and better dynamic properties. The effects of zinc oxide addition on processing properties, in addition to the viscosity change noted above, are well illustrated in Figure 3.3.



ZnO with Silica **ZnO after Silica**



ZnO 2nd Stage **High Temperature ZnO 2nd Stage**

Figure 3.3 ZnO Addition and Temperature Effect: Garvey Die Extrusion

Here, extrusion properties in terms of rugosity and swell are drastically influenced by the time of zinc oxide addition. Early addition, with attendant long contact time with silica, almost completely eliminates silica structure effects and produces poor edge/surface ratings along with extensive extrudate swelling. The low viscosity values in Table 3.8 correlate well with poor extrusion performance.

Table 3.8 Zinc Oxide Addition, Effects on Compound Viscosity

	Viscosity, $ML_4$100°C	
Zinc oxide addition:	**SBR 1708**	**SBR 5102**
Banbury 1 with silica	59	42
Banbury 1 after silica	90	40
Banbury 2 (or mill)	110	70
Mill mixed, ZnO last	110	140

The reaction of soluble zinc with silica is subject to influence by addition order and also by mixing temperature. Comparison of the pre-cure portions of rheometer curves in Figure 3.4 illustrates the effect of first stage mixing temperature over a range of 140 to 185ºC. At lower temperatures with first stage zinc addition we see pronounced agglomeration effects, in terms of a slight viscosity increase followed by a relatively high minimum. At 165ºC where the silica network has been partially destroyed by zinc intervention, these phenomena disappear. Mixing temperature shows little influence on rheology when zinc oxide or zinc octoate is withheld until the second stage. As noted above, the major effect of second stage addition is a substantial increase in viscosity accompanied by reduced shrinkage and nerve. Cure rate is faster for second stage addition. At temperatures of 185ºC and above, cure retardation occurs when loss of silica free water allows greater amounts of soluble zinc to react with silica silanols and thus become unavailable for cure activation. By the same mechanism, high mixing temperatures lead to increased compression set.

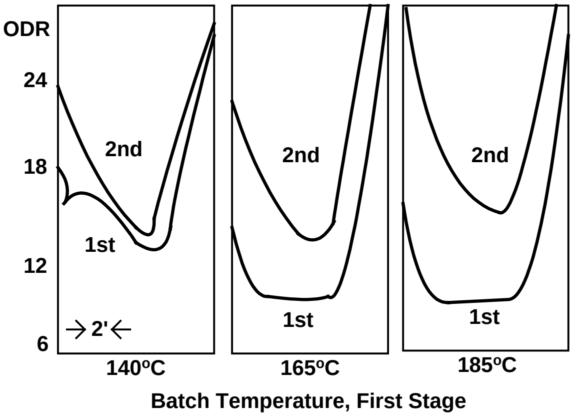


Figure 3.4 Zinc Addition and Mixing Temperature: Rheometer Curing

Some vulcanizate properties respond to both mixing order and temperature. Trouser tear strength offers the most striking example, as seen in Figure 3.5.

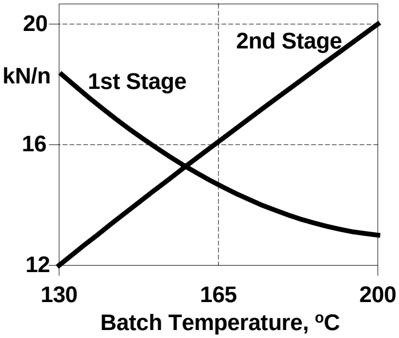


Figure 3.5 Zinc Addition and Mixing Temperature: Trouser Tear

In this case, tear strength response to temperature is completely reversed when zinc is withheld from the first Banbury stage. Similar trends, although minor in extent, are seen in abrasion indices and cut growth resistance. Stress-strain and flexometer heat build-up properties generally show no significant dependence on either mixing order or batch temperature. However, a slight but definite increase in 100 to 500% extension modulus occurs with second stage zinc addition. Stress relaxation measurements have failed to reveal any variation related to zinc addition or mixing temperatures.

3.5 CURE SYSTEM: MAGNESIUM OXIDE ACTIVATION

The addition of magnesium oxide to a normal zinc oxide cure system produces a strong activating effect. Since magnesium oxide alone is not effective, this appears to be a classic case of synergism. Significant property effects are noted in Table 3.9.

Table 3.9 Cure Activation by Magnesium Oxide

Zinc oxide	5	5	0
Magnesium oxide	0	3	6
MDR cure rate, 150°C, T_{90} minutes	23	17	40
Mooney scorch, 135°C,T_5 minutes	20	16	23
Mooney viscosity, ML_4100	25	19	76
Compression set, 70 hrs,100°C, %	49	30	74
Elongation, %	640	580	
Elongation, aged 70 hrs, 121°C, %	340	500	
Goodrich flexometer: 100°C; 22.5%; 1 MPa			
Permanent set, %	12	4	20
Heat build-up, °C	42	33	43

The combination of magnesium and zinc oxides provides significant improvement in crosslink related properties: cure rate, set, heat build-up and aging resistance. The extent of such changes in other situations depends on the presence of other activators and curatives. For example, higher amounts of glycols, thiurams or sulfur mitigate the magnesia effects. On the other hand, magnesia can replace polyethylene glycol with no loss in cure rate and reduced compression set.

The processing behavior of magnesia activated SBR compounds can, in certain circumstances, be less than satisfactory. Severe mill sticking occurs with rosin acid SBR types such as 1500 and 1502. Fatty acid 1503 compounds are free from sticking. As with zinc oxide, addition order can influence properties. Banbury 2 addition provides faster cure rate and increased tensile, but these are accompanied by an increase in compression set.

3.6 CURE SYSTEM: LEAD OXIDE (LITHARGE) ACTIVATION

Before toxicity considerations eliminated lead compounds from compounding use, litharge was used, in combination with zinc oxide and alone, as an effective activator for silica reinforced compounds. With zinc, the synergistic effects were similar to those of magnesia. Increased modulus and lower heat build-up were obtained, although compression set was unchanged. Trouser tear, tensile and scorch safety were reduced. Unlike magnesia, litharge alone produced a satisfactory state of cure and was uniquely effective in providing low water absorption.

3.7 CURE SYSTEM: STEARIC ACID

The primary function of stearic acid, normally 1 to 2 phr, is its reaction with zinc oxide to supply a reactive form of zinc for accelerator complexing. Higher concentrations (8 phr) produce minor reductions in viscosity, hysteresis and scorch safety. Swelling in 70ºC water is substantially reduced from 15% to 8% at the 8 phr level in SBRs 1502 and 1509 (but not 1500). In a magnesia-zinc activated system, increased stearic acid at 6 phr was, except for reduced tensile, without effect.

3.8 CURE SYSTEMS: PRIMARY, SECONDARY ACCELERATORS

Early cure systems for silica compounds contained thiazole-guanidine (MBTS-DPG) combinations, accelerator types which were less sensitive to zinc concentration than dithiocarbamates and thiurams. In later work it was found that combinations of sulfenamides and thiurams, at lower concentrations, provided considerable improvements in cure rate, scorch safety, crosslink density and vulcanizate properties. Cure and scorch characteristics of a medium gravity soling formula, in Table 3.10, are typical.

Table 3.10 Acceleration Systems

	A	**B**
MBTS	1.2	--
MBS (MOR)	--	0.6
DPG	1.5	0.6
TMTM	0.2	0.6
ODR cure rate, 165°C, T_{90} minutes	13	8.0
Mooney scorch, 135°C, T_5 minutes	13	26

As indicated above, TMTM (tetramethylthiuram monosulfide) acts to provide a very efficient rheometer cure curve with long scorch time and short 90% cure time, both accomplished with a 40% reduction in accelerator content and cost. Other thiurams, such as DPTH, and dithiocarbamates also increase cure rate, but with considerable sacrifice in scorch safety. A contour curve study in a passenger tread base formula which contained 15 phr silica compared the cure rate and vulcanizate property influence of TMTM and mercaptosilane A189 over a range of 0.2 to 0.7 phr. The two variables had equal influence on all properties except abrasion resistance. At additions of 0.5 phr the PICO abrasion indices were 115 for TMTM and 130 for mercaptosilane, a gap which widens at higher concentrations of both silane and silica. Since abrasion resistance is determined primarily by filler-polymer bonding (as well as filler particle size), the lack of accelerator impact is not surprising.

3.9 CURE SYSTEMS: SINGLE ACCELERATORS

The most basic and uncomplicated approach to cure system evaluation is to study single accelerator effects over a wide range of concentrations. The purpose of such studies is not to supply formula recommendations for specific service conditions, but to provide the compounder with basic information of the characteristics of each accelerator alone. Plots of compound properties versus single accelerator concentration reveal relative reactivity as well as accelerator solubility in SBR. The materials in this study represent several classes of accelerators and include those listed in Table 3.11.

Table 3.11 Evaluation of Single Accelerators

DPG	Diphenyl guanidine
DETU	Diethyl thiourea
MBTS	Benzothiazole disulfide
MBS	Morpholino thio benzothiazole
TBBS	Tertiarybutyl benzothiazole sulfenamide
TBTD	Tetrabutyl thiuram disulfide
TCS (OTOS)	Thiocarbamyl sulfenamide
TMTM	Tetramethyl thiuram monosulfide
ZBDC	Zinc dibutyl dithiocarbamate
ZEPDC	ethylphenyl dithiocarbamate
Formula: SBR 1502-100; Hi-Sil 255-50; CI resin-10; S.A.-2; ZMTI-2; PEG 3350-2; ZnO-3; Sulfur-2; Accelerator-1 to 4	

Plots of crosslinking delta torque and cure rate, in Figures 3.6 and 3.7, show wide variation in both rate and extent of crosslink formation. TCS is the most effective in respect to crosslinks and second only to TMTM in the rate at which they are produced. At the lowest concentration, 1 phr, only

DPG and DETU are noticeably less efficient. Most interesting is the anomalous behavior of ZBDC: unchanging crosslinks at all concentrations, and a precipitous change in cure rate at 2 phr. The relatively low compression set values provided by ZBDC offer an explanation in terms of an increase in mono- and disulfide crosslinks, which produce lower rheometer torque and modulus than do the polysulfide varieties.

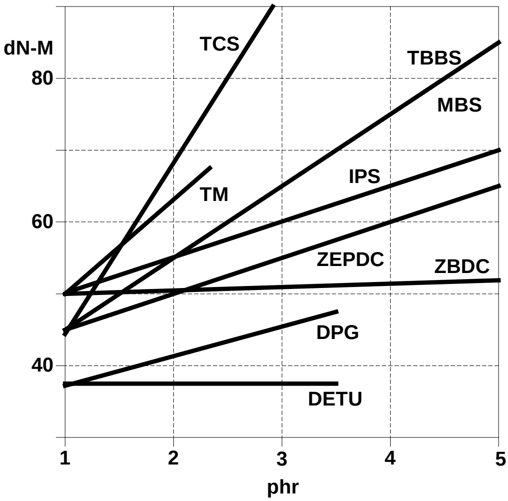


Figure 3.6 Effect of Accelerator Concentration on Crosslinking

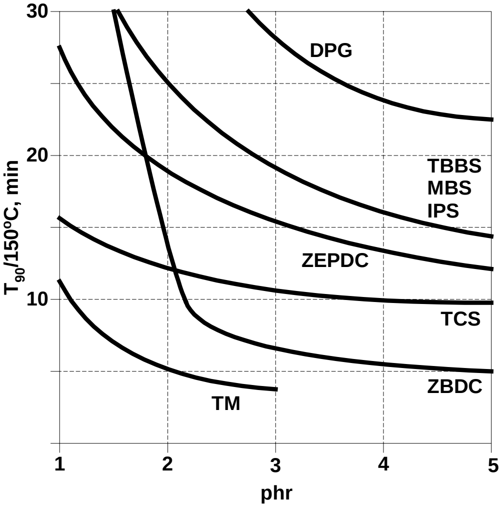


Figure 3.7 Effect of Accelerator Concentration on Cure Rate

In contrast to ZBDC, the cure rate and crosslinking behavior is reversed for TCS. A sharp increase in crosslink content between 1 and 2.5 phr has little or no effect on cure rate or scorch safety which remain almost unchanged over the 1 to 4 phr range. This kinetic stability can possibly relate to the presence of the sulfenamide structure in TCS. In any case, the extremely high crosslink content must involve a correspondingly high percent of mono-sulfide links, a supposition which is confirmed by the lowest set and trouser tear values of any accelerator.

As seen in Figure 3.8, the lowest compression set values are those for TCS and TMTM, indicating that these accelerators are the most efficient in eliminating the polysulfide crosslinks normally associated with silica reinforced SBR. However, Figure 3.9 shows that scorch safety is questionable with TMTM above 1 phr, and with ZBDC above 2.5 phr.

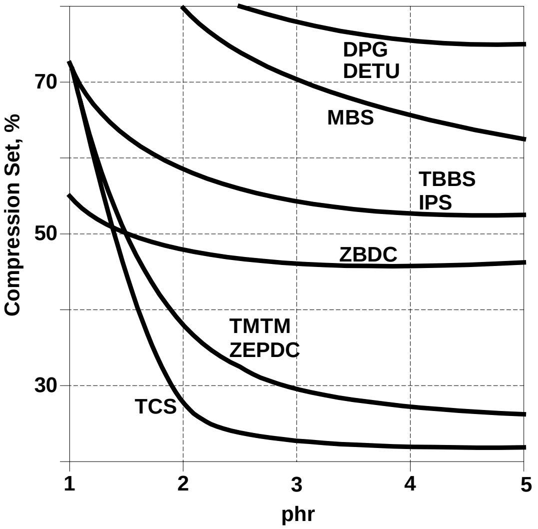


Figure 3.8 Effect of Accelerator Concentration on Compression Set

A complete summary of TCS and ZBDC accelerated compounds together with an HAF black control appears in Formulary compound SBR 25A. In this equal hardness, comparable crosslink comparison with HAF, set and trouser tear properties favor the silica compounds with either accelerator, and other properties, with the usual exception of abrasion index, are comparable.

Perhaps the major question here and in any comparison of silica and black compounds is that of processing safety. In this case, T5 scorch values at 130°C indicate a 2 to 1 safety margin in favor of the HAF compound. It is apparent that scorch safety comparable to that of carbon blacks is not likely to be achieved with the dosage of single accelerators required to attain efficient crosslinking. The alternative is the usual use of primary and secondary accelerator combinations which allow greater processing safety. As noted above, the value of these studies of single accelerators is to reveal the basic characteristics which can be considered in selecting the primary and secondary materials. A Formulary example of the result of such selection can be seen in compound SBR 25, where a combination of MBS and TMTM has produced a compound with excellent safety together with a superior combination of trouser tear strength, low set, high resilience and low heat build-up.

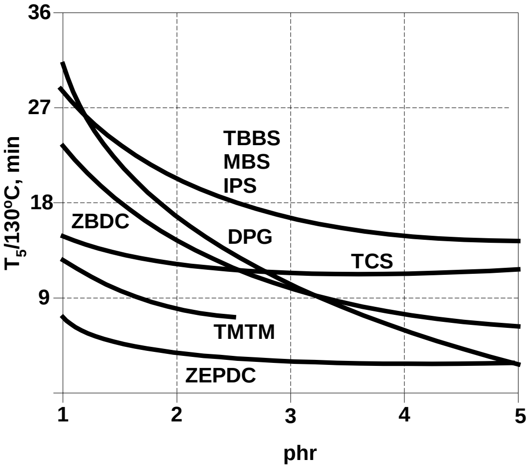


Figure 3.9 Effect of Accelerator Concentration on Scorch Delay

3.10 CURE SYSTEMS: SULFUR CONCENTRATION

Reduced sulfur concentrations in the 0 to 0.6 phr range are used to attain superior heat resistance, through an increase in monosulfide crosslinks. The evaluation in Table 3.12 is based on a rosin acid SBR, 1500, with sulfur donor TMETD and sulfenamide MBS (MOR). Optimum heat resistance, in terms of aged elongation and tensile, is attained at sulfur concentrations of 0.3 to 0.6 phr. This range also provides the lowest set and heat build-up values. Among other property relationships, those involving flexometer compression, DeMattia cut growth and tear are subject to significant change as sulfur content increases. Although durometer readings remain essentially unchanged, flexometer compression stiffness, static and dynamic, clearly responds to these relatively small sulfur additions. This lack of correlation with hardness suggests that, in similar situations, flexometer compression data would be more predictive of rheological behavior than would durometer hardness. Although the DeMattia test for cut growth is recognized to be dependent on hardness, increased modulus (higher crosslink density) and reduced trouser tear at higher sulfur contents are also in large part responsible for the precipitous fall in cut growth resistance.

Table 3.12 Sulfur Concentration in a Sulfur Donor Cure System

Sulfur, phr	0	0.15	0.3	0.6
ODR cure rate, 150°C; T_{90} minutes	17	16	15	12
Mooney scorch, 135°C; T_5 minutes	12	12	11	10
Durometer hardness	70	70	70	72
M300 modulus, MPa	1.2	1.7	2.3	3.1
Tensile, MPa	15	18	19	21
Elongation, %	970	800	750	650
Aged 170 hrs, 135°C				
Tensile, MPa	4.2	4.8	8.6	8.0
Elongation, %	90	100	200	130
MG Trouser tear, kN/m	19	18	17	13
Compression set, 70 hrs, 100°C	38	22	18	17
Goodrich flexometer:				
100°C; 22.5%; 1 MPa				
Static compression, %	40	31	25	18
Dynamic compression	18	19	15	9
Permanent set	10	6.1	5.2	35
Heat build-up, ºC	39	39	36	19
DeMattia cut growth, kc to 500%	200	120	60	17
Other ingredients: SBR1500-100; Hi-Sil 210-50; 100C resin-20; Stearic acid-4; ZnO-4; TMQ-1; HPPD-2; PEG 3350-2; MBS-1.5; TMETD-2.5				

Since the data above are based on the thiuram sulfur donor TMETD it is of interest to examine, in Table 3.13, a comparison of other donors in the same base formula with sulfur at 0.3 phr . Obviously, DTDM and MDB are incapable of producing an adequate state of cure, even with the accompaniment of MBS. This is not surprising in view of their lack of the dithiocarbamate accelerating unit. TMTD (not shown) at 2.5 phr reproduces the properties found with TMETD. Unfortunately, the fastest material, DPTH, entails questionable scorch safety. The sulfur donor TCS at 2.5 phr (not shown) is somewhat less effective than TMETD, but with silane treated silica (Ciptane), provides excellent trouser tear resistance and more than adequate dynamic properties (Formulary compound SBR 16).

At the 2.5 phr level of TMETD, the MBS present in all these compounds can be omitted or reduced with a slight loss in scorch safety. Formulary compound SBR 24 describes the superior aging performance and other properties of the TMETD compound.

Table 3.13 Sulfur Donor Accelerators Compared

	DTDM		**MDB**		**TMETD**		**DPTH**	
Sulfur donor content, phr	1.5	2.5	1.5	2.5	1.5	2.5	1.5	2.5
ODR 150°C, T_{90} minutes	29	35	29	30	19	16	12	10
Scorch 135°C, T_5 minutes	21	23	20	18	15	12	8.3	5.9
Durometer	59	57	58	55	59	64	60	62
Tensile, MPa	11	13	13	10	19	22	17	24
Compression set, %	72	68	67	59	32	25	39	28
Flexometer HBU,ºC	74	49	86	51	44	39	40	25

3.11 PLASTICIZATION

Reducing the viscosity of silica reinforced SBR is accomplished by one or both of two distinct methods: 1. Use of oils and resins to plasticize the polymer; 2. Use of additives to modify the silica network structure.

It is well known that mineral filled SBR compounds plasticized with resins (natural, aromatic or aliphatic), incur less property degradation than those plasticized with petroleum oils, esters and other materials. Thus, coumarone-indene resins have been used for many years in soling compounds where the silica content may be as high as 60 phr. The example in Table 3.14 demonstrates the processing and reinforcing advantages of an aromatic resin, 20 phr cumar MH, in SBR reinforced with 50 phr of 150m^2/g N_2SA silica.

Table 3.14 Effect of Plasticization: Resin vs Oil on Compound Properties

Plasticizer, 20 phr	**100°C CI resin**	**Aromatic oil**
ODR, 160°C, T_{90} minutes	5.5	5.0
Mooney viscosity, $ML_4$100	100	85
Garvey die Extrusion	smooth	rough
Durometer hardness	68	64
M300 modulus, MPa	4.2	3.8
Tensile, MPa	27	16
Elongation, %	680	600
Trouser tear, grooved, kN/m	15	10
PICO abrasion index	75	63
Flexometer HBU,ºC	37	36

Notwithstanding the slight difference in hardness and viscosity, the improvement with resin plasticization in extrusion behavior and in reinforcing properties such as tensile, tear and abrasion is quite impressive. Hydrogenated rosin and rosin esters are also effective in viscosity reduction with minimal effect on reinforcement. An interesting aspect of rosin related behavior is seen in Table 3.15 in a comparison of SBR polymers based either on fatty acid (1503) or rosin acid (1500) emulsifiers.

Table 3.15 Plasticization: Polymer Emulsifier Effects

SBR grade	1503	1500
Mooney viscosity, ML_4100	92	81
Extrusion swell, %	31	25
M300 modulus, MPa	2.8	2.4
MG trouser tear, kN/m	9.5	12
Compression set, 70 hrs, 100°C, %	29	36

Formation of zinc resinate from the rosin in SBR 1500 evidently provides more plasticizing activity than zinc stearate from 1503, and at the same time interferes to a greater extent with crosslinking activity. As a result, both set and tear increase and 300% modulus falls in the SBR 1500 compound.

The second method of plasticizing silica reinforced SBR involves a de-agglomeration of the silica network structure rather than a softening of the polymer. Additives to produce this type of viscosity reduction are either soluble zinc compounds or amine derivatives such as HMT (hexamethylenetetramine). Magnesium oxide performs a similar function but produces a fairly severe loss in reinforcement. SBR1500 compounds (55 phr silica, 15 phr resin; cure system of sulfur 2.5, MBS 0.8, and TMTM 0.5 phr, with zinc oxide in second stage) undergo significant viscosity and extrusion swelling changes with zinc and amine additives as shown in Table 3.16.

Table 3.16 Plasticization: Zinc and Amine Additives

	A	**B**	**C**	**D**
Additive type	None	Zn octoate	Zn methacrylate	HMT
Content, phr	--	3	0.5	0.5
Banbury stage	--	1st	2nd	2nd
Viscosity, ML_4100	91	67	61	77
Original	81	57	52	68
Remilled				
Garvey extrusion swell, %	33	44	52	33
Durometer hardness	73	71	70	75
M300 modulus, MPa	2.8	2.5	2.6	3.1

Cure rate and vulcanizate properties not listed above were not significantly affected by the additives. As the silica network forces are blocked by the additives, viscosity falls and swell increases. Among the three additives described above, zinc methacrylate is most effective; a 0.5 phr addition reduced Mooney viscosity by 30 points. For both zinc methacrylate and HMT, point of addition affects viscosity. In this example, second stage addition of these additives produced lower viscosity (7 points) than occurred in Banbury 1 addition. There are many other materials, including accelerators and antioxidants, that act to reduce viscosity in this manner, but many of these incur unfavorable changes in processing and vulcanizate properties.

No discussion of silica processing technology in SBR would be complete without reference to silane-silica coupling effects. Although the coupling of silica with mercaptosilane is designed primarily to enhance abrasion resistance, it also offers a very effective way to reduce the normal silica agglomerate structure and thereby reduce viscosity. The most efficient coupling agent for silica reinforced SBR is mercaptopropyl trimethoxy silane. Addition of 1 phr in the formula above can be expected to reduce viscosity to the same range as the zinc additives and HMT. Discussion of the reinforcing effects of silane coupling appears in a later section.

3.12 ANTIOXIDANTS

In Table 3.17, a comparison of five antioxidants includes both staining and non-staining varieties at the 2 phr level in a typical all-silica SBR 1502 base compound. In terms of aged hardness, tensile and elongation, TMQ is most effective, with ZMTI and DPA445 only slightly removed. For non-black compounds, ZMTI would be recommended. Repetition of this study with antioxidant contents at 4 phr revealed improvement in aged tensile and elongation only with ZMTI. Observation after one year of shelf aging, showed no evidence of bloom, even at 4 phr, except for the NBC compounds. Trouser tear, PICO abrasion and pendulum rebound tests are not affected by either antioxidant type or content. There is, however, a significant drop in viscosity with ZMTI. Previous evidence of the de-agglomerating power of soluble zinc on silica makes this a predictable phenomenon.

Table 3.17 A Comparison of Antioxidants in SBR

Antioxidant type	TMQ	HPPD	NBC	ZMTI	DPA445
ODR cure rate 150°C, T_{90} min	14	12	13	14	14
ODR crosslinks, MH-ML;dN-m	66	65	67	64	63
Mooney viscosity, ML_4100	102	94	118	66	98
Vulcanizate color	brown	black	green	tan	tan
Durometer hardness:					
Original	71	72	73	68	72
Aged 520 hours, 100°C	80	82	87	79	80
Tensile, MPa:					
Original	25	22	24	24	23
Aged 520 hours, 100°C	14	12	8.9	13	13
Elongation,%:					
Original	735	685	680	705	730
Aged 520 hours, 100°C	365	250	80	340	210
Other ingredients: SBR1502-100; Hi-Sil 210-50; C.I. resin-10; Oil-3; Stearic acid-2; ZnO-3; Sulfur-2; MBS-1.5; TMTM-0.6; PEG 3350-1.5					

3.13 TEAR RESISTANCE: SILICA PRIMARY PARTICLE SIZE

The primary particle size (expressed as surface area) of a particular silica is of great importance in attaining high values of trouser tear strength. High surface area silicas (small ultimate particle size) provide high tear strength, as illustrated in Table 3.18.

Table 3.18 Tear Resistance: Silica Surface Area Effect

CTAB surface area, m^2/g	130	148	170	220
Durometer hardness	64	64	63	68
MG trouser tear, kN/m	11	17	40	45
MDR cure rate,150°C, T_{90} minutes	8	11	22	37
MDR crosslinks, dN-m	23	18	19	20
M300 modulus, MPa	3.1	2.7	2.3	2.9
Mooney viscosity, ML_4100	51	60	78	125
PICO abrasion index	50	60	60	64
Cure: 25 min/150°C				
Ingredients: SBR1502-100; silica-50; 100C resin-10; 510 oil-5; ODPA-1; Stearic acid-2; ZnO-3; sulfur-2; MBS-1.5; TMTM-0.6				

The sharp increase in trouser tear which occurs between CTAB surface areas of 148 and 170 m^2/g (N_2SA between 180 and 220 m^2/g) can be related to crosslink modification (increased polysulfides) as well as to an increase in surface area. The reductions in high strain 300% modulus and cure rate are good evidence of a reduction in crosslink density. The absence of any significant change in abrasion index with smaller primary particle size silicas may be due to this crosslink deficiency as well as to surface modification by soluble zinc. Hardness does not appear to be involved in the tear behavior here.

3.14 TEAR RESISTANCE: SILICA CONTENT

In SBR compounds reinforced with both silica and carbon black or other fillers, trouser tear strength increases in direct proportion to silica content. When silica content exceeds 50 phr, it is possible to attain extremely high tear resistance even in the presence of silane coupling (see Formulary compound SBR 29). Formulary compounds SBR 4, 10, 13, 16, 19, 25, 27, 28, 30, 31, 35 and 39 are all examples of trouser tear strengths unattainable with carbon black reinforcement.

If silica content is increased without regard to hardness, the properties of the higher silica content compounds are significantly affected by the resulting increase in durometer values. To avoid these hardness effects, the studies in Table 3.19 have been made in which higher silica contents are accompanied by added oil .

Table 3.19 Trouser Tear Strength: Silica Surface Area Effects

180 m^2/g N2SA Silica, phr	40	50	60	70
Naphthenic oil	10	17	25	33
MDR cure rate, T_{50} minutes	7.6	7.3	11	20
Cure time, 150°C, minutes	15	15	40	40
Durometer: 23°C	58	59	60	66
100°C	57	58	58	60
MG trouser tear, kN/m	4.5	13	29	63
Mooney viscosity, $ML_4$100	48	65	75	89
Compression set, 70 hrs, 100°C, %	54	71	91	98
DeMattia cut growth, kc	1	5	12	33
Transparency, %	11	19	24	24
M300 modulus, MPa	2.9	2.5	2.3	1.9
Tensile, MPa	8.9	15	15	13
Elongation, %	555	765	845	985
PICO abrasion index	45	48	50	55
Other ingredients: SBR1502-53; SBR715-34; BR S200-13; TMQ-0.5; ODPA-1; Pine tar-1; Stearic acid-2; 2nd stage: ZnO-3;Sulfur-2.5; MBTS-1.5; TMTM-0.7; DEG-2				

With no significant change in hardness, the rise in trouser tear strength at higher silica contents is exponential. Undesirable changes include reduced cure rate, reduced 300% modulus, increased viscosity and increased compression set. In the latter case, extremely high set values, together with the increase in tear strength, indicate that the crosslinking is almost completely polysulfidic. These changes, including an increase in transparency, are directly related to greater soluble zinc-silica attachment at higher silica contents. Thus, a major factor in silica induced tear strength is this change in sulfur crosslink type. The second major factor in achieving high tear strength, noted in the preceding section, is a reduction in silica particle size (increased surface area). Abrasion resistance is essentially unchanged by either surface area or content.

3.15 FABRIC ADHESION

As is the case with natural rubber and other elastomers, the adhesion of SBR compounds to untreated and treated textile fabrics increases in proportion to silica content. The improved adhesion appears to be the result of enhanced wetting of the oxygenated fabric surface by silica silanols. Much of the development work on SBR adhesion has involved the combination of silica with resorcinol and hexamethyltetramine (HMT or hexa) or resorcinol resins and hexamethylenemethylmelamine (HMMM), These combinations are sometimes known as the HRH bonding system (acronym by D.D.Dunnom). Incorporation of resorcinol and HMT in the mixed compound eliminates the need for RFL fabric treatment or serves as insurance against defective treatment. Empirical recommendations for these direct bonding formulas in SBR include 1-3 phr minimum for resorcinol, resins and HMT (resorcinol must be separate from HMT until final mixing stage); 15 phr minimum silica or 1/3 total filler, early addition of zinc oxide; 1 phr minimum stearic acid to produce soluble zinc ion; (glycols and silanes reduce adhesion). A typical example is described in Formulary compound SBR 6.

The recommendations for zinc oxide and stearic acid indicate that soluble zinc, as well as resorcinol, silica and HMT, is involved in bond formation, and that a study of the adhesion mechanism must include the zinc oxide function.

One such study of adhesion reaction kinetics is based on variation in compounding and processing materials, rather than on an analytical approach [2]. The procedure here is to plot rubber-to-nylon (untreated) static adhesion data for 11 compounds which represent all possible masterbatch combinations of the four variables. Each masterbatch was mixed at three temperatures, 115°C, 140°C and 165°C. Peel adhesion specimens were cured over a time range of 15 to 60 minutes at 150°C. If two or more components are mutually reactive, their reaction rate will increase at the higher mixing temperature and the corresponding bond development will be faster and possibly greater.

The highest strip adhesion, 16 kN/m, attained at the lowest mixing temperature occurred only with the masterbatch combination of zinc oxide and resorcinol, with or without silica. The combination of zinc oxide and HMT required a mixing temperature of 165°C to reach the same point. The cure time required for development of maximum adhesion values is also shortest with the zinc oxide-resorcinol combination. It can thus be concluded that the reaction of soluble zinc with resorcinol is a vital precursor to the actual resin formation at the bond interface. Lack of kinetic response by silica indicates that wetting is its principal function.

This proposed mechanism effectively explains all of the empirical rules noted above. Stearic acid is required to ionize zinc for subsequent reaction with resorcinol. To perform the wetting function, a minimum silica content is needed to overcome the dilution effect of carbon black. Materials such as glycols and silanes, which modify the silica silanol surface, will interfere with the wetting function. The entire system can be considered to be a typical example of how to meet the two major requirements for adhesion: intimate interfacial contact and a high strength interfacial matrix.

3.16 HEAT RESISTANCE

The heat resistance of silica reinforced SBR has been compared to that of SBR compounds based on carbon black in preceding sections. In these examples silica supplies superior heat resistance in terms of both actual aged elongation and percent retention after aging. The accelerated aging temperatures of 90°C to 135°C and the extended aging period of 700 hours used in these evaluations are far in excess of the 70ºC and 70 hours stipulated for SBR compounds in ASTM D2000. Formulary compounds SBR 2, 11, 24, 25 and 32 describe heat resistant silica reinforced compounds. Compound SBR 24, based on a sulfur donor cure system, is particularly outstanding with 210% elongation after 7 days at 135°C.

3.17 SILANE COUPLING

Silane coupling of silica in SBR compounds produces the same effects noted in the natural rubber discussion of silanes. In Table 3.20 the effects of adding 3% of mercaptopropyltrimethoxysilane (MPTMS), the simplest mercaptosilane, to silica reinforced SBR are summarized (Chapter 1, reference [4]).

Table 3.20 Silane Coupling: Mercaptopropyltrimethoxysilane

	A	**B**
MPTMS A189, phr	0	1.2
MDR cure rate, 150°C, T_{95} minutes	40	25
Mooney viscosity, ML_4100	103	77
Durometer hardness	71	68
M300 modulus, MPa	4.9	13
Tensile, MPa	18	28
Elongation, %	580	510
Flexometer heat build-up, ºC	47	27
Tire abrasion, road wear index (Black control = 100)	79	114
Other ingredients: SBR1502-100; Hi-Sil210-60; oil-10; Stearic acid-2; HPPD-2; Zinc oxide-4; Sulfur-2.8; MBTS-1.5; DOTG-1.5		

The major point here is the remarkable increase in tire wear resistance. In this particular sectional tire road test, the silane coupled silica tread produced a higher index than that of the ISAF black control. The major disadvantage is in the lower elongation, a change which forecasts reduced cut and chip resistance.

The coupling process involves attaching the functional groups of the silane to silica surface silanols and to polymer unsaturation to form a permanent bond between silica and polymer. After hydrolysis of the silane alkoxy groups, attachment to silica silanols occurs on contact during the first moments of mixing. This same reaction takes place during the blending production of silica pretreated silane. The second part of the coupling reaction occurs at normal curing temperatures when the mercaptan group of the silane bonds to the polymer double bond. As noted below, high mixing temperatures do not produce premature silane-polymer bonding. The scorching problems associated with polysulfidic silanes (TESPT) arise from the release of free sulfur which initiates crosslinking during processing.

Depending on the polymer type and silica surface area, the modification of silica by MPTMS to a point of abrasion reinforcement equal to that of HAF black varies from 4 to 6% silane, silica basis. The polysulfide TESPT requires double these amounts. Unpublished studies by J.D.Borroff (1969) of mercaptosilane coupling of SBR 1708 with a 150 m^2/g N_2SA silica used modified Mullins softening curves to illustrate the rheological equivalence of HAF black to silica treated with 4% MPTMS.

Mixing temperature of non-productive silane batches is a sensitive parameter for the polysulfide types of mercaptosilanes. These materials (e.g.., TESPT) require a minimum temperature to become active by breaking sulfide linkages, and at the same time, must not exceed a maximum temperature above which premature crosslinking occurs. In contrast to these processing restrictions, MPTMS with its unblocked mercaptan group is ready to complete its polymer coupling function without molecular modification. As already noted, the superior efficiency of MPTMS can lead to scorch safety problems unless appropriate selection and reduction in accelerators are made. For applications where abrasion resistance requires no more than a 3% silane presence, MPTMS is clearly preferred to TESPT. Table 3.21 contrasts the two silanes in a solution SBR compound, Banbury mixed in one pass to 130°C. If material cost considerations allow a doubling of the TESPT content, these abrasion and modulus gaps disappear, with no loss in scorch safety

Table 3.21 Mercaptosilanes Compared: 220 m^2/g N_2SA Silica

	A	B
Mercapto silane type	MPTMS	TESPT
Mercapto silane content, phr	1.5	1.5
MDR cure rate 150°C, T_{50} minutes	13	15
Mooney scorch, 121°C, T_5 minutes	30+	30+
Durometer hardness	71	73
M300 modulus, MPa	7.4	3.9
PICO abrasion index	72	57
DIN abrasion loss, mg	158	176
Other ingredients: SSBR 1215-100; 220 m^2/g N_2SA Silica -50; CI resin-10; Stearic acid-2;HPPD-2; ZnO-3; PEG-2; Sulfur-2; TBBS-2		

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A more risky solution to the scorch problem is illustrated in Table 3.22 where higher mixing temperatures are seen to significantly prolong scorch life, with some disadvantageous changes in other properties. Property changes at higher mixing temperatures are primarily due to loss of silica free water, which, through subsequent zinc sequestering, degrades crosslink density. Crosslink degradation can be mitigated by the use of a glycol, not present in this instance. In this example the presence of TMTM at 0.7 phr aggravates scorching tendencies. Alternatives to TMTM include acceleration with sulfenamides (2-3 phr) and addition of dithiodimorpholine (DTDM), either of which is effective in ameliorating the scorch problem [3]. Other methods of extending scorch life with MPTMS involve use of silicas pretreated with silane.

Table 3.22 Silane MPTMS Coupling: Mixing Temperature Effects

Banbury Stage 1 temperature, °C	135	160	190
Mooney scorch, 121°C T_5 minutes	10	22	30+
ODR cure rate, 150°C T_{90} minutes	18'	31	45
Mooney viscosity, ML_4100	80	90	85
Durometer hardness	71	68	62
M300 modulus, MPa	6.8	4.8	3.8
Tensile, MPa	23	18	15
Elongation, %	660	690	710
Trouser tear, kN/m	14	22	20
Compression set, 70 hrs, 100°C, %	52	82	79
Flexometer heat build-up, °C	43	48	65
PICO abrasion index	101	106	101

Ingredients: SBR 1500-100; Silane A189-1; 150 m^2/g N_2SA Silica -65; Oil-25; HPPD-1; Stearic acid-1; 2nd stage: ZnO-3; Sulfur-2.8; MBS-1; TMTM-0.7

Silanes without mercaptan functionality are not effective in producing improved abrasion resistance in SBR (Chapter 1 references [1] and [4]). However, vinyl and amino silanes can be used with peroxide curing systems. In the Table 3.23 comparison of various silanes (from M.P.Wagner) it is seen that viscosity reductions, through silica de-agglomeration, are possible with any of these silanes, but improvements in modulus, low heat build-up and tread wear resistance are achieved only by a silane with mercaptan functionality.

Table 3.23 Silane Functional Group Effects

Silane	Viscosity ML_4100	M300 MPa	HBU °C	Tread Wear Index
None	168	4.9	49	100
Methyl	80	3.7	42	95
Vinyl	125	5.2	38	98
Glycidyl	88	5.2	34	100
Amino	112	6.5	31	104
Mercapto	77	12.0	28	140

3.18 SILANE COUPLING: COMPETITION

There are several formula ingredients which can interfere with silane alkoxy bonding to silica surface silanols [4]. These include zinc oxide, amine derivatives, glycols, stearic acid and some resins, all normal components of silica reinforced compound formulas. A study of the competitive effects of these materials indicated that zinc oxide is a major obstacle to efficient silane coupling. The control in these mixing experiments is the initial mixing (0.5 minute addition) of silane to silica and SBR. Evaluation of the competitive activity of other ingredients is ascertained by their addition *before* silane at 0.5 minutes in the Banbury masterbatch; silane is added at 3 minutes and the remaining ingredients are added on the mill with sulfur and accelerator. The resulting compound properties, in Table 3.24 provide the basis (in terms of the PICO abrasion index and modulus data) to make an activity ranking list for each competing ingredient.

Table 3.24 Silane Coupling: Competitive Materials

First added compound	PICO Abrasion Index	M300 MPa	Dynamic Modulus E'	Tan delta
Silane (MB Control)	103	11	6.6	0.126
Zinc oxide	82	7.0	13.0	0.196
HPPD	90	8.8	9.2	0.159
Stearic acid	95	10	7.2	0.133
Polyethylene glycol	97	11	6.7	0.123
Aromatic resin	102	10	9.4	0.148
Ingredients: SBR1502-100; Hi-Sil 210-50; Silane A189-1.5; C.I.resin-10; HPPD-2; Stearic acid-2; PEG 3350-2; ZnO-3; Sulfur-2; TBBS-2				

The most important functions of silane coupling are to increase abrasion resistance and reduce loss modulus or tan delta (i.e., reduce tire rolling resistance). The major interference with these objectives comes from zinc oxide and its addition before silane. Previous discussion of the strong affinity of soluble zinc for the silica silanol surface makes this behavior entirely plausible. The same silanol bonding predilection of amines and amine derivatives explains the competitive degradation of abrasion, modulus and tan delta by HPPD (dimethylbutylphenyl p-phenylenediamine). Polyethylene glycol, notwithstanding a slight loss of abrasion resistance, has little effect on dynamic or static modulus and provides the lowest tan delta. This behavior is an indication that, even with silane coupling, the zinc blocking action of glycols is necessary to produce the most efficient crosslink network. An aromatic resin can be added before silane with no change in abrasion resistance and only a slight increase in tan delta. Other properties such as hardness, trouser tear and hot rebound are also sensitive to mixing order, but to a lesser extent. In these cases early addition of zinc oxide and HPPD are also the major influence in diluting silane coupling effects. Rheometer crosslinks (not shown) are at a maximum when resin precedes silane addition.

Formulary examples of compounds based on silane coupling include SBR 7, 28, 36, 40, and 43. Formulas based on silane-pretreated silica include compounds SBR 10, 12, 14, 16, 17, 23, 29, 30 and 32.

References

1. Hewitt, N.L., "Processing Technology of Silica Reinforced SBR", Elastomerics, March 1981
2. Hewitt, N.L., “Adhesion Mechanisms”, Rubber Age, January, 1972
3. Fetterman, M.Q., U.S.Patent 4,002,594
4. Hewitt, N.L., “Silane Coupling”, Poster at A.C.S. Rubber Div., Louisville, May,1992

Emulsion SBR Formulary

The silica surface areas indicated in the following compounds are N_2SA (BET) surface areas. A listing of commercially available precipitated silica products by surface area is provided in Appendix A. The common abbreviations used in these compounds are provided in Appendix E.

SBR 1

Elastomer: SBR/NR Durometer: 35
Application: General

SBR 1708	50	PEG 3350	2	
SMR	50	Zinc oxide	3	
35 m^2/g Silica	40	Sulfur	2.7	
Whiting	40	MBTS	0.5	
Naphthenic oil	30	DPG	0.3	
100C Resin	12			
ODPA	1	Specific gravity		1.21

Mooney Scorch, 121°C, T_5 minutes	15
Mooney Viscosity, $ML_4$100	24
40 minute cure, 136°C:	
M300, MPa	1.1
Tensile, MPa	8.5
Elongation, %	780
Permanent Set, %	5
Die C tear, kN/m	12.2
NBS Abrasion Index	20
Ross flex cut growth, kc to 500%	>100K

SBR 2

Elastomer: SBR Durometer: 45
Application: General; RS 405 ABF2

SBR 1502	100	Zinc oxide	4
65 m^2/g Silica	40	Sulfur	2
100C Resin	10	CBS	1
Dioctyl Sebacate	12	DPG	0.5
ODPA	1	Specific gravity	1.12

Mooney Scorch, 121°C, T_5 minutes	>30
Mooney Viscosity, ML_4100	38

10 minute cure, 160°C:	Original	70 hrs, 70°C
Durometer	45	49
M300, MPa	1.4	1.7
Tensile, MPa	10.0	9.8
Elongation, %	700	720

Permanent Set, % (D470)	4
Compression Set, 22 hrs,70°C, %	39
Low Temperature Flexibility, -54°C, D736	Pass

SBR 3

Elastomer: SBR/NR Durometer: 51(Black)
Application: General MRG; Tear

SBR 1712	48	PEG 2250	2
SBR 1808	113	Stearic acid	2
SMR 5	15	MC Wax	1
150 m^2/g Silica	45	Zinc oxide	4
100C Ar. Resin	20	Sulfur	2.5
Aromatic Oil	10	MBS (MOR)	1.5
Rosin Ester	4	TMTM	0.4
TMQ	1		
HPPD	2	Specific gravity	1.18

ODR Cure Rate 150°C, T_{90} minutes	25
Mooney Scorch 132°C, T_5 minutes	25
Mooney Viscosity, ML_4100	62

30 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer	51	72
M300, MPa	3.1	
Tensile, MPa	14	10
Elongation, %	780	300

Trouser Tear, Grooved, kN/m	16
PICO Abrasion Index	50

SBR 4

Elastomer: SBR Durometer: 52
Application: Tear; Footwear

SBR 1500	100	PEG 3350	2
150 m^2/g Silica	50	Zinc oxide	5
100C Ar. Resin	15	Sulfur	0.5
Aromatic Oil	20	DTDM	2
Arofene 7209	2.5	TMETD	0.6
TMQ	1		
HPPD	2		
Stearic acid	2	Specific gravity	1.12

ODR Cure Rate, 150°C, T_{90} minutes	17
Mooney Scorch 121°C, T_5 minutes	23
Mooney Viscosity, ML $_4$100	35

30 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer	52	83
M300, MPa	1.5	
Tensile, MPa	14	8.3
Elongation, %	840	140

MG Trouser Tear, kN/m:	
with grain	21
cross grain	17

Compression Set, 70 Hrs, 100°C	30

Goodrich Flexometer: 100°C, 22.5%; 1 MPa	
Permanent Set, %	14
Heat Build-up	41°C

SBR 5

Elastomer: SBR/IR Durometer: 55
Application: Translucent amber soling

SBR 8107	60	PEG 3350	3
IR 400	40	Sulfur	2.5
150 m^2/g Silica	60	MBS (MOR)	0.6
Naphthenic Oil	30	TMTM	0.6
Phenolic AO	1	DOTG	0.6
Stearic acid	1		
Zinc oxide	3	Specific gravity	1.13

ODR Cure Rate, 150°C, T_{90} minutes	6
Mooney Scorch, 121°C, T_5 minutes	15
Mooney Viscosity $ML_4$100	40
6 minute cure, 150°C:	
Durometer	55
M300, MPa	1.7
Tensile, MPa	12
Elongation %	760
NBS Abrasion Index	80

SBR 6

Elastomer: SBR Durometer: 55
Application: Fabric adhesion; Tear strength

Banbury 1		Banbury 2	
SBR 1502	100	Zinc oxide	6
150 m^2/g Silica	65	HMT 50% MB	3
Resorcinol 60% MB	4	Sulfur	2.6
Aromatic Oil	25	TBBS	1.2
Stearic Acid	2	TMTM	0.6
		DPG	0.6
		Specific gravity	1.14

ODR Cure Rate 150°C, T_{90} minutes	30
Mooney Scorch 121°C, T_5 minutes	26
Mooney Viscosity ML_4100	49

30 minute cure, 150°C:	Original	96 hrs, 100°C
Durometer	55	67
M300, MPa	2.7	
Tensile, MPa	13.5	10.4
Elongation, %	680	400

Trouser Tear, Grooved, kN/m	35
PICO Abrasion Index	61

Strip Adhesion to Untreated Fabric, kN/m

	Cure	Original	Water Immersed 24 Hrs, 23°C
Nylon*:	30 minutes, 150°C	11.4	7.8
	60 minutes, 150°C	15.6	12.4
Rayon:	30 minutes, 150°C	11.4	6.2
Polyester,*:	30 minutes, 150°C	2.6	
(activated)	60 minutes, 150°C	3.2	

*Oven aging of press cured laminates showed no loss in fabric tensile strength after 48 hours at 150°C

SBR 7

Elastomer: SBR/EPDM Durometer: 55
Application: Ozone and heat resistance; 170°C Cure

SBR 1707	96	Zinc oxide	2		
EPDM 505*	30	PEG 3350	1.5		
Silane A189*	0.2	Sulfur	0.2		
150 m^2/g Silica	50	TMETD	1		
Naphthenic Oil	10	DPTH	1		
Hydrogenated Rosin	3				
MC Wax	1.5	Specific gravity			1.11

*separate MB with 12 phr silica

MDR Cure Rate 170°C, T_{90} minutes	4
Mooney Scorch 121°C, T_5 minutes	11
Mooney Viscosity ML_4100	68
Garvey Extrusion, 120°C	10A; 30% swell

6 minute cure, 170°C:	Original	72 Hrs, 121°C
Durometer	55	66
M300, MPa	4.1	
Tensile, MPa	7.4	9.9
Elongation, %	480	500

Compression Set: 70 Hrs, 100°C	24%
Ozone Exposure: 50 pphm; 38°C; 125 hour	
Static: bent loop	No cracking
Dynamic, 60 cpm	No cracking
Fatigue to failure, 100% strain	136 kilocycles

SBR 8

Elastomer: SBR/NR Durometer: 56
Application: Low HBU; Heat resistance

Banbury 1		Banbury 2	
SBR 1215	60	Zinc oxide	5
SMR	40	Sulfur	0.4
Ciptane I	31	Vultac 7	1.5
Naphthenic oil	8	TBBS	3
Stearic acid	2	TCS	0.5
TMQ	2		
HPPD	2		
PEG 3350	1	Specific gravity	1.10

MDR Cure Rate, 155°C, T_{90} minutes	8.9
Mooney Scorch 121°C, T_5 minutes	29
Mooney Viscosity, ML_4100	30

10 minute cure, 155°C:	Original	700 hrs, 100°C
Durometer, 23°C	56	64
100°C	52	
M300, MPa	3.8	
Tensile, MPa	23	11
Elongation, %	765	345

Compression Set: 70 hrs, 100°C, %	56.8
PICO Abrasion Index	50

Dynamic Properties, Cure 20 minutes, 155°C

Goodrich Flexometer: 100°C, 22.5%; 1 MPa

Permanent Set, %	3.3
Heat Build-Up	14°C

Dynamic Modulus, DMA: 1 Hz; 10% Strain, MPa

	Original	350 hrs, 100°C
E' at -20°C	46	32
Tangent Delta at -20°C	0.78	0.79
E'at +10°C	7.0	8.4
E' at +60°C	4.6*	6.0*
Tangent Delta at +60C	0.158*	0.148*

*Values unchanged from 20°C to 100°C

Pendulum Rebound (Z), %, 23°C	55.5
100°C	68.8

SBR 9

Elastomer: SBR Durometer: 58
Application: General; Footwear; Injection molding

SBR 1778	55	Sulfur	3
SBR 1502	60	MBTS	1.5
65 m^2/g Silica	60	DOTG	1
Naphthenic oil	23	PEG 3350	2
Stearic acid	3		
Zinc oxide	5		
ODPA	1	Specific gravity	1.16

ODR Cure Rate, 138°C, T_{90} minutes	23
ODR Scorch, 138°C, T_2 minutes	11
Mooney Viscosity, ML_4100	33
25 minute cure, 138°C:	
Durometer	58
M300, MPa	4.5
Tensile, MPa	11.2
Elongation, %	530
NBS Abrasion Index	88

SBR 10

Elastomer: SBR Durometer: 60
Application: Ciptane; Tear; Fast cure

SBR 1502	100	Zinc oxide	3
Ciptane I	55	PEG 3350	2
100C Resin	10	Sulfur	1.3
Red Iron Oxide	5	OTOS	1.8
ODPA	2		
Stearic acid	2	Specific gravity	1.20

MDR Cure Rate, 150°C, T_{50} minutes	5.5
T_{90} minutes	8.2
Mooney Scorch 121°C, T_5 minutes	27
Mooney Viscosity, ML_4100	45

18 minute cure, 150°C:	Original	700 hrs, 95°C
Durometer	60	77
M300, MPa	5.8	
Tensile, MPa	26	23
Elongation, %	775	530
MG Trouser Tear, kN/m	29	39

PICO Abrasion Index	89
Compression Set, 70 hrs, 100°C	35.6%

Goodrich Flexometer: 100°C; 22.5%; 1 MPa

Permanent Set, %	11.0
Heat Build-Up	46°C

Pendulum Rebound (Z), %, 23°C	40
100°C	53

SBR 11

Elastomer: SBR Durometer: 60
Application: Heat resistance; Low set

SBR 1500	100	PEG 3350	2
150 m^2/g Silica	50	DTDM	2
100C Ar. Resin	20	TMTD	0.8
TMQ	1	MBS (MOR)	1.5
HPPD	2		
Zinc oxide	10	Specific gravity	1.21

ODR Cure Rate 150°C, T_{90} minutes	29
Mooney Scorch 135°C, T_5 minutes	12
Mooney Viscosity ML_4100	70

40 minute cure, 150°C:	Original	700 hrs, 110°C	120 hrs, 121°C
Durometer	60	80	73
M300, MPa	3.4		
Tensile, MPa	20	14	21
Elongation, %	730	320	620

MG Trouser Tear, kN/m	11
Compression Set, 70 hrs, 100°C	17%

Goodrich Flexometer: 100°C, 22.5%; 1 MPa

Static compression, %	20
Dynamic compression	10
Permanent Set, %	4.4
Heat build-up	35°C

SBR 12

Elastomer: SBR Durometer: 60
Application: Heat resistance; Silane

SBR 1502	100	Zinc oxide	3
Silica/Ciptane	40/41	Sulfur	0.8
100C Ar. Resin	10	TCS	2.8
Stearic Acid	2		
ZMTI	2		
PEG 3350	2	Specific gravity	1.10

Silica	160 m^2/g Silica	Ciptane 255*
MDR Cure Rate 150°C, T_{90} minutes	12	10
Mooney Scorch 130°C, T_5 minutes	13	11
Mooney Viscosity ML_4100	63	58

*3% mercaptosilane on 160 m^2/g silica

17 minute cure, 150°C:		
Durometer 23°C	60	61
M300, MPa	2.9	4.7
Tensile, MPa	26	32
Elongation, %	765	750

Aged 700 hours:	100°C	125°C*	100°C	125°C*
Durometer	69	81	67	71
Tensile, MPa	8.1	3.4	9.6	10.1
Elongation, %	320	10	330	280

*150 hours

Compression Set ,%, 70 hrs, 100°C	25.0	18.8
PICO Abrasion Index	41	52
Pendulum Rebound (Z), % 23°C	49.0	50.2
100°C	63.2	65.6
Goodrich Flexometer: 100°C, 22.5%; 1 MPa		
Permanent Set, %	3.6	2.3
Heat Build-up, °C	29	22
DMA Dynamic Modulus: 1 Hz; 15% Strain		
E'at 30°C, MPa	8.9	8.4
E' at 100°C	4.9	4.6
Tangent Delta, 60°C	0.164	0.166

SBR 13

Elastomer: SBR/NR Durometer: 61 (black)
Application: Tear, grader tread; Sulfur donor

SBR 1712	89	Zinc oxide	4
150 m^2/g Silica*	30	PEG 3350	1.5
SMR	35	Sulfur	0.3
HAF N330	40	MDB	2
100C Resin	5	MBS	1.5
MC Wax	3	DPTH	0.3
Stearic acid	2		
TMQ	1		
HPPD	2	Specific gravity	1.20

*add at 0' with 1712

ODR Cure Rate 150°C, T_{90} minutes	19
Mooney Scorch 130°C, T_5 minutes	20
Mooney Viscosity ML_4100	63

	30 minute cure, 150°C	200 minute cure,138°C
Durometer	61	62
M300, MPa	4.9	4.9
Tensile, MPa	19.0	18.8
Elongation, %	680	660

MG Trouser Tear, kN/m: 23°C	19.0
100°C	8.2
PICO Abrasion Index	54

Goodrich Flexometer: 200 minute cure, 138°C

	Heat Build-up, °C
100°C; 22.5; 1 MPa	37
93°C; 25%; 1.6 MPa	81

DeMattia Cut Growth: 200 minute cure, 138°C

KC to 500% growth	53

Stanley London Skid Index

Dry Smooth Glass	133
Wet Textured Glass	60

SBR 14

Elastomer: SBR/BR/NR Durometer: 62
Application: Low rolling resistance tread; Black

SBR 1204	45	Stearic acid	1
BR 1203	30	Zinc oxide	3
SMR	25	PEG 3350	0.5
Ciptane (6% A189)	20	Sulfur	1.5
ISAF N299	33	TBBS	1.3
100C Resin	5	DTDM	0.3
Aromatic Oil	5		
HPPD	1.5	Specific gravity	1.14

ODR Cure Rate 150°C T_{90} minutes	11
Mooney Scorch 130°C T_5 minutes	15
Mooney Viscosity ML_4100	52

15 minute cure, 150°C:	
Durometer	62
M300, MPa	8.8
Tensile, MPa	22.6
Elongation, %	620

MG Trouser Tear, kN/m: 23°C	8.0
100°C	3.3
PICO Abrasion Index: 23°C	117
100°C	112
Sectional Tire Road Wear: 16,000 miles; 3 tire averages	
Mils/1000 miles	6.06
Miles to wear bar	47,200

DMA Dynamic Modulus: 1 Hz; 15% Strain	
E’, MPa, -15°C	17
60°C	6.9
Tangent Delta, 0°C	0.173
60°C	0.149

Pendulum Rebound (Z), %: 23°C	53
100°C	62

SBR 15

Elastomer: SBR Durometer : 64
Application: TCS acceleration; Low set, HBU

Banbury 1		Banbury 2	
SBR 1502	100	Zinc oxide	3
150 m^2/g Silica	50	PEG 3350	2
100C Ar. Resin	10	Sulfur	0.8
ZMTI	2	TCS	2.8
Stearic acid	2		
		Specific gravity	1.13

ODR Cure Rate 150°C, T_{90} minutes	13
Mooney Scorch 130°C, T_5 minutes	11
Mooney Viscosity ML_4100	75

20 minute cure, 150°C:	Original	700 hrs, 95°C
Durometer	64	82
M300, MPa	2.8	
Tensile, MPa	20	6.4
Elongation, %	705	5

MG Trouser Tear, kN/m	15
PICO Abrasion Index	52
Compression Set, 70 hrs, 100°C	21%
Pendulum Rebound (Z), %: 23°C	43
100°C	59

Goodrich Flexometer: 100°C; 22.5%; 1. MPa

Permanent Set, %	3.9
Heat Build-up	28°C

DMA Dynamic Modulus: 30°C, 1 Hz

E', MPa	16
E"	2.36
Tangent Delta	0.147

DeMattia Cut Growth, KC to 500%	45

SBR 16

Elastomer: SBR Durometer: 64
Application: TCS acceleration; Ciptane I

Banbury 1		Banbury 2	
SBR 1502	100	Zinc oxide	3
Ciptane I	52	PEG 3350	2
100C Ar. Resin	10	Sulfur	0.8
ZMTI	2	TCS	1.8
Stearic Acid	2	Specific gravity	1.15

MDR Cure Rate 150°C T_{90} minutes	16
Mooney Scorch 130°C T_5 minutes	12
Mooney Viscosity, $ML_4$100	74

20 minute cure, 150°C:	Original	700 hrs, 95°C
Durometer	64	80
M300, MPa	5.7	
Tensile, MPa	25	8.3
Elongation, %	745	75

MG Trouser Tear, kN/m	22
Compression Set, 70 hrs, 100°C, %	32.3
Pendulum Rebound (Z), %: 23°C	46
100°C	56

Goodrich Flexometer: 100°C; 22.5%; 1 MPa

Permanent Set, %	5.8
Heat Build-up	32°C

DMA Dynamic Modulus: 30°C, 1 Hz

E’, MPa	12.4
Tangent Delta	0.181

DeMattia Cut Growth, kc to 500% 100

SBR 17

Elastomer: SBR/BR Durometer: 64
Application: HP tread; Ciptane

Banbury 1		Banbury 2	
SBR 1721	41	Zinc oxide	3
SBR 1712	41	PEG 3350	1
BR 1203	40	Sulfur	1.3
Ciptane (3.5% A189)	18/0	TBBS	1.5
HAF N339	67/75	DTDM	0.6
100C Arom. Resin	12/0	TMTD	0.1
Aromatic Oil	8/12		
HPPD	2		
TMQ	1		
Stearic Acid	2	Specific gravity	1.14

	Ciptane	N339 Control
ODR Cure Rate, 160°C, T_{90} minutes	6.5	8.0
Mooney Scorch, 130°C, T_5 minutes	15	20
Mooney Viscosity, ML $_4$100	57	60
12 minute cure, 160°C:		
Durometer	64	66
M300, MPa	8.2	12.3
Tensile	20	16
Elongation, %	370	650
20 minute cure, 160°C:		
DMA Dynamic Modulus: 1 Hz; 15% Strain, MPa		
E” at 0°C	14.0	10.2
S” at 0°C	7.9	9.6
E’ at 30°C	18.3	17.7
Tangent delta at 80°C	0.24	0.24
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Static Compression, %	19	18
Dynamic Compression	8.8	6.5
Permanent Set	8.5	6.7
Heat Build-up, °C	43	44
Pendulum Rebound (Z), %: 23°C	38.2	44.6
100°C	62.6	66.8
PICO Abrasion Index	100	157
DeMattia Cut Growth, KC to 500%	30	8

SBR 18

Elastomer: SBR/NR Durometer: 65
Application: General purpose; Hose; Lead cure; Heat resistance

SBR 1503	75	PEG 3350	2
SMR	25	DTDM	2
35 m^2/g Silica	50	TBTD	0.5
Mistron Talc	50	TMETD	1
100C Resin	10		
Paraffinic Oil	10		
Stearic Acid	1		
Zinc Oxide	5	Specific gravity	1.27

ODR Cure Rate 157°C, T_{90} minutes	21
Mooney Scorch 121°C, T_5 minutes	30
Mooney Viscosity, ML_4100	50

30 minute cure, 157°C:	Original	72 hrs, 121°C
Durometer	65	64
M300, MPa	3.5	
Tensile, MPa	11.1	9.5
Elongation, %	640	640

No discoloration in lead cure.

SBR 19

Elastomer: SBR/NR Durometer: 65
Application: General Purpose; Extended cure

SBR 1500	80	Zinc oxide	3
SMR	20	PEG 3350	2
150 m^2/g Silica	50	Sulfur	2
100C Ar. Resin	10	MBS (MOR)	1.5
Aromatic oil	3	DPG	0.5
Stearic acid	2		
HPPD	2	Specific gravity	1.14

ODR Cure Rate 150°C, T_{90} minutes	19
Mooney Scorch 135°C, T_5 minutes	20
Mooney Viscosity, ML_4100	92

Cure:	30 min, 150°C	150 min, 150°C	300 min, 135°C
Durometer	66	65	67
M300, MPa	2.3	1.9	2.5
Tensile, MPa	23	21	23
Elongation,%	780	800	740
MG Trouser Tear, kN/m			
Original	22	24	22
Remilled	25	32	19
DeMattia Cut Growth; Kc to 500% Growth	25	35	15
Monsanto Fatigue to Failure: Kilocycles	80	75	45
Yerzley Resilience, %	48		
Benzene Solubles; 72 hours at 23°C, %	13.13	13.15	

SBR 20

Elastomer: SBR/NR Durometer: 65
Application: Footwear sole; Pale crepe color

SBR 1502	82	Stearic acid	2
SMR	10	DEG	2
High Styrene Resin	20	Zinc Oxide	3
150 m^2/g Silica	50	Sulfur	2.3
35 m^2/g Silica	2	CBS	1.2
Naphthenic Oil	40	TMTM	0.6
MC Wax	0.5		
Phenolic AO	0.5	Specific gravity	1.12

ODR Cure Rate 150°C, T_{90} minutes	20
Mooney Scorch 121°C, T_5 minutes	30
Mooney Viscosity, ML_4100	58

20 minute cure, 150°C:

Durometer	65
M300, MPa	2.0
Tensile, MPa	12.5
Elongation, %	780

NBS Abrasion Index	63

SBR 21

Elastomer: SBR/NR Durometer: 65
Application: Flame resistance; Textile adhesion

SBR 1502	80	<u>2^{nd} Stage</u>	
SMR	20	Bonding Agent M-3	3
65 m^2/g Silica	40	Sulfur	2.5
150 m^2/g Silica	15	TBBS	1.3
Zinc Oxide	8	DPG	0.4
Antimony Oxide	15		
Chlorowax 70	20		
Chlorowax 500C	15		
Bonding Agent R6	4		
Stearic Acid	3	Specific gravity	1.38

ODR Cure Rate 150°C, T_{90} minutes	40
Mooney Scorch 130°C, T_5 minutes	30
Mooney Viscosity, ML_4100	50

40 minute cure, 150°C:

Durometer	65
M300, MPa	3.4
Tensile, MPa	15
Elongation, %	740

Strip Peel Adhesion to Fabric, kN/m

Untreated Nylon	>23
RFL Treated Nylon	>26

SBR 22

Elastomer: SBR/BR Durometer: 65 Black
Application: Agricultural tread; Tear

SBR 1714	45	Stearic Acid	2
SBR 1500	40	PEG 3350	1
BR 1220	30	Zinc Oxide	4
150 m^2/g Silica	30	Sulfur	2.2
FEF N539	60	TBBS	1
Aromatic Oil	30	TMTM	0.3
MC Wax	2		
HPPD	2		
TMQ	1	Specific gravity	1.20

ODR Cure Rate 150°C, T_{90} minutes	12
Mooney Scorch 135°C, T_5 minutes	13
Mooney Viscosity, ML_4100	60
Garvey Extrusion:	
Swell, %	20
Rating	10A

30 minute cure, 150°C:	Original	250 hrs, 90°C
Durometer	65	85
M300, MPa	6.6	
Tensile	12	10
Elongation, %	580	180

Trouser Tear, kN/m	14
Weathering Effect on Durometer Hardness:	
500 hours weatherometer	70
2 yrs outdoor aging (Pittsburgh)	65
PICO Abrasion Index	82
Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent set, %	21
Heat build-up	58°C
DeMattia Cut Growth, kc to 500%	30

SBR 23

Elastomer: SBR Durometer: 65
Application: Translucent; Silane effects

SBR 1502	100	PEG 3350	1.5
Silica	50	Sulfur	2
Resin (Nevtac 100)	10	MOR	1.5
Naphthenic Oil	5	TMTM	0.6
Stearic Acid	2		
ODPA	1		
Zinc Oxide	3	Specific gravity	1.14

Silica	150 m^2/g Silica	Ciptane 255*
MDR Cure Rate, 150°C, T_{50} minutes	9.4	7.3
T_{90} minutes	20	20
Mooney Scorch, 121°C, T_5 minutes	30+	30+
Mooney Viscosity, ML_4100	71	63

*3% mercaptosilane on 160 m^2/g silica

Stress/Strain:	Original	Aged*	Original	Aged*
Durometer	66	76	67	76
M300, MPa	3.0	5.9		
Tensile, MPa	20	9.3	26	13
Elongation, %	750	380	680	310

*Aged 700 hours at 90°C

MG Trouser Tear, kN/m	17	12
PICO Abrasion Index	55	78
DIN Abrasion Loss, ml	180	140
Transparency (Hunterlab), %	37	20
Haze	87	88
Compression Set, %, 70 hrs, 100°C	55	53
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Permanent set, %	Blow out	4.4
Heat build-up, °C		22
DeMattia Cut Growth, KC to 500%	2	3
Pendulum Rebound (Z), %, 23°C	38	41
100°C	55	60

SBR 24

Elastomer: SBR Durometer: 69
Application: Heat resistance; Low set; Tear

SBR 1500	100	PEG 3350	2
150 m^2/g Silica	50	Sulfur	0.3
100C Arom. Resin	20	MBS (MOR)	1.5
HPPD	2	TMETD	2.5
TMQ	1		
Stearic Acid	4		
Zinc Oxide	4	Specific gravity	1.20

ODR Cure Rate 150°C, T_{90} minutes	15
Mooney Scorch 135°C, T_5 minutes	11
Mooney Viscosity, ML_4100	83

20 minute cure, 150°C	Original	700 hrs,100°C	170 hrs,135°C
Durometer	69	80	84
M300, MPa	2.3		
Tensile, MPa	19	12	9
Elongation, %	760	420	200

Trouser Tear, Grooved, kN/m	18
Compression Set, %, 70 hours, 100°C	18
Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent set, %	5.2
Heat build-up, °C	36

DeMattia Cut Growth, kc to 500%	60

SBR 25

Elastomer: SBR Durometer: 69
Application: General Purpose; Non-discoloring

SBR 1502	10	Sulfur	2
150 m^2/g Silica	50	MBS	1.5
100C Resin	10	TMTM	0.6
ZMTI	2	PEG 3350	1.5
Stearic Acid	2		
Zinc Oxide	3		
Naphthenic Oil	3	Specific gravity	1.14

MDR Cure Rate 150°C, T_{90} minutes	24
Mooney Scorch 130°C, T_5 minutes	22
Mooney Viscosity, ML_4100	66

30 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer	68	75
M300, MPa	3.6	
Tensile, MPa	24	15
Elongation, %	705	435

MG Trouser Tear, kN/m	17.5
PICO Abrasion Index	55
Compression Set, %, 70 hrs, 100°C	46.3

Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent Set, %	14
Heat build-up	45°C

Pendulum Rebound (Z), %	23°C	47.8
	100°C	66.8
DeMattia Cut Growth: kc to 500%		18

Monsanto Fatigue to Failure, 100% Strain, kc	17

SBR 25A

Elastomer: SBR Durometer: 69

Application: Accelerators TCS and ZBDC; Black control

SBR 1502	100	Zinc Oxide	3
Silica or HAF	50	PEG 3350	2
Picco 6100	10	Sulfur	2
Stearic Acid	2	Accelerator	2
ZMTI	2		

160 m^2/g Silica	50	50	-
HAF N330	-	-	55
TCS (Curite 18)	2	-	-
ZBDC	-	2	-
TBBS	-	-	2
ODR Cure Rate, 150°C, T$_{90}$ minutes	20	23	21
ODR Crosslinks, dN-m	65	53	75
Mooney Scorch, 130°C, T$_5$ minutes	12	16	27
Mooney Viscosity, ML$_4$100	110	110	64
Cure, minutes, 150°C:	35	40	20
Durometer	71	69	70
M300, MPa	4.3	2.9	13
Tensile, MPa	24	21	24
Elongation, %	660	770	535
Aged 72 hours, 121°C:			
Durometer	82	79	78
Tensile, MPa	12	9.4	13
Elongation, %	220	305	125
MG Trouser Tear, kN/m	13	29	11
PICO Abrasion Index	-	57	124
Compression Set, %, 70 hrs, 100°C	30	45	55
Goodrich Flexometer: 100°C, 22.5%; 1 MPa			
Permanent Set, %	5.0	-	9.4
Heat build-up, °C	39	65	38
Pendulum Rebound (Z), %, 23°C	43	51	41
100°C	61	61	63
DMA Dynamic Modulus: 30°C; 1 Hz			
E', MPa	20.3	-	17.1
E"	2.61	-	2.81
Tangent Delta	0.129	-	0.162

SBR 26

Elastomer: SBR/NR Durometer: 70
Application: Fabric adhesion; Hot air cure for coated fabric

SBR 1006	90	Zinc Oxide	5
SMR	10	DTDM	1
65 m^2/g Silica	60	MBS	1
Hard Clay	70	TMTM	0.4
100C Aro. Resin	10	Sulfur	1.2
Naphthenic Oil	10	HMT	1.5
Stearic Acid	2		
ODPA	1		
Resorcinol	3	Specific gravity	1.36

ODR Cure Rate 142°C, T_{90} minutes	30
Mooney Scorch 121°C, T_5 minutes	11
Mooney Viscosity, ML_4100	55

40 minute cure, 142°C:

Durometer	71
M300, MPa	6.6
Tensile, MPa	8.3
Elongation, %	470

Strip Adhesion to Untreated Fabrics, kN/m:

2.1 MPa Air Pressure	Nylon	Cotton
60 minutes, 142°C	7.1	2.7
120 minutes, 142°C	7.1	3.5

SBR 27

Elastomer: SBR/NR Durometer: 71 (Black)
Application: OTR tread; Tear; w/wo silane;

SBR 1500	65	DEG	1.5
SMR	35	Zinc Oxide	4
150 m^2/g Silica	30	Sulfur	0.3
ISAF N231 black	30	MDB	2
100C Aro. Resin	10	MBS	1.5
MC Wax	3	DPTH	0.3
TMQ	1		
HPPD	2	Specific gravity	1.17

Silane A189:	0	0.4
ODR Cure Rate, T$_{90}$ minutes, 138°C	38	32
154°C	15	13
Mooney Scorch 130°C, T$_5$ minutes	22	18
Mooney Viscosity, ML$_4$100	51	49
200 minute cure, 138°C:		
Durometer	70	72
M300, MPa	5.2	8.0
Tensile, MPa	21	22
Elongation, %	640	580

MG Trouser Tear, kN/m	23°C	100°C	23°C	100°C
Cure 30 minutes, 154°C	24	15	20	13
Cure 200 minutes, 138°C	22	11	18	10

Goodrich Flexometer:
(A: 100°C; 22.5%; 1 MPa; B: 93°C; 25%; 1.6 MPa)

	A	B	A	B
Permanent Set, %				
30 minute cure, 154°C	12	19	8	16
200 minute cure, 138°C	9	16	5	13
Heat build-up, °C				
30 minute cure, 154°C	49	78	46	68
200 minute cure, 138°C	48	73	44	64

PICO Abrasion Index	79	91
DeMattia Cut Growth: kc to 500%	65	45

SBR 28

Elastomer: SBR/NR Durometer: 72
Application: Fabric adhesion; Lead adhesion

SBR 1500	85	Resorcinol Resin	3
SMR	15	HMMM 963	3
65 m^2/g Silica	80	Sulfur	2
Aromatic Resin	10	MBS (MOR)	1.2
Aromatic Oil	10	TMTM	0.8
Stearic Acid	2		
ODPA	1		
Zinc Oxide	5	Specific gravity	1.20

ODR Cure Rate, 150°C, T_{90} minutes	35
Mooney Scorch, 132°C, T_5 minutes	11
Mooney Viscosity, ML_4100	50
40 minute cure, 150°C;	
Durometer	72
M300, MPa	5.6
Tensile, MPa	13
Elongation, %	680
Strip Peel Adhesion to Untreated Nylon Fabric, kN/m	
40 minutes, 150°C	5.2
60 minutes, 150°C	7.0
Strip Peel Adhesion to Lead Sheet, kN/m	
40 minutes, 150°C	1.2
60 minutes, 150°C	5.2
Compression Set, %, 70 hours, 100°C	67

SBR 29

Elastomer: SBR Durometer: 73
Application: Tear strength; Heat resistance; Zinc dimethacrylate

SBR 1502	100	PEG 3350	2
Ciptane 1	65	Sulfur	1.3
Picco 6100	15	OTOS	1
Red Iron Oxide	5	TBBS	1.5
Stearic Acid	2		
TMQ	2		
Zinc Oxide	3	Specific gravity	1.23

Zinc dimethacrylate :	0	2
MDR Cure Rate, 150°C, T_{90} minutes	10	8.0
Mooney Scorch, 121°C, T_5 minutes	>30	>30
Mooney Viscosity, ML_4100	84	69
Garvey Extrusion:		
% Swell	25	40
Edge/surface rating	8A	8A
15 minute cure, 150°C:		
Durometer (button), 23°C	72	74
100°C	62	59
M300, MPa	7.0	6.0
Tensile, MPa	26	27
Elongation, %	685	755
Aged 700 hours, 95°C		
Durometer	75	73
Tensile, MPa	19	20
Elongation, %	425	475
MG Trouser Tear, kN/m	32	41
Die C Tear	53	54
PICO Abrasion Index	102	89
DIN Abrasion Loss, ml	122	126
Compression Set, %, 70 hrs, 100°C	62	63
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Permanent Set, %	12	16
Heat build-up, °C	37	42
Pendulum Rebound (Z), %, 23°C	32	28
100°C	52	48

SBR 30

Elastomer: SBR/BR Durometer: 74 Black
Application: HP tread; Traction; Tear

SBR 1721	60	Zinc Oxide	3
BR 1203	40	PEG 3350	1
Ciptane (3.8% A189)	40	Sulfur	1.3
SAF N110 Black	36	DTDM	1.2
Aromatic 100C Resin	20	TBBS	1.5
Aromatic Oil	6	TMTD	0.1
Stearic Acid	2		
HPPD	2		
TMQ	1	Specific gravity	1.15

MDR Cure Rate, 160°C, T_{90} minutes	7.5
Mooney Scorch, 130°C, T_5 minutes	16
Mooney Viscosity, ML_4100	60
12 minute cure, 160°C:	
Durometer	74
M300, MPa	9.4
Tensile, MPa	23
Elongation, %	650
MG Trouser Tear, kN/m	21
PICO Abrasion Index	95
DMA Dynamic Modulus: 1 Hz; 15% Strain; MPa	
E” at 0C	28.0
E’ at 90C	9.8
Tangent Delta at 90°C	0.254
Pendulum Rebound (Z), %, 23°C	39.6
100°C	59.4
Goodrich Flexometer; 100°C; 22.5%; 1 MPa	
Permanent Set, %	5.8
Heat build-up, °C	41
DeMattia Cut Growth, kc to 500%	18

SBR 31

Elastomer: SBR   Durometer: 73
Application: General; Tear

SBR 1500	100	Zinc Oxide	3
150 m^2/g Silica	55	PEG 3350	2
Aromatic 100C Resin	15	Sulfur	2.5
Zinc Octoate	2	MBS (MOR)	0.8
Stearic Acid	4	TMTM	0.5
HPPD	2		
TMQ	1	Specific gravity	1.19

	Original	Remilled
ODR Cure Rate, 150°C, T_{90} minutes	16	16
Mooney Scorch, 135°C, T_5 minutes	11	11
Mooney Viscosity, ML_4100	73	64
Garvey Extrusion, 121°C		
% Swell, width	38	46
Edge/surface rating	10A	10A

20 minute cure, 150°C:	Original	170 hrs, 100°C	70 hrs, 121°C
Durometer	73	80	86
M300, MPa	3.0		
Tensile, MPa	21	20	12
Elongation, %	720	450	270

Trouser Tear, Grooved, kn/m	18.4
PICO Abrasion Index	68
Compression Set: 70 hrs/100°C, %	54

Pendulum Rebound (G-H),	Percent	Durometer
At -20°C	17	90
At +20°C	45	72
At 100°C	63	60

Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent Set, %	13
Heat build-up, °C	42
DeMattia Cut Growth: kc to 500%	35
Water Immersion, 100°C, % Volume Change	
24 hours	7
72 hours	12
160 hours	9

SBR 32

Elastomer: SBR/NR Durometer: 73 (Black)
Application: Heat resistance; Fabric adhesion

SBR 1500	75	Resorcinol	1.5
SMR	25	Sulfur	0.5
150 m^2/g Silica	40	MDB (Morfax)	2
HAF N351black	25	TBTD	1.2
Aromatic 100C Resin	15	HMT	1
Stearic Acid	3		
TMQ	1		
HPPD	2		
Zinc Oxide	8	Specific gravity	1.25

ODR Cure Rate, 160°C, T_{90} minutes	10
Mooney Scorch, 121°C, T_5 minutes	15
T_{35} minutes	22
Mooney Viscosity, ML_4100	59

15 minute cure, 160°C:	Original	700 hrs, 100°C
Durometer	73	84
M300, MPa	7.2	
Tensile	22	17
Elongation, %	650	320

Strip Peel Adhesion to Untreated Nylon Fabric, kN/m	
20 minutes, 160°C	4.1
40 minutes, 160°C	4.8

Compression Set, %, 70 hrs, 100°C	34
Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent Set, %	5.7
Heat Build-up, °C	31
DeMattia Cut Growth, kc to 500%	10
Monsanto Fatigue to Failure (100% strain), kc	
Original	57
Aged 48 hrs, 121°C	51

SBR 33

Elastomer: SBR/BR/NR Durometer: 75
Application: Zinc-free; Abrasion resistance

SSBR 1215	60	Sulfur	2
BR 1220	30	TBBS	2
SMR	10	HMT	2
Ciptane 1	52	Zinc Oxide	0.5
Arom. 100C Resin	10		
Phenolic AO	1	Specific gravity	1.12

MDR Cure Rate, 160°C, T_{50} minutes	3.2
T_{90} minutes	18
Mooney Scorch, 130°C, T_5 minutes	12
Mooney Viscosity, ML_4100	96
Garvey Extrusion (Brabender):	
% Die Swell	5
Edge and Surface	7A

25 minute cure, 160°C:	Original	700 hrs, 90°C
Durometer, 23°C	75	83
100°C	74	
M300, MPa	9.8	
Tensile, MPa	20	8.4
Elongation, %	515	115

PICO Abrasion Index, 23°C	145
100°C	100
MG Trouser Tear, kN/m	7.9
Compression Set, %, 100°C, 70 hrs	56

DMA Dynamic Modulus: 30°C; 1 Hz; 20% Strain	
E’, MPa	19
Tangent Delta	0.123

Pendulum Rebound (Z), %, 23°C	49
100°C	63

SBR 34

Elastomer: SBR	Durometer: 74
Application: Fire resistant	

SBR 1500	100	PEG 3350	2
150 m^2/g Silica	55	Sulfur	2.6
Antimony Oxide	15	TBBS	0.8
Chlorowax 70S	25	TMTM	0.3
Stearic Acid	4	Zinc Oxide	3
TMQ	1		
HPPD	2	Specific gravity	1.31

ODR Cure Rate, 150°C, T_{90} minutes	19
Mooney Scorch, 135°C, T_5 minutes	10
Mooney Viscosity, ML_4100	82

30 minute cure, 150°C:	Original	700 hrs, 80°C
Durometer	74	80
M300, MPa	2.8	
Tensile, MPa	23	19
Elongation, %	740	460

Trouser Tear, Grooved, kN/m	21
Compression Set, %, 70 hrs. 100°C	69
DeMattia Cut Growth, kc to 500%	24

Water Immersion, 100°C	% Volume Change
24 hours	12
72 hours	18
168 hours	13

SBR 35

Elastomer: SBR Durometer: 78(black)
Application: Tear strength; MRG

SBR 1503	100	Zinc Oxide	4
150 m^2/g Silica	40	PEG 3350	1.5
HAF N330 black	70	Sulfur	2.5
100C Arom. Resin	20	MBS (MOR)	1.5
Aromatic Oil	25	TMTM	0.2
TMQ	1		
HPPD	2		
Stearic Acid	2	Specific gravity	1.24

ODR Cure Rate, 150°C, T_{90} minutes	15
Mooney Scorch, 130°C, T_5 minutes	15
Mooney Viscosity, ML_4100	75

30 minute cure, 150°C	Original	600 hrs, 90°C
Durometer	78	90
M300, MPa	9.1	
Tensile, MPa	15	11
Elongation, %	500	100

Trouser Tear, Grooved, kN/m, 23°C	19
70°C	7.0

PICO Abrasion Index	105

Goodrich Flexometer: 100°C; 22.5%; 1 MPa

Static Compression, %	18
Dynamic Compression	8
Permanent Set	14
Heat Build-up, °C	48

SBR 36

Elastomer: SSBR/BR/NR Durometer: 79
Application: Zinc-free and silane; Abrasion; Footwear

SBR 715	50	Zinc Oxide	1
BR 1220	40	Sulfur	2
SMR	10	TBBS	1.5
150 m^2/g Silica	60	MBTS	1
Silane SI69	2	HMT	2
100C HC Resin	10		
ODPA	1	Specific gravity	1.15

MDR Cure Rate, 150°C, T_{50} minutes	7
Mooney Scorch, 121°C, T_5 minutes	22
Mooney Viscosity, $ML_4 100$	126
Durometer (20 min, 150°C; C. Set Disk)	
23°C	79
100°C	74

13 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer	76	86
M300, MPa	10	
Tensile, MPa	19	12
Elongation, %	475	150

Abrasion Indices: PICO at 23°C	155
PICO at 100°C	105
DIN Loss, ml	120
NBS	201
MG Trouser Tear, kN/m	13
Ross Flex, kc to 500% cut growth	50
Dynamic Coefficient of Friction, wet aluminum	0.77
DMA Dynamic Modulus: 1 Hz, 15% strain, MPa	
E’ at 30°C	13
Tan Delta at 30°C	0.129
E’ at 0°C	19
E” at 0°C	3.1
Tan Delta at 0°C	0.160
Pendulum Rebound (Z), %, 23°C	48
100°C	59

SBR 37

Elastomer: SBR/NR Durometer: 80
Application: General purpose; White; Processing

SBR 1502	80	Zinc Oxide	3
SMR CV60	20	PEG 3350	1
High Styrene S6B	20	Sulfur	3
220 m^2/g Silica	20	TBBS	1.5
65 m^2/g Silica	30	OTOS	0.5
Titanium Dioxide	15	Stearic Acid	2
Nevtac 100	5		
ODPA	1	Specific Gravity	1.16

MDR Cure Rate, 150°C, T_{50} minutes	20
T_{90} minutes	30
Mooney Scorch, 121°C, T_5 minutes	30
Mooney Viscosity, ML_4100	56
Durometer: 23°C	80
100°C	63
30 minute cure, 150°C:	
M300, MPa	9.2
Tensile, MPa	17
Elongation, %	530
MG Trouser Tear, kN/m	11
PICO Abrasion Index	74
Compression Set, %, 70 hrs, 100°C	60
Pendulum Rebound (Z), %, 23°C	40
100°C	53

SBR 38

Elastomer: SBR/NR Durometer: 81
Application: Hose; Fire resistance; Brass adhesion

SBR 1778	55	Zinc Oxide	5
SBR 1507	35	HPPD	2
SMR	25	PEG 3350	2
65 m^2/g Silica	100	Sulfur	3
Hard Clay	100	MBS	1
Antimony Oxide	10	DPG	1
Chlorowax 70	25	TMTM	0.5
Naphthenic Oil	10		
Stearic Acid	4		
MC Wax	3	Specific Gravity	1.51

ODR Cure Rate, 150°C, T_{90} minutes	10
Mooney Scorch, 121°C, T_5 minutes	20
Mooney Viscosity, ML_4100	60
Garvey Extrusion, 121°C: % Swell	13
Edge/surface	10A
15 minute cure, 150°C:	
Durometer	81
M300, MPa	4.8
Tensile	6.8
Elongation, %	480
Brass/Steel Wire (6+3) Adhesion, Cure 30 minutes, 150°C:	
Pull-out, kN/m	16

Flame Test, 2 mm 1” Wide Strip Held 1” in Flame, minutes to self-extinguish:	
Horizontal	1.6
Vertical	0.5
Compression Set, %, 22 hrs, 70°C	34
PICO Abrasion Index	33

Water Immersion, % Volume Change	70°C	100°C
24 hours	9.7	11.3
160 hours	9.7	10.6
340 hours	9.3	10.0

SBR 39

Elastomer: SBR Durometer: 83
Application: Tear strength; Fire resistance; Low cost flooring

SBR 1500	100	Stearic Acid	4
150 m^2/g Silica	55	PEG 3350	2
Hard Clay	50	TBBS	1
Antimony Oxide	15	ZMDC	0.5
Chlorowax 70S	25	Sulfur	2.8
Hydrog, Rosin	10	Zinc Oxide	3
TMQ	2		
Color	2	Specific Gravity	1.42

MDR Cure Rate, 150°C, T_{90} minutes	30
Mooney Scorch, 135°C, T_5 minutes	10
Mooney Viscosity, ML_4100	97

30 minute cure, 150°C	Original	700 hrs, 80°C
Durometer	83	90
M300, MPa	3.4	
Tensile, MPa	15	15
Elongation, %	750	420

MG Trouser Tear, kN/m	26
PICO Abrasion Index	72
DeMattia Cut Growth, kc to 500%	>100

SBR 40

Elastomer: SBR/NR Durometer: 85
Application: Abrasion; Tack; silane; Zinc octoate

SBR 1502	80	PEG 3350	2
SBR 1904	20	Zinc Oxide	3
SMR	10	Zinc Octoate	2
150 m^2/g Silica	70	Sulfur	3
Silane A189	2.4	TBBS	2
Arom. 100C Resin	10	DTDM	1
Stearic Acid	2		
ODPA	1	Specific Gravity	1.23

MDR Cure Rate, 150°C, T_{90} minutes	19
Mooney Scorch, 130°C, T_5 minutes	17
Mooney Viscosity, $ML_4$100	75
Building Tack	Good
30 minute CURE, 150°C:	
Durometer	85
M200, MPa	13.7
Tensile, MPa	19.8
Elongation, %	285
PICO Abrasion Index*	181

*PICO values on 80-90 durometer compounds are likely to be overstated.

SBR 41

Elastomer: SBR/BR/NR Durometer: 89
Application: Resilient flooring; Emulsion vs. solution SBR; Zinc-free

Elastomers	100	Sulfur	3
High Styrene Resin	15	TBBS	2
150 m^2/g Silica	30	HMT	2
Hard Clay	100	OTOS	variable
25C Resin	9		
Stearic Acid	2	Specific Gravity	1.38

SBR	1502-100	715-60
BR 1220	0	30
SMR	0	10
OTOS	1	0
MDR Cure Rate, 150°C, T_{50} minutes	9.2	6.7
T_{90} minutes	34	26
Mooney Scorch, 121°C, T_5 minutes	21	22
Mooney Viscosity, $ML_4$100	76	100
20 minute cure, 150°C:		
Durometer (button)		
23°C	88	90
100°C	70	74
M20, MPa	2.5	3.0
M300, MPa	8.9	11.3
Tensile, MPa	18	13
Elongation, %	545	380
Taber Abrasion: H22 Wheels; 1000 Rev; mg lost	130	105
NBS Abrasion Index	40	37
Pendulum Rebound (Z), %, 23°C	32	38
100°C	40	74
DeMattia Cut Growth: kc to 500%	4	3
Compression Set, Method A, Constant Force: 70 hours, 45°C		
Initial Deflection, mm	0.51	
Creep, % Final Deflection	69.0	
Permanent Set, % Final Deflection	77.0	

SBR 42

Elastomer: SBR/HSR Durometer: 92
Application: Soling

SBR 1509	70	PEG 3350	2
SBR 1094	63	Sulfur	2
220 m^2/g Silica	45	TBBS	1.5
100C Resin	5	TMTD	0.3
ODPA	1	DPG	0.3
Stearic Acid	2		
Zinc Oxide	5	Specific Gravity	1.14

MDR Cure Rate, 150°C, T_{50} minutes	24
T_{90} minutes	31
Mooney Scorch, 121°C T_5minutes	>30
Mooney Viscosity, ML_4100	65
Durometer(button)	
23°C	91
100°C	57
NBS Abrasion Index	106
PICO Abrasion Index	55
DIN Abrasion Loss, ml	196
MG Trouser Tear, kN/m	31
30 minute cure, 250°C:	
Durometer	93
M300, MPa	8.0
Tensile, MPa	18
Elongation, %	580
Ross Flex Cut Growth: kc to 500%	40
Pendulum Rebound (Z), %, 23°C	32
100°C	32

SBR 43

Elastomer: SBR Durometer: 91
Application: Rolls; Rice hulling

SBR 1502	80	Zinc Octoate	2
SBR 1900 (HSR)	20	Zinc Oxide	2
SMR CV60	10	PEG 3350	2
150 m^2/g Silica	90	Insol. Sulfur, 80%	9
Silane A189	2.4	MBS(MOR)	2
Titanium Dioxide	3	DTDM	1
100C Resin	10		
Stearic Acid	4		
ZMTI	1	Specific gravity	1.26

MDR Cure Rate, 150°C, T_{90} minutes	26
Mooney Scorch, 121°C, T_5 minutes	19
T_{30} minutes	>30
Mooney Viscosity, ML_4100	66
Garvey Extrusion, 120°C: Die Swell	2%
Edge/Surface	8A
40 minute cure, 150°C:	
Durometer(button)	
23°C	91
100°C	82
M100, MPa	11.0
Tensile, MPa	20.8
Elongation, %	230
Pendulum Rebound(Z), %, 23°C	23
100°C	60
PICO Abrasion Loss, mg, 70°C	25
100°C	45

CHAPTER 4

COMPOUNDING PRECIPITATED SILICA IN SOLUTION SBR AND BR

4.1 INTRODUCTION

The advent of stereo specific, solution types of SBR and BR created a new and advantageous polymer environment for silica to function as a reinforcing filler. Absence of fatty acids in these elastomers precludes the formation of soluble zinc contamination of the silica surface and resultant loss in silica-polymer bond strength. In terms of compound properties, solution elastomers brought about significant improvements in abrasion resistance, high strain modulus and hysteresis effects in silica reinforced compounds. In formulas which make use of “zinc-free” curative systems, abrasion resistance comparable to that of carbon black can be attained without the use of silane coupling agents.

4.2 SILICA AND CARBON BLACK

Although precipitated silica provides the highest level of reinforcement among inorganic fillers, comparisons with carbon black reveal severe deficiencies in abrasion resistance. This behavior was particularly mystifying as silica ultimate particle size is generally smaller, and surface area greater, than those of reinforcing blacks. A search for an explanation of this anomalous reinforcement behavior led to studies of silica interaction with normal cure activators such as zinc oxide, stearic acid and glycols [1], [2], [3]. This work indicated that the lack of abrasion resistance was due not to a defect inherent in the silica, but to silica surface modification by soluble zinc (zinc oxide plus stearic acid) attachment. As a result, zinc is partially removed from its role as accelerator activator, and , at the same time, becomes a barrier to effective silica-polymer bonding. With elimination of solubilizing fatty acids and use of accelerators that act more or less independently of soluble zinc, compounds of vastly enhanced cure state and abrasion resistance can be attained. With the introduction of solution polymers, this process was simplified to a matter of eliminating stearic acid, to achieve a soluble zinc-free cure system.

Solution SBR and BR compounds based on this approach allow comparisons of silica to carbon black, as in Table 4.1, that differ considerably from those previously described with emulsion polymers. Abrasion resistance is now equal for the relatively low surface area silica and HAF black. Of equal interest is the retention of the usual silica advantage in low tan delta. A durometer increase of 10 to 20% is characteristic of zinc-free systems. Major reservations in these data are lower scorch safety and much higher viscosity, both to be addressed below.

Table 4.1 Silica and Carbon Black: Zinc-Free Cure System

	150 m^2/g N_2SA Silica	**HAF, N330 Carbon Black**
Stearic acid	0	2
Zinc oxide	0	3
TBBS	2	1
MDR cure rate, 160°C, T_{90} minutes	16	9.2
Mooney scorch, 130°C, T_5 minutes	7.1	30+
Mooney viscosity, $ML_4$100	164	73
Durometer hardness	69	63
M300 modulus, MPa	4.8	7.6
PICO abrasion index	126	116
DMA tangent delta,	0.096	0.151
Ingredients: BR1220-60; SBR1215-30; SMR-10; Filler-50; 100C resin-12; ODPA-1; Sulfur-2; variables		

Carbon black compounds without silica also respond to the elimination of soluble zinc, as shown in Table 4.2. In this case, however, retention of insoluble zinc oxide in the formula is necessary to produce significant change.

Table 4.2 Zinc-free Cure System: Carbon Black

Stearic acid	0	0
Zinc oxide	0	3
MDR crosslinks, dN-m	25	32
Durometer hardness	63	68
M300 modulus, MPa	9.3	12
Tensile, MPa	20	15
Elongation, %	520	350
Compression set, 70 hrs, 100°C, %	58	39
DMA tangent delta, 60°C	0.133	0.103
Formula of Table 4.1 with TBBS 2 phr & HAF 50 phr		

Improvements in crosslink density, modulus, set and tan delta all relate to more efficient sulfur usage, in respect to both total crosslinks and a reduction of polysulfide types. Of particular interest is the reduction of tan delta to a level close to that of silica compounds. Since accelerators vary to a considerable extent in their reactivity with insoluble zinc oxide, conclusions from these results must be limited to accelerations by TBBS and similar sulfenamides. Other accelerator evaluations with silica reinforcement are discussed below.

4.3 ZINC-FREE CURE SYSTEMS

Tables 4.3 and 4.4 summarize the effects of removing soluble zinc from the cure system in solution SBR 1215 and BR 1220 compounds. In this case, the reduced tan delta is the result of a considerable increase in dynamic stiffness E', rather than a reduction in loss modulus E".

Table 4.3 Zinc-Free Cure System: SBR 1215

Zinc oxide(3), stearic acid(2)	Present	Absent
ODR cure rate, 160°C, T_{90} minutes	33	29
ODR crosslinks, dN-m	60	90
Mooney scorch, 130°C, T_5 minutes	30+	10
Viscosity, ODR minimum	15	22
Durometer hardness	70	80
M300 modulus, MPa	3.2	9.0
PICO abrasion index	53	84
DMA tan delta, 60C	0.110	0.067
Other ingredients: SBR 1215-100; 150 m^2/g N_2SA Silica-50; resin-10; ODPA-1; Sulfur-2; TBBS-2		

Table 4.4 Zinc-Free Cure System: BR/SBR1215

Zinc oxide, stearic acid, PEG	Present	Absent
MDR cure rate, 160°C, T_{90} minutes	5.1	6.1
MDR crosslinks, dN-m	22	27
Mooney viscosity, ML_4100	140	158
Durometer hardness	71	74
M300 modulus, MPa	5.7	6.5
Tensile, MPa	13	19
Elongation, %	540	680
PICO abrasion index	70	102
Compression set, 70 hrs, 100°C, %	78.4	81.0
E" DMA loss modulus, 30°C, MPa	1.7	2.37
SEM agglomerates, microns	0.05-0.12	0.03-0.08
Ingredients: BR1220-60; SBR1215-30; NR-10; 150 m^2/g N_2SA Silica -50; resin-10; ODPA-1; Sulfur-2; accelerators		

In Table 4.4, the comparison in BR/SBR1215 involves the elimination of polyethylene glycol (PEG) as well as zinc oxide and stearic acid. If soluble zinc is not available to react with silica, there is no need for the glycol barrier. TBBS at 3 phr in the control has been replaced by TBBS- 1 and DOTG- 1.5 in the zinc-free system.

In both solution SBR and the BR blend, elimination of stearic acid, zinc oxide and glycol has produced a dramatic improvement in abrasion resistance and tensile. In SBR 1215 the increase in rheometer crosslink density and 300% modulus are outstanding. In the BR/SBR blend, the change in durometer and dynamic stiffness make it difficult to draw valid comparisons for other properties. In particular, the increase in E" loss modulus can be taken to mean that there is probably no favorable change in dynamic behavior in a zinc-free system. The change in relationship between durometer and abrasion index is one of the principal characteristics of a zinc-free system. Figure 4.1 illustrates the linear relationship between these properties for normal and zinc-free compounds which differ in silica content over the 20-50 phr range. At equal hardness, zinc-free compounds produce abrasion indices 20 points greater than those of the normal zinc activated cure system. An equal abrasion index is attained with a zinc-free compound at a hardness 15 points below that of the normally accelerated control.

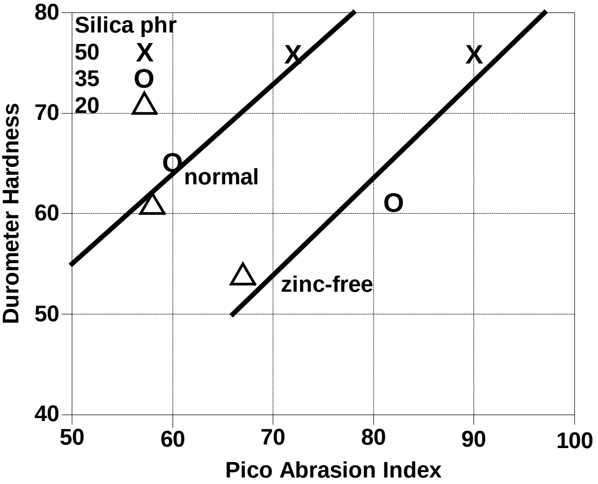

Figure 4.1 Effect of Silica Concentration on Abrasion and Hardness; Zinc-Free Compound

The scanning electron micrographs in Figure 4.2 provide evidence of the silica structural changes which take place in the zinc-free compounds in the BR/SBR/NR blend described above.

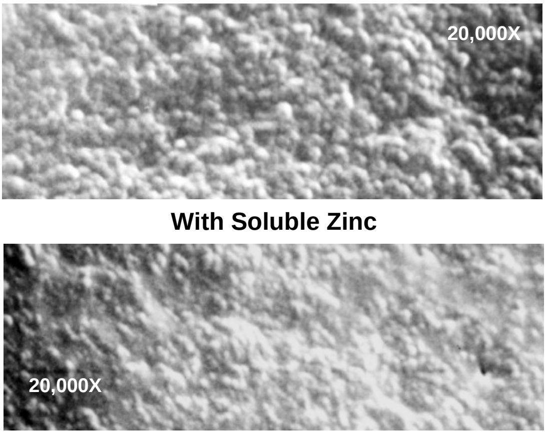

Figure 4.2 Effect of Soluble Zinc on Silica Agglomerate Size

In particular, the elimination of soluble zinc has produced a silica agglomerate size reduction from 0.09 to 0.05 microns. Generally, silica agglomerate reduction can be viewed as a change in the ratio of silica-silica and silica-polymer bond strengths. As the ratio shifts in favor of the latter, more de-agglomeration occurs during mixing. The smaller agglomerate size as well as the stronger polymer bond produce enhanced reinforcement in terms of increased modulus, tensile and abrasion resistance and hardness. Since these changes parallel those associated with silane coupling, it can be inferred that the mechanism is similar, that is, an increase in silica-polymer bond strength, which is the result of eliminating the soluble zinc barrier on the silica surface. At this point, reduced scorch safety and high viscosity indicate that more compounding changes must be investigated before the zinc-free concept will enter commercial practice. Subsequent sections address these problem areas.

4.4 ZINC-FREE CURE SYSTEMS: ACCELERATORS AND SULFUR

Selection of accelerators compatible with a zinc free environment in the previous examples has been based on evaluation of several accelerators representing basic types such as thiazoles, thiurams, sulfenamides, dithiocarbamates, guanidines and HMT (hexamethylene tetramine). In Table 4.5 these are ranked in order of their efficiency in reducing abrasion loss. The major dividing line in respect to abrasion resistance occurs between HMT and ZBDC, and places the latter together with TMTD and ZMBT in the ineffective group. Inadequate crosslinking occurs with ZBDC and ZMBT. As noted below, the presence of 1 to 3 phr insoluble zinc oxide, with or without HMT, alters much of the unmodified accelerator behavior.

Table 4.5 Zinc-free Cure System: Accelerators Compared

Accelerator 2 phr	MDR Xlinks dN- m	PICO mg loss	M300 MPa	Comp. Set %
MBTS	20	19	4.3	90
TBBS	25	22	5.3	88
DPG	23	22	5.5	80
DPTH	28	24	6.3	81
HMT	28	26	3.2	92
ZBDC	13	41	2.6	83
TMTD	28	46	5.3	82
ZMBT	15	50	1.9	96
Other ingredients: BR1220-55; SBR1205-35; NR-10; 150 m^2/g N_2SA Silica -50; C.I.resin-12; ODPA-1; Sulfur-2				

Explanation of the effectiveness of thiazoles, sulfenamides and guanidines in zinc-free systems can be related to their dissociation capabilities. These accelerator types, as well as HMT, are known to dissociate completely to the corresponding amines - without the presence of zinc oxide. The failure of the methyl thiurams to act in a zinc-free system can also be related to their normally slight dissociation to amine forms. Because of its favorable combination of abrasion resistance, crosslinking, modulus and safety, TBBS (modified with insoluble zinc oxide and HMT) has been the accelerator of choice in many of the zinc-free development studies described below.

Most of the zinc-free formulas reported in these pages contain 2 phr sulfur. Since these zinc-free compounds are somewhat deficient in age resistance and dynamic properties, the possibilities of improvement through low sulfur (0.5 phr) content are of obvious interest. Results vary, dependent on both accelerator and polymer types. In the BR/NR polymer blend, which forms the basis for the most successful examples of zinc-free compounding, low sulfur compounds all suffered unacceptable losses in PICO abrasion indices. Accelerators evaluated included TBBS (also in the 2 phr control), TBzTD, Zisnet, DPTH, and TDTM. Age resistance, in terms of both actual and retained elongation, is considerably improved in all low sulfur compounds. As seen in Table 4.6, the situation changes when the polymer blend includes SBR 1215 in place of natural rubber with DPTH as the sole accelerator.

Table 4.6 Zinc-free Cure Systems; Sulfur Content

Sulfur	2	2	1	0.5
DPTH	2	2	2	2
Zinc oxide	2	0	0	0
ODR cure rate 160°C, T_{70} minutes	9.6	19	16	11
Mooney scorch 130°C, T_5 minutes	2.5	12	11	9.8
Durometer: Original	70	70	69	67
Aged 700 hrs, 90°C	79	90	87	80
Elongation, %, Original	525	455	690	705
Aged 700 hrs, 90°C	95	2	5	85
PICO abrasion index	95	100	95	100

The objective of improving age resistance is achieved here, with no sacrifice in abrasion resistance. Addition of zinc oxide to the 2 phr sulfur compound is also effective but only with a complete loss of scorch safety. The three non-zinc compounds show no significant differences in abrasion index or compression set. Flexometer set and heat build-up are slightly higher at 0.5 sulfur. A more detailed discussion is available in reference [1].

4.5 ZINC-FREE CURE SYSTEMS: POLYMER EFFECTS

Accelerator efficiency, as defined by compression set reduction, depends to a surprising degree on polymer type, in respect to whether BR or solution SBR predominates. Compression set in a BR/NR blend is not affected by any of the accelerators noted above, with the exception of TBzTD, which also degrades abrasion. However, the replacment of NR by only 25 phr solution SBR1215 produces significant reductions in both set and heat build-up, strong evidence of a reduction in polysulfide crosslinks. This response is probably related to the high vinyl content of the SBR. The comparison in Table 4.7 between BR and solution SBR at the 70 phr level reveals the significant differences.

No significant changes are found in Mooney viscosity, pendulum rebound at 23°C and 100°C, flexometer heat build-up or dynamic modulus and tan delta. The most startling difference in the solution SBR compound is the lack of aging resistance (700 hours at 90°C). Predictably, both abrasion index and tear resistance decline in SBR, although the combination of 99 PICO index and 15 kN/m trouser tear predicts a high level of performance.

Table 4.7 Zinc-free Cure System: Polymer Effects

BR 1220	70	30
SBR 715	--	70
SMR	30	--
MDR cure rate 150°C, T_{90} minutes	8.0	21
Mooney scorch 130°C, T_5 minutes	18	16
Mooney viscosity, ML_4100	104	110
Durometer hardness	73	79
M300, MPa	4.9	5.9
Elongation, %	800	615
Aged elongation, %	300	65
PICO abrasion index	145	99
MG trouser tear, kN/m	22	15
Compression set, 70 hrs, 100°C, %	90	79
Other ingredients: 150 m^2/g N_2SA Silica -50; Resin-10; SW-PC-1; Sulfur-2; TBBS-2; Zinc oxide-1; HMT 2		

4.6 ZINC-FREE CURE SYSTEMS: ZINC OXIDE AND HMT

It became apparent from initial compounding studies that, without insoluble zinc oxide in the formula, heat aging resistance was seriously compromised, as illustrated in Figure 4.3. However, it was also apparent that introduction of 1 or 3 phr can lead to significant losses in process safety, abrasion index, modulus, 100°C resilience and rheometer crosslinks. But these unfavorable changes do not occur with all accelerators, and, in some cases, the reverse is true.

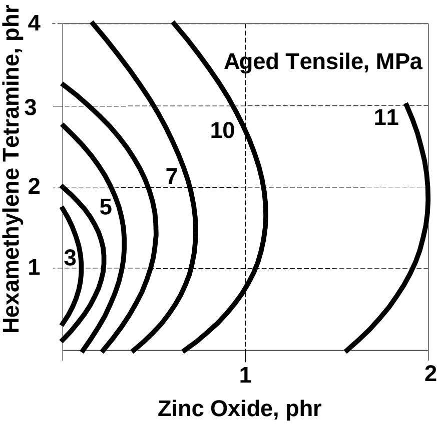

Figure 4.3. Effect of HMT and ZnO Concentration on Aged Tensile

Table 4.8 Zinc-Free Cure Systems: Accelerators and Zinc Oxide

Accelerator 2 phr	**T_{50} 150°C**	**T_5 121°C**	**Xlink dN-m**	**Duro A**	**M300 MPa**	**PICO index**	**DIN ml**
T\BBS	9	9	17	63	3.7	192	64
TBBS +1 ZnO	11	7	16	64	4.3	106	129
CBS	11	7.1	11	62	3.7	196	83
CBS +1 ZnO	11	10	13	62	3.6	131	141
DCBS	8.5	15	10	64	4.4	199	68
DCBS +1 ZnO	9.3	13	19	63	4.2	198	69
MBTS	24	29	6	63	3.3	89	89
MBTS +1 ZnO	9.5	30+	4	63	3.6	86	86
MBTS/DPTH	10	25	14	64	5.5	156	61
MBTS/DPTH +1 ZnO	9.5	30+	9	62	4.7	139	97
TBzTD	18	30	4	60	2.9	102	102
TBzTD +1 ZnO	5.9	19	12	66	4.6	316	69
ZBzDC	6.5	23	9	61	2.9	150	70
ZBzDC +1 ZnO	6.1	16	9	65	4.4	264	69

Ingredients: BR1220-70; NR-30; 160 m^2/g N_2SA Silica -45; Vest.8012-10; CI resin-10; ODPA-1; Sulfur-2; accelerator; zinc oxide

The only accelerators in Table 4.8 that achieve optimum abrasion resistance without zinc oxide are TBBS, DCBS, MBTS/DPTH and, possibly, ZBzDC. Contrary to the initial findings in a BR/SBR base formula, MBTS is lacking in abrasion resistance (DIN), but addition of 0.5 DPTH corrects the problem with accompanying improvements in crosslinks, cure rate and modulus. Property *degradation* by zinc oxide is seen with TBBS, CBS and DPTH/MBTS. Among those sulfenamide accelerators which function independently of zinc, TBBS achieves highest crosslink density. ZBzDC, although deficient in crosslink density, provides significantly lower compression set (not shown) than any of the others. This reduction in set (to 70%) is one of the rare instances in zinc-free compounds where a lower proportion of polysulfide crosslinks is attained. Zinc oxide addition offers the greatest improvement to the benzyl modified thiuram, TBzTD, and in fact this compound offers the best combination of scorch safety, cure rate, hardness, modulus and abrasion resistance. Benzyl modified thiurams and dithiocarbamates also have the advantage of being environmentally acceptable. A ZBzDC compound is provided as Formulary compound BR 7 and others in the section on plasticization.

As noted above, zinc is necessary for heat resistance in zinc-free compounds. This requirement presents a problem for those accelerators, TBBS, CBS, and MBTS/DPTH, which lose their effectiveness in the presence of insoluble zinc. A sufficient remedy in the case of TBBS was found in the use of HMT at the 2 phr level to serve as a barrier to whatever amount of abrasion degrading silica-zinc reaction was taking place, as seen in Figure 4.4. As seen in Table 4.9, HMT also has the remarkable ability to change the shape of the rheometer curve, to produce both added scorch safety and faster crosslinking, with lower viscosity and increased crosslink density.

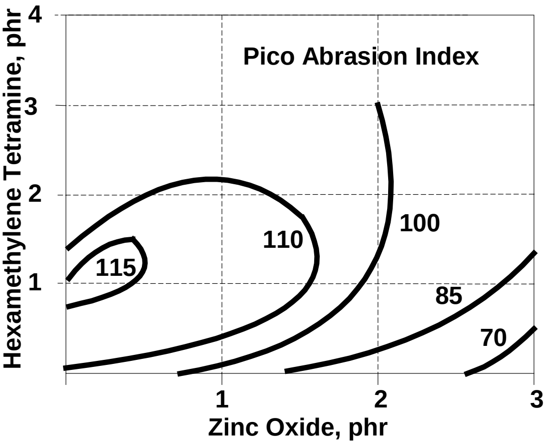

Figure 4.4. Effect of HMT and ZnO Concentration on Abrasion

Table 4.9 Zinc-Free Cure System: HMT Effects

	Silica Surface Area					
	150 m^2/g N_2SA			**180 m^2/g N_2SA**		
Zinc oxide	0	3	3	0	3	3
HMT	0	0	2	0	0	2
MDR cure rate, 160°C, T_{90} min	13	9	17	14	27	9
MDR crosssllinks, dN-m	30	26	31	32	26	38
Mooney scorch, 130°C, T_5 min	8	16	17	13	15	19
Mooney viscosity, $ML_4$100	127	129	115	142	136	117
Durometer hardness	74	70	74	79	70	79
M300 modulus, MPa	5.0	4.5	4.4	4.1	3.1	4.7
Pendulum rebound,100°C, %	56	52	58	51	45	52
PICO abrasion index	82	69	76	110	69	96
Flexometer heat build-up, ºC	41	Blow	38	52	Blow	47
Other ingredients: BR1220-60; SBR1205-30; NR-10; silica-50; 100C resin-10; ODPA-1; Sulfur- 2; TBBS- 2						

HMT has succeeded in eliminating or reducing the property degradation associated with the presence of zinc oxide alone. The higher surface area silica compounds suffer more zinc induced degradation in modulus, abrasion and rebound. A summary of the benefits of the HMT-zinc oxide additive system includes major improvements in heat aging resistance, scorch safety, and compression set. A good example of the HMT compounding technique appears in Formulary compound B4A. Materials evaluated as replacements for HMT include butraldehyde aniline (Accelerator 808), piperidinium pentamethylene dithiocarbamate (PPD), trimethylthiourea(TMTU), hexamethylenediamine carbamate (DIAK #1), and Echo A. Unfortunately all of these are prohibitively more active at processing temperatures than is HMT. The accelerating effect of HMT is not evident in normal cure systems.

The action of HMT in eliminating zinc contamination of silica relates to two possible mechanisms: HMT forms a zinc complex not reactive with silica silanols, or HMT buffers the silica surface to prevent soluble zinc contamination. Since the desirable alteration in the rheometer curves occurs with or without zinc present, the silica surface buffer mechanism appears to be the more likely explanation.

If the assumption that HMT acts as a barrier to zinc contamination of the silica surface is true, then a similar function may be expected from a glycol, the original barrier material of choice in silica compounding technology. However, In the example in Table 4.10, a reversal of the HMT behavior occurs (greater DIN loss and lower PICO index) when DEG is present with zinc oxide.

Table 4.10 Zinc-free Cure System: Diethylene Glycol (DEG) Effect

Diethylene Glycol (DEG)	0	2	0	2
Zinc Oxide	0	0	1	1
MDR cure rate, 150°C, T50	2.9	3.8	4.4	2.4
MDR crosslinks @ 10', dN-m	14	12	9	22
Durometer hardness (15 min/150°C)	64	64	62	68
PICO abrasion index	156	143	139	83
DIN abrasion loss, mg	61	70	97	121
M300 modulus, MPa	5.5	4.3	4.7	6.2
Pendulum rebound, 100°C, %	62	64	53	73
Flexometer heat build-up, ºC	42	41	53	18
Compression set, 70 hrs, 100°C, %	84	90	84	62
Other ingredients: BR1220-70; NR-30; 150 m^2/g N_2SA Silica -45; 100C resin-10; ODPA-1; Vest.8012-10; Sulfur-2.7; MBTS- 2; DPTH 0.5 single pass Banbury to 133°C				

The accompanying marked improvement in both crosslink density and the properties dependent on crosslinking indicate that DEG , in contrast to HMT, has made zinc more available for accelerator complexing and silica contamination.

4.7 ZINC-FREE CURE SYSTEMS: EFFECTS OF ADDITIVES

Another view of additives to a zinc-free cure system, in Table 4.11, makes use of a BR/SBR/IR translucent formula based on 35 phr of a 145 m^2/g N_2SA silica and no zinc oxide, which is used to evaluate soluble and insoluble zinc compounds (zinc octoate and zinc stearate), two glycols (DEG and hexane diol) and HMT.

Table 4.11 Zinc-Free Cure System: Various Additives

Additive:	None	octoate	stearate	DEG	diol	HMT
MDR 150°C, T_{50} min	3.7	4.9	4.0	7.0	9.7	5.9
MDR crosslinks,dN-m	16	15	14	12	14	16
Scorch T_5 min/121°C	13	18	15	26	30+	23
Mooney visc, ML_4100	109	110	86	75	71	87
Mill sticking	sl	sl	none	sl	sl	sl
Durometer hardness	52	53	53	52	49	53
Aged durometer	90	70	86	86	86	71
M300 modulus, MPa	2.6	2.6	2.3	2.1	2.1	2.5
Tensile strength, MPa	20	20	18	14	12	19
PICO abrasion index	85	72	74	85	77	82
Light transmittance, %	17	48	31	34	41	48
Color shade	gray	lt yl	tan	dk tan	lt yl	yl
Ingredients: SBR1215-40; BR1220-30; IR2200-30; 150 m^2/g N_2SA Silica -35; DOP-10; ODPA-1; sulfur-1; TBBS-1; OTBS-1; additives-2						

The relatively low silica content reduces the prospect of finding any startling property changes. However, hexane diol interaction with silica is sufficient to produce a significant drop in durometer and viscosity. Both glycols have a fatal influence on tensile and modulus, a further indication of silica - polymer blocking. Although the formula contains no zinc oxide, there is sufficient soluble zinc from zinc octoate to block polymer bonding and produce the lowest abrasion index. The unavailability of active zinc from zinc stearate is reflected in its lack of aging resistance. In contrast , only zinc octoate and HMT provide any hardness stability during aging (100°C for 330 hours), although the latter would appear to operate more in the conventional amine antioxidant functionality. This function, rather than silica - polymer blocking, is also indicated by its high abrasion index. Light transmittance is improved by all additives with HMT and zinc octoate being the most effective. Their function appears to be one of removing cure reaction residues, reducing the size of silica agglomerates and preventing oxidative discoloration of organic ingredients.

All additives act to reduce cure rate and scorch, but only DEG shows significant loss in crosslink density, A fairly linear relation appears between crosslinks and 300% modulus, but not so with abrasion index. In respect to crosslinking and other properties, HMT is the preferred additive here, as it is also in zinc-free systems which contain insoluble zinc oxide. HMT appears in many of the zinc free formulas in the formulary section.

4.8 ZINC-FREE CURE SYSTEMS: SULFUR CONTENT

The primary interest in sulfur content is to achieve improved age resistance at low concentrations, without sacrificing abrasion resistance. In Table 4.12, based on a formula without added zinc oxide or HMT, the anticipated improvement at low sulfur content does not occur. Resistance to aging degradation (700 hours at 90°C) is unaffected by sulfur content, and is improved only by the addition of 1 phr zinc oxide and HMT. Zinc oxide alone (not shown), lowers abrasion resistance , particularly at 0.5 phr sulfur.

Table 4.12 Zinc-free Cure System: Sulfur, Zinc Oxide and HMT

Sulfur	0.5	0.5	1.0	2.0	2.0	4.0
TBBS	3	3	2	2	2	2
Zinc oxide	0	1	0	0	1	0
HMT	0	2	0	0	2	0
MDR, 160°C, T_{50} minutes	5.2'	5.1'	3.6'	3.4'	3.0	3.7
MDR.crosslinks,dN-m	16	15	21	29	26	38
Durometer, original	56	63	63	68	73	74
Durometer, aged*	85	75	90	86	81	88
M300 modulus, MPa	2.1	3.2	3.4	4.9	5.3	7.8
Tensile, original, MPa	7.3	10	15	14	19	9.2
Tensile, 700 hrs, 90°C, MPa	5	8	6	6	9	4
Elongation, %, original	805	700	890	660	725	345
Elongation, aged*	1	330	1	1	170	1
PICO abrasion index	72	55	93	104	94	93
Compression set, 70hr, 100°C	88	97	81	74	89	67
Other ingredients: BR1220-65; SBR1215-35; NR-10; 150 m^2/g N_2SA Silica - 50; resin-10; ODPA-1						

Further attempts to achieve a satisfactory combination of aging and abrasion resistance at 0.5 sulfur through the use of sulfur donors and TBBS are also based on a 70/30 blend of BR and natural rubber, the combination used in many of the zinc free compounds described previously. It is obvious, in Table 4.13, that these donors, though promising in various aspects, are, with sulfur at 0.5, not capable of matching the 100 - 160 abrasion index range of compounds cured with normal sulfur content and a zinc-free system.

Table 4.13 Zinc-free Cure System: Sulfur Donors, Low (0.5 phr) Sulfur

TBBS	3	2	2	2	2
TBzTD	0	1	0	0	0
triazine trithione	0	0	2	0	0
DPTH	0	0	0	2	0
DTDM	0	0	0	0	2
MDR crosslinks, dN-m	13	25	15	28	26
Durometer	63	69	64	70	71
PICO abrasion index	55	76	53	77	84
Aged elongation, %	330	230	310	155	175
Other ingredients: BR1220-70; NR-30; 150 m^2/g N_2SA Silica -50; resin-8; oil-8; ODPA-1; sulfur-0.5; Zinc oxide-1; HMT-2					

If a sulfur content of 2 phr is accepted as a minimum, accelerator TBBS offers the most promising compound performance in terms of aging, abrasion resistance and trouser tear strength, in either BR /NR or solution SBR, as seen in Table 4.14.

Table 4.14 Zinc-free Cure System: TBBS in BR/NR and Soln SBR

BR1220	70	30
SBR 1215	0	70
SMR	30	0
150 m^2/g N_2SA Silica	50	40
Ciptane® I	0	11
TBBS	2	2
MDR, 150°C, T_{90} minutes	6	6.7
Mooney scorch, 130°C, T_5 minutes	15	16
Mooney viscosity, ML_4100	109	110
Durometer hardness	76	79
Elongation, %	665	615
Elongation, 700 hrs, 90°C, %	430	65
PICO abrasion index	155	99
MG trouser tear,kn/m	22	15
Comp.set, 70hrs, 100°C, %	90	77
Flexometer heat build-up, ºC	34	30
Other ingredients: 100°C resin-10; AO PC-1; Zinc oxide-1; HMT-2; sulfur-2; TBBS- 2		

Acceleration by 2 phr TBBS alone avoids the questionable loss of scorch safety which accompanies the use of TBzTD, Zisnet and DPTH. In respect to abrasion index, the property of most interest, we find all compounds, except that with TBzTD, to have PICO indices in the HAF carbon black range of 100 to 200. This range is characteristic of zinc-free BR/NR 70/30 blends; a similar ratio of BR and *solution SBR* provides significantly lower PICO indices, but with lower compression set. This trend continues as solution SBR (715) becomes the dominant elastomer.

In Table 4.15, addition of 2 phr triazine trithione (Zisnet®) to the TBBS acceleration provides a faster cure rate and a significant reduction in compression set - with no meaningful loss in either abrasion index or trouser tear strength. However, a decline in scorch safety at 2 phr indicates that commercial trials should begin with triazine trithione at 1 phr. The other accelerators in this series (TBzTD, TIBTD, and ZIBDC, not shown) failed to maintain either tear strength or abrasion resistance.

Table 4.15 Zinc-free Cure System: Solution SBR and Zisnet

TBBS	2	2
triazine trithione	0	2
MDR cure rate, 150°C, T_{50} minutes	6.7	4.0
Mooney scorch, 130°C, T_5 minutes	16	7.0
Mooney viscosity, ML_4100	110	118
Durometer	79	82
Elongation,original, %	615	525
Elongation, 700 hrs, 100°C, %	65	115
PICO abrasion index	99	101
MG trouser tear, kN/m	15	12
Compression set, 70 hrs, 100°C, %	79	42
Other ingredients SBR715-70; BR1220-30; 150 m^2/g N_2SA Silica-40; Ciptane 1-11; Resin-5; Oil-5; A.O. HP-1; Sulfur-2; ZnO-1; HMT-2		

The relatively high set values in many zinc free compounds signify a high proportion of polysulfide crosslinks, a condition which is necessary to produce high trouser tear strengths. The combination of trouser tear strength and high abrasion resistance in all zinc-free compounds appears to be unattainable by other compounding technologies.

4.9 ZINC-FREE CURE SYSTEM: ANTIOXIDANTS

It is to be expected that the unprotected silica surface in a zinc-free environment will be sensitive to reaction with amine and phenolic antioxidants. This prediction is partially verified in the study described in Table 4.16 where various antioxidants at the 2 phr level produce a significant reduction in the PICO abrasion index. *However, no such reduction takes place at antioxidant concentrations of 1 phr,* except in the case of HPPD where the index actually rises, to 217 (not shown).

Table 4.16 Zinc-free Cure System: Antioxidants

Antioxidant, 2 phr	None	PC	ODPA	ZMTI	HPPD	TMQ
MDR,150°C, T_{90} min	7.5	9.3	8.0	4.8	6.7	6.9
Scorch, 130°C, T_5 min	16	18	17	8.0	16	19
Durometer: Original	74	74	73	72	74	70
Aged 100°C	85	82	83	84	86	82
Aged 90°C	83	80	84	82	84	81
Tensile, MPa:						
Original	17	17	18	18	19	19
Aged 100°C	2.9	8.0	7.0	4.8	7.9	8.4
Aged 90°C	7.0	12	13	8.5	14	12
Elongation, %:						
Original	755	810	810	710	775	795
Aged 100°C	25	185	135	75	120	170
Aged 90°C	175	325	270	210	290	310
PICO abrasion index	135	107	103	106	110	89
Sun exposure, skin	yes	yes	yes	yes	no	sl.

Other ingredients: BR1220-70; NR-30; 150 m^2/g N_2SA Silica-50; resin-10; Sulfur-2; TBBS-2; ZnO-1; HMT-2

No significant antioxidant influence is found on hardness, 300% modulus, compression set or rebound. ZMTI (zinc mercaptotoluimidazole) is the exception in respect to cure rate (faster), modulus (higher) and aging resistance (poorer). Surprisingly, the usual superiority of HPPD (dimethylbutylphenyl p-phenylenediamine) and TMQ (polymerized dihydrotrimethylquinoline) is not much in evidence in respect either to aged tensile or to aged elongation. Not unexpectedly, the only materials effective in resisting hard skin formation during sunlight exposure are the two which offer an ozone resistance function. It appears that any of these antioxidants, except ZMTI and including the phenolic derivative, PC, is suitable to provide adequate age resistance to zinc free compounds. As noted previously, the presence of a minimum of 1 phr zinc oxide is required to attain satisfactory age resistance.

4.10 ZINC-FREE CURE SYSTEMS: PROCESSING

Mixing procedures for BR/NR zinc free compounds involve no unusual procedures for either addition order or temperature. Many of the preceding examples were mixed in a 00 Banbury to stock temperatures of 135 to 140ºC with zinc oxide, HMT, sulfur and accelerators added in a second Banbury stage. Accelerator evaluations directed to footwear applications were mixed in a single stage to 130ºC, with sulfur added on the mill. Zinc oxide addition in the first Banbury stage produces improved Garvey extrusion ratings in terms of edge definition; reductions in viscosity and rheometer crosslinks are barely significant.

When the Banbury 1 batch temperature is increased to 165°C and beyond, significant changes take place in viscosity, hardness and dynamic modulus, as sen in Table 4.17.

Table 4.17 Zinc-Free Cure System: Mixing Times and Temperatures

Banbury Time and Temperatures minutes / ºC	3 / 138	6 / 166
MDR cure rate, 150°C, T_{50} minutes	5.4	8
T_{90} minutes	21	22
MDR crosslinks, dN-m	27	25
Mooney viscosity, $ML_{4}100$	108	88
Durometer hardness,(21 min/150°C)	75	69
DMA dynamic modulus, 60°C		
E', MPa	18.5	11.9
E"	1.65	1.19
Tangent delta	0.089	0.101

Ingredients: BR1220-70; NR-30; 150 m^2/g N_2SA Silica -50; Vest.8012-10; resin-5; ODPA-1; Banbury 2: ZnO-1; HMT-2; sulfur-2.7; TBBS-2

Properties (not shown) with no significant change due to mixing temperature include scorch safety, extrusion swell, pendulum rebound, stress/strain, trouser tear, aging and heat build-up. Because of the normally higher viscosity of zinc-free compounds, the 20% drop in Mooney is probably the most important effect here. This, and the lower durometer and dynamic modulus, are mainly de-agglomeration effects, brought on by free water loss at the high mixing temperature. When accelerators such as MBTS and DPTH (not shown) are included in the first Banbury at stock temperatures above 140°C, tear and tensile strengths degrade, but abrasion indices (DIN and PICO) remain unchanged.

High temperature mixing effects for BR compounds with *normal acceleration* also show major reductions in viscosity and hardness, and also, in contrast to the zinc-free compounds, a significant reduction in cure rate.

Blends of BR and SBR in the zinc-free mode suffer from poor milling characteristics: stiffness, lack of tack, ballooning, etc. This situation is best corrected by the substitution (for SBR) of 10 to 30 phr natural rubber or polyisoprene. It is because of this processing requirement that many of the compounding studies under discussion make use of a 70/30 blend of BR1220 and natural rubber, a combination which has proven to provide excellent processing behavior. When solution SBR (particularly oil extended) is the predominant elastomer, mill sticking becomes a problem. One solution to this is illustrated in Formulary compound BR 26 where stearic acid (in its lubricant role) replaces the usual 1 phr of zinc oxide. In this case, the absence of soluble zinc maintains the zinc-free mechanism and associated improvement in abrasion resistance - with a sacrifice in heat resistance. Mill sticking can also be ameliorated by an amide wax additive (Armoslip® CP), but increasing the BR content is the most effective corrective for mill sticking.

These processing considerations all lead to a recommendation for BR blended with natural rubber or IR in a 70/30 ratio as the preferred vehicle for zinc free compounding. Formulary examples include compounds BR 4, 6, 7, 8, 9, 13, 17, 20, and 21.

An increase of NR content to 50/50 produces desirable changes in viscosity and tear strength, at the expense of abrasion resistance; Formulary examples are compounds BR 2, 5, and 10.

4.11 ZINC-FREE SYSTEMS: PLASTICIZERS

Plasticizers are defined here as those materials which improve flow properties by interaction with the elastomer. In contrast to this, additives such as soluble zinc compounds interact with the silica filler to produce similar reductions in viscosity, by silica de-agglomeration. A summary of both mechanisms, presented in Tables 4.18 and 4.19, is based on a formula of BR/IR with 45 phr silica and accelerated with ZBzDC.

Plasticizer contents were selected to produce significant changes in viscosity, but as with any plasticizer study, the accompanying change in durometer makes it impossible to evaluate plasticizer effects on vulcanizate properties on an equal hardness basis. However, in this case, it is apparent that the rosin ester resin is the most effective viscosity reducer - with a relatively minor effect on DIN abrasion loss. PICO index, in contrast, shows a much greater sensitivity to reduced hardness. The effectiveness of the rosin ester is in keeping with some of the very early studies of plasticizers for silica reinforced compounds, particularly those of natural rubber, where many materials of vegetable origin were found to be the most efficient viscosity reducers. Compression set (70 hours at 100°C) combined with MDR crosslink data indicates that the plasticizing superiority of the rosin ester is achieved with an alarming loss of crosslink density and increase in set. The aliphatic resin presents less of a problem in this respect, but suffers a slightly greater loss in the DIN abrasion test.

Table 4.18 Zinc-Free Cure System: Plasticizers

Plasticizer Type	None	Naphthenic Oil	Aliphatic 100°C resin	Rosin Ester
Plasticizer Content, phr	0	15	20	20
MDR.cure rate,150°C, T_{50} min	3.0	3.0	3.0	5.0
MDR crosslinks, dN-m	11	13	9.0	6.0
Mooney viscosity, ML_4100	154	100	92	77
Durometer hardness	69	62	57	51
M300 modulus, MPa	6.2	3.7	3.9	2.3
DIN abrasion loss, ml	80	95	106	94
PICO abrasion index	211	129	88	85
Compression set, %	59	72	61	81

Other ingredients: BR1220-70; IR2200-30; 150 m^2/g N_2SA Silica 45; ODPA-1; ZnO-1; ZBzDC-2; Sulfur-2 (mill)

Table 4.19 Zinc Dimethacrylate (ZDMA): Viscosity Reduction

ZDMA 634, phr	0	2	4	6
MDR cure rate, 150°C, T_{90} minutes	5.0	15.0	30	23
MDR crosslinks at T90, dN-m	13	14	12	16
Mooney viscosity, ML_4100	149	120	93	69
Durometer hardness	69	68	62	59
M300 modulus, MPa	6.6	4.3	2.4	2.4
DIN abrasion loss, ml	71	73	80	86
100C Rebound (Z), %	57	56	52	52
Flexometer Heat build-up, ºC	36	41	46	46
Compression set, 70 hrs, 100°C,%	69	79	92	91
DMA dynamic modulus, 60°C, 1Hz				
E', MPa	7.8	7.7	5.2	4.4
E", MPa	0.83	0.91	0.88	0.85
Tangent delta	0.107	0.109	0.159	0.195

base formula in Table 4.18

4.12 ZINC-FREE SYSTEMS: ADDITIVE PLASTICIZERS

The action of additives on silica structure produces many of the process and vulcanizate changes noted for the plasticizers above, but through a different mechanism. In this case the mechanism is silica de-agglomeration rather than polymer plasticization. In normal zinc systems, several glycols fall under the classification of additives. In a zinc-free system, diethylene glycol (DEG) has a positive effect on crosslinking and set, but little influence on viscosity or vulcanizate properties. The major additive activity is found from zinc compounds such as zinc soaps and zinc dimethacrylate (see Table 4.19). These materials have been found to surpass HMT as viscosity reducers.

The lack of any significant variation in rheometer crosslinks indicates that reduced silica-polymer bonding is the major cause of the degradation in modulus, abrasion and dynamic properties which occurs as ZDMA content rises. At the same time, rising compression set values indicate an increase in polysulfide crosslinking. Results similar to these for ZDMA are also obtained with a zinc soap (e.g., Struktol® A50). Formulary examples of the use of ZDMA include compounds BR 2, 5, 10 and 15. Everything considered, this is not an encouraging route to plasticizing zinc-free compounds. A more promising approach is discussed in the following section.

4.13 SILANE COUPLING: PRETREATED SILICA

Before a discussion in detail on the role of mercaptosilane coupling agents in improving silica reinforcement of solution polymers, it will be helpful to describe a commercial silane treated silica, Ciptane, in respect to the advantages of avoiding Banbury addition of silanes. The purpose of developing a mercaptosilane treated silica was to eliminate the noxious odor of mercaptopropyltrimethoxysilane (MPTS), the most efficient of all silanes, during mixing and processing operations. The Ciptane products are odor free and subject to no mixing temperature limitations. The odor problem was also solved by the development of di- and tetrasulfide products. Unfortunately, the higher molecular weight of these products required a doubling of concentration to attain reinforcement equal to that by MPTS. There are a number of Ciptanes, which include various silica types and silane contents. In a comparison of pre-treatment versus separate silane addition, Table 4.20, the silica surface area is 180 m^2/g and the silane concentration is 3% (silica basis). Five replicates of each zinc free compound are averaged.

The Banbury mixing conditions here are at minimums for both time and temperature in order to produce a maximum of possible variability between and within batches. Expectations of pre-treatment or masterbatching are generally based on a belief that they will reduce variability among successive batches. In this case, only durometer and 300% modulus show an advantage (lower range) for pre-treated silica in this respect. Of greater interest here is the unexpectedly wide divergence in some properties between Ciptane and separate silane addition compound averages. Faster cure rate, lower viscosity, and increased modulus are all evidence of more silane reactivity with separate addition. However, the abrasion differences, which favor Ciptane, point in the opposite direction. Explanations include the unavoidable difference in production batch identity of the two silicas. Generally, in other polymers and other cure systems, comparisons of treated silica versus separate silane addition have shown a loss of efficiency of up to 20% in the pre-treated form. This difference is possibly due to a greater heterogeneity in the room temperature dry blended product. The hydrolyzed alkoxy groups react immediately on contact with silica surface silanols.

Table 4.20 Silane Treated Silica; Zinc-Free Cure System

	Silane-Treated Silica		**Separate Silane Addition**	
	Average	Range	Average	Range
MDR.cure.rate 150C,T_{50} minutes	4.5	0.6	3.6	0.3
Mooney scorch 121C,T_5 minutes	17.6	3	15.4	1
Mooney viscosity ML_4100	68	1	59	2
Durometer hardness	68	3	68	6
M300 modulus, MPa	7.5	0.2	8.5	0.6
Tensile, MPa	17	4	14	4
Elongation, %	575	100	435	100
DIN abrasion loss, ml	65	9	75	12
PICO abrasion index	205	65	165	25

Ingredients: BR1220-65; SBR303-25; IR2200-10; Silica-40; MPTS-1.2; Oil-5; ODPA-1; ZnO-1; HMT-2; TBBS-2; Sulfur(mill)-2; Banbury single stage 3 min to 100°C stock temperature

4.14 SILANE COUPLING

The major benefit arising from the use of mercaptosilane in silica reinforced solution SBR and BR compounds is an improvement in abrasion resistance, to the point of equaling that of carbon black. Auxiliary benefits include low heat build-up and set, improved dynamic properties and lower viscosity. The major disadvantage is loss of trouser tear strength. In zinc free systems, which are characterized by high viscosity, viscosity reduction is of particular importance. The action of mercaptopropyltrimethoxysilane (MPTS), in the form of Ciptane silane treated silica, to reduce viscosity in both normal and zinc-free curing systems is demonstrated in Table 4.21 in the same BR/NR, 70/30 base formula used in preceding studies.

Table 4.21 Silane Coupling: Viscosity Reduction

Cure system;	**Soluble zinc**		**Zinc-free**	
150 m^2/g N2$_S$A Silica	50	-	50	-
Ciptane I, 3% MPTS	-	51	-	51
MDR cure rate, 150°C, T$_{90}$ minutes	9.9	9.4	6.9	4.6
MDR crosslinks, dN-m	32	34	23	25
Mooney scorch, 130°C, T$_5$ minutes	30+	30+	16	20
Mooney viscosity, ML$_4$100	88	72	112	82
Durometer	74	74	73	75
M300 modulus, MPa	4.5	9.7	5.6	10.3
Elongation, %	640	470	660	485
Compression set, %	77	64	87	74
PICO abrasion index	86	137	126	193
MG trouser tear, kN/m	7.8	3.9	12	6.0
DMA dynamic modulus, 1 Hz, 60°C				
E', MPa	17	10	16	12
E"	1.4	0.8	1.8	1.2
Tan delta	0.81	0.82	0.110	0.104
E' at 0ºC	23	12	21	15

The significant reduction in viscosity of the silane compounds is achieved without change in cure rates or crosslink density. Unfortunately, this viscosity reduction is the result of a partial destruction of the silica network structure, which leads to increased extrusion swell and roughness. The data in this study also reveal some interesting differences between normal (stearic acid) and zinc-free curing systems. The latter provide increased curing and scorch activity and, at equal 2 phr sulfur content, a considerable loss of crosslinks. However, this drop in crosslink density has little impact on the vulcanizate properties of these compounds, an observation which provides another example of the strong influence of zinc-free silica on improving polymer bonding and, thereby, reinforcement.

Of major interest here, in addition to improved abrasion resistance, is the reduction in both elastic and loss dynamic modulus. The reduced loss modulus, E", in particular, relates directly to the effectiveness of silane coupled silica in lowering the rolling resistance of tire treads. A less well known silane effect is the reduction in low temperature modulus, E', a phenomenon which may have led to the use of coupled silica in winter tire treads.

The two principal forms of mercaptosilane are MPTS, noted above, and TESPT (triethoxysilylpropyltetrasulfide). Disulfide versions are also available. Molecular weight differences require a TESPT dosage double that of MPTS to achieve equal coupling efficiency. In addition to this requirement, TESPT use involves a minimum mixing temperature, to unblock the active mercapto group, and a maximum temperature to avoid scorching from its free sulfur content. A comparison of these materials in a BR/SBR compound in Table 4.22 includes Ciptane, the pre-treated silanized silica.

Table 4.22 Mercaptosilanes Compared; Zinc-free Cure

	Ciptane	**150 m^2/g N_2SA Silica**	
Silica, phr	42	40	40
MPTS %, silica basis	3	3	0
TESP %, silica basis	0	0	5
MDR cure rate 150°C, T_{90} minutes	7	6	10
Mooney viscosity,$ML_4$100°	92	80	92
Durometer hardness	72	72	72
PICO abrasion index: 23°C	173	196	216
70°C	133	102	92
DIN abrasion loss, ml	79	83	87
Compression set 70 hrs, 100°C, %	76	72	87
Other ingredients: BR1220-65; SBR303-25; IR2200-10; Oil-5; ODPA-1; ZnO-1; HMT-2; sulfur-2; MOR-2; single stage Banbury 3 min' to 120°C; sulfur on mill			

Obviously, restricting the mixing temperature to 120°C presents a question as to the complete dissociation of TESPT. Evidence that a higher temperature would be advisable for this material is seen in the higher set, DIN and cure rate values for the TESPT compound. These deficiencies are also evidence of the better processing flexibility of the silanized silica, Ciptane. In other respects, scorch, crosslink density, durometer, stress/strain and rebound properties show little variation.

The data here and other observations on silane coupling of silica in solution polymers are summarized in Table 4.23.

Table 4.23 Features of Silane Coupling in Solution Polymers

Positive Features	**Negative Features**
Viscosity reduced	Scorch safety variable
Abrasion resistance increased	Tear strength reduced
Set and heat build-up reduced	Elongation reduced
Dynamic modulus reduced	Aged tensile reduced
Low temperature flexibility	
Aged elongation retention	

When the silane content is increased from the 3% (silica basis) in the preceding examples to the 5-6% level used in tire tread applications, and the polymer blend contains 25 phr emulsion SBR, relationships between normal and zinc-free systems with silane coupled silica are somewhat different, as seen in Table 4.24.

Table 4.24 Silane Coupling at 5-6%: Normal and Zinc-free Systems

	Cure system	
	Normal	Zinc-free
Stearic acid	2	0
PEG 3350	1	0
HMT	0	1
Ciptane, % mercaptosilane (MPTS)	6	5
MDR cure rate, 150°C, T_{90} minutes	14	20
MDR 150°C crosslinks, dN-m	25	34
Mooney scorch 121°C, T5 minutes	11	30+
Mooney viscosity, ML_4100	64	58
Durometer hardness	64	66
Elongation, %	310	375
DIN abrasion loss, ml	73	88
Dynamic coefficient of friction, wet Al	0.54	1.24
Pendulum rebound, 100°C, %	67	65

Ingredients: BR1220-65; SBR1502-25; IR2200-10; Ciptane-53/52; Vest.8012-10; 510 oil-10; ODPA-1; ZnO-2; Sulfur-2.5/ 3.0; TBBS-1/ 2; MBTS-1.5/ 1.0; Banbury mixed 3 min to 140°C stock

The fatty acid content of the SBR1502 probably alters the insoluble zinc content of the zinc-free compound and thereby modifies the usual lower crosslink density and higher viscosity characteristics of zinc-free compounds. PICO abrasion indices are essentially equal for the two compounds, but DIN losses (73 and 88 ml, respectively) favor the normal cure system. Compression set remains higher with a zinc-free cure, 82 versus 62%. Of great interest in footwear applications is the remarkable increase in the coefficient of friction in the zinc-free compound, which occurs notwithstanding a slightly higher compound hardness.

Examples in the Formulary of silane coupled silicas, mainly in zinc-free curing systems, include compounds BR 3, 11, 12, 16, 17, 20, 22, 24, 26, 27, 28 and 31.

4.15 ZINC-FREE CURE SYSTEMS: SURFACE AREA EFFECTS

In normal cure systems, the influence of surface area (primary particle size) on reinforcement properties is marginal. In contrast, a zinc-free environment allows the reinforcing advantages of smaller particles and agglomerates to become apparent in terms of enhanced abrasion resistance at high surface areas, as seen in Table 4.25.

Table 4.25 Zinc-free Cure Systems: Silica Surface Area Effects

Silica Surface Area, m^2/g N_2SA	150	220	250
MDR cure rate 150°C, T_{50} minutes	5.3	4.8	4.5
MDR crosslinks, MH-ML, dN-m	25	26	24
Mooney viscosity ML_4100	86	107	134
Durometer hardness	69	69	71
M300 modulus, MPa	5.2	5.3	6.6
PICO abrasion index	96	117	161
MG trouser tear, kN/m	9.7	12	9.3
Compression set, 70 hrs, 100°C, %	83	81	82
DMA dynamic modulus, 1 Hz, 30°C			
E", MPa	1.33	1.55	1.96
E'	13.2	14.3	17.3
Ingredients: BR1220-70; SBR715-20; NR-10; silica-42; 100°C resin-10; ODPA-1; Zinc Oxide-1; HMT-2; sulfur-2; TBBS-2			

The major surface area effects in the zinc-free system appear in viscosity, dynamic modulus, and abrasion resistance. These changes take place without significant change in crosslink density, cure rate, durometer, 300% modulus, trouser tear strength, flexometer heat build-up or set. The stability in these properties points directly to increased quantity and improved quality of silica-polymer bonding as the source of improved reinforcement by high surface area silicas.

Table 4.26 contains a more detailed examination of silica surface area (CTAB) effects, and makes use of a zinc-free system which includes TBzTD and excludes HMT. As noted in Chapter 1, the silanol configuration of the Rhodia 1165 product eliminates applicability of the usual surface area classification. Electron micrographs indicate a primary agglomerate size of 1165 equal to that of Hi-Sil 190G.

In this zinc-free system, surface area has little effect on cure rate, crosslink density, durometer, modulus, elongation, resilience, heat build-up or dynamic modulus. The lack of response of crosslink related properties to surface area is expected in a compounding environment which is free from soluble zinc reactions. Properties that respond positively to increasing surface area include tear and abrasion resistance; negative responses include viscosity and compression set. Among these commercial silicas, Rhodia 1165 has a slight advantage in both abrasion and tear resistance.

Table 4.26 Surface Area Effects in Zinc-free BR/NR with TBzTD

	PRODUCER*					
	A	**A**	**B**	**C**	**A**	**C**
Grade	180H	255	7000	175GR	190G	1165
CTAB surface area, m^2/g	133	145	148	161	171	NA
MDR cure, 150°C, T_{90} min	6	5	6	4	5	4
MDR crosslinks, dN-m	12	12	12	12	12	13
Mny scorch 121°C, T_5 min	15	13	13	12	12	11
Mooney visc, $ML_4/100$	96	106	108	119	124	127
Durometer hardness	67	69	68	70	69	72
DIN abrasion loss, ml	80	82	76	65	77	71
PICO abrasion index	196	192	261	321	232	334
MG trouser tear, kN/m	13	14	13	13	18k	23k
M300 modulus, MPa	5.0	5.2	5.4	6.1	5.7	5.7
Tensile, MPa						
Original	17	17	17	16	19	19
700 hrs, 90°C	2.7	2.6	3.8	2.8	3.0	3.2
Elongation, %						
Original	810	795	760	750	810	825
700 hrs, 90°C	65	50	100	50	40	75
Compression set, %	65	67	66	65	74	74
100°C rebound (Z), %	58	58	58	56	58	56
Flexometer HBU,°C	37	37	36	35	38	36
DMA dyn mod, 1Hz, 60°C						
E”, MPa	0.37	0.57	0.58	0.63	0.63	0.66
E’, MPa	4.9	5.1	4.9	5.3	6.5	6.3
Tangent delta	0.075	0.112	0.117	0.118	0.098	0.105
Dynamic frict coeff, wet Al	0.61	0.53	0.53	0.54	0.54	0.51

*A: PPG, B: DeGussa, C: Rhodia

Ingredients: BR 1220-70; NR-30; silica-45; vest.8012-10; 100°C resin-10; ODPA-1; zinc oxide-1; TBzTD-2; Sulfur-2 (mill); single stage Banbury 3 min to 130°C

The importance of the relationship between surface area and abrasion resistance in a zinc free system is demonstrated in the graph in Figure 4.5. The three curves show the response of PICO abrasion index to silica surface area for BR/SBR/NR compounds (formula above) which represent (1) a normal soluble zinc cure system control, (2) a zinc-free system, and (3) a zinc-free system with silane coupled silica. The normal cure system shows little abrasion response to surface area. The zinc-free compounds, freed from silica contamination by soluble zinc, respond to increased surface area with higher abrasion indices. Silane coupling (TESPT, 5%) of the zinc-free compounds produces the same response to surface area, but at a significantly higher level. This graph provides a simple but definitive summary of the realization of precipitated silica's full reinforcement capability through zinc-free curing systems.

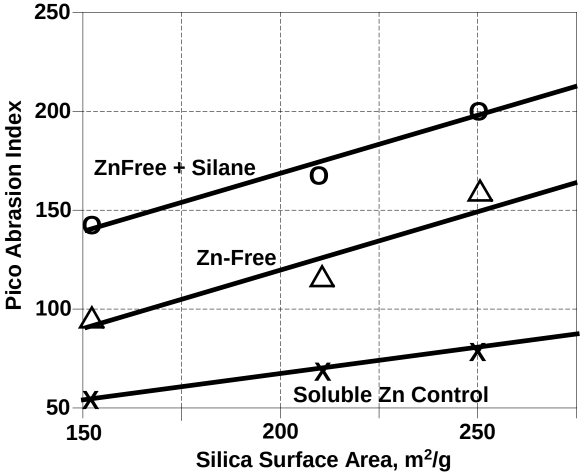

Figure 4.5 Effect of Silica Surface Area on Abrasion

4.16 ZINC-FREE CURE SYSTEMS: TROUSER TEAR STRENGTH

Trouser tear geometry, in contrast to that of other tear test procedures, provides the only tear evaluations which relate to the performance quality of rubber products. The test is described in reference [4] of Chapter 2 (Rubber World, June 1982). The high trouser tear values associated with silica compounds in general are also found, although at somewhat reduced levels, in zinc-free compounds based on solution polymers. Trouser tear strength relates directly to a high incidence of polysulfide crosslinks and associated predominance of stress relaxation during deformation. Soluble zinc curing of silica compounds has always been characterized by a high proportion of polysulfide crosslinks, and this is also the case for zinc-free systems. Evidence for this is seen in the relatively high compression set values noted in the foregoing discussions. Rearrangement of polysulfides during compound compression at 100°C leads to a retention of the deformed state and resulting high set values.

In soluble zinc systems, procedures designed to increase trouser tear values frequently compromise abrasion resistance; improvement in abrasion resistance is invariably accompanied by loss in tear strength. A solution to this compounding impasse is the major characteristic of a zinc-free cure system. The use of zinc-free cures produces compounds of good abrasion resistance and, at the same time, retains the high trouser tear strengths associated with silica reinforcement. This unique combination of properties is readily explained in terms of improved silica-polymer bonding combined with a large polysulfide crosslink content. Illustrative compounds of outstanding trouser tear strength are found in Formulary compounds BR 2, 4, 4a, 5, 10, 15, 20, 22, 28 and 29.

4.17 ZINC-FREE CURE SYSTEMS ; SILICA CONTENT

Examination of silica content effects can be approached from two possible compounding positions: a simple increase in silica content with no other formula changes, or an increase in silica content with concurrent oil addition to maintain constant hardness. The maintenance of unchanged hardness avoids the intrusion of hydrodynamic effects which have little to do with the nature of the filler. In either case, the controlling factor in compounds of varying filler content is the corresponding variation in the elastomer content. Lower elastomer contents produce a decline in elastic properties such as resilience, dynamic loss modulus, and flexometer heat build-up. The study described here involves silica contents of 50, 60 and 75 phr for both a high surface area grade, Hi-Sil 190G, and a 3% MPTS silane treated grade, Ciptane 255. Only significant property changes are listed in Table 4.27; the complete data appear in Table 4.28.

Table 4.27 Zinc-free Cure System: Silica Content Effects

220 m^2/g N$_2$SA Silica (190G)	50	60	75	--	--	--
Ciptane 255	--	--	--	50	60	75
Naphthenic oil	20	30	45	10	20	35
MDR cure 150°C, T$_{50}$ minutes	8.4	17	24	6.5	5.9	5.5
MDR crosslinks,dN-m	15	15	16	16	14	13
Durometer hardness	64	66	68	63	63	64
PICO abrasion index	105	99	99	119	68	57
100°C rebound (Z), %	51	49	45	57	53	50
DMA E', 30°C, MPa	14	18	25	8.3	8.7	13

The most striking item here is the catastrophic loss in abrasion index of the Ciptane compounds at 60 and 75 phr. Evidently, higher oil contents have overwhelmed the silane coupling effect. Even in a zinc-free system, untreated silica exhibits its usual cure retarding effect at increased concentrations. As expected, both rebound resilience and dynamic loss modulus are adversely affected as silica content increases.

Table 4.28 Effect of Silica Content, With and Without Silane

	Silica			**Mercaptosilane-Treated Silica**		
Silica N_2SA, m^2/g	220			180		
Silica Content, phr	50	60	75	50	60	75
Oil Content, phr	20	30	45	10	20	35
MDR, 150°C, T_{50} min	8.4	17	24	6.5	5.9	5.5
T_{90} min	47	50	49	33	37	41
MDR crosslinks, dN-m	15	15	16	16	14	13
Mooney visc, $ML_4/100$	86	94	108	60	56	50
Cure rate at 150°C, min	20	20	30	20	20	20
Durometer, 23°C	64	66	68	63	63	64
100°C	55	56	61	54	54	54
M20 modulus, MPa	0.92	0.93	0.98	0.96	0.92	0.95
M300 modulus, MPa	5.0	4.7	4.8	8.0	6.8	6.4
Tensile, MPa	11	9	9	11	8.4	7.0
Elongation, %	600	570	570	380	360	325
MG trouser tear, kN/m	13	14	14	6	6	5
Light Transmittance, %	18	15	11	14	16	18
Haze, %	86	87	88	88	86	85
Pendulum rebound (Z), %						
23°C	56	54	49	58	56	52
100°C	51	49	45	57	53	50
Flexometer HBU,°C	37	43	Blow	Blow	32	Blow
DMA dynamic mod, 1Hz						
E" at 0°C, MPa	2.3	2.8	2.37	1.76	1.84	2.95
E" at 30°C, MPa	1.75	1.99	2.37	1.23	1.34	1.98
E' at 0°C, MPa	19	25	25	12	12	18
E' at 30°C, MPa	14	18	25	8.3	8.7	13
Tangent delta at 0°C	0.125	0.116	0.096	0.152	0.157	0.166
Tangent delta at 30°C	0.130	0.114	0.096	0.148	0.155	0.159
Dyn frict coeff, wet Al						
Rate: 150 mm/min						
Dry	0.55	0.55	0.77	0.67	0.78	0.54
Wet	0.83	0.81	0.77	1.05	1.14	1.00
Rate: 500 mm/min						
Dry	0.80	0.96	0.72	0.96	0.67	0.90
Wet	1.17	1.15	0.84	1.01	1.00	1.06
Banbury 1-5 min, to °C	164	163	160	145	146	146

Other ingredients: BR1220-70; SBR715-35; SBR205-15; IR2210-10; Vest. 8012-15; ODPA-1; TMQ-0.5; MC wax-1; amide wax-1; ZnO CR41-1; TBBS-2; HMT-2

Although compound hardness shows only a minor increase, dynamic modulus, both storage and loss, rises rapidly with higher silica contents. Since abrasion resistance is not favorably affected, the only advantage of high silica contents appears to be a financial one: lower pound-volume material costs at greater silica and oil contents.

A closer look at Table 4.28 affords some interesting comparisons between coupled and unmodified silica. With silane, cure rates are definitely faster and do not change with silica/oil content. Rheometer crosslinks at 50 and 60 phr, however, remain at comparable values. The usual viscosity reduction provided by silane remains in effect at all silica/oil contents, and supplies further evidence of the two, unrelated functions of mercaptosilane: silica de-agglomeration and polymer bonding. In this case only the de-agglomeration function takes place; modulus and abrasion losses indicate that higher oil contents have mitigated the polymer bonding function. Increased E" loss modulus, with and without silane, also provides evidence of deterioration in polymer bonding at high silica and oil contents.

Dynamic friction data are included for those compounders in the shoe soling and related industries. Despite no friction coefficient improvement with silica content, the powerful wetting effect characteristic of silica is evident in the higher coefficients obtained under wet testing conditions. Also of interest for translucent soling applications is the slight improvement in light transmittance with Ciptane in contrast to the loss with unmodified silica.

4.18 ZINC-FREE CURE SYSTEMS: DUROMETER EQUIVALENTS

A practical compounding matter closely related to silica content is the determination of hardness equivalents for silica and softener content. How many phr of silica or oil are needed to change hardness plus or minus 1 durometer point? A study in which silica and oil contents are varied, in Table 4.29, provides an estimate of the required amounts. These values are most readily obtained from the graph of durometer versus content in Figure 4.6. One durometer point, plus or minus, equals 1.2 phr 180 m^2/g N_2SA silica or 1.9 phr oil. Data appear in Table 4.29.

The complete processing and vulcanizate data for these compounds affords several interesting observations. Higher silica and oil contents (70/20 vs. 55/5) lead to a sacrifice in cure rate, modulus, tensile, abrasion , resilience and heat build-up, but with little change in dynamic modulus and tangent delta. A similar study in a BR/SBR blend yields 1.1 phr for a higher surface area silica, and 1.6 phr for naphthenic oil per durometer point.

Table 4.29 Zinc-Free Cure system: Durometer Equivalents: Silica and Oil

180 m^2/g N_2SA Silica, phr	25	40	55	40	55	70
Naphthenic oil 510	5	5	5	20	20	20
Durometer: 23°C	51	61	75	53	67	78
Other ingredients: BR1220-50; SMR-50; 100C resin-10; OPDA-1; ZnO-1; TBBS-2; HMT-2; sulfur (mill)-2. Banbury, 3 min to 125°C stock						

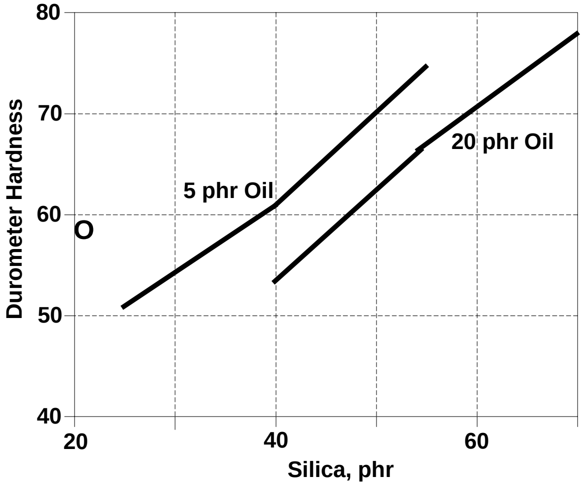

Figure 4.6. Hardness Equivalents for Silica and Softener Content

References

1.Hewitt, N.L., “Zinc-Free Curing Systems for Silica”, Rubber World, September 1992

2.Hewitt, N.L., "Improving Silica Reinforcement", paper presented at ACS Rubber Division Meeting, Pittsburgh, PA, October 1994

3.Wartmann, H.J., Strauss, C.R., “Analysis of Cure Parameters to Define Vulcanization and Reinforcement”, paper presented at ACS Rubber Division, Spring Meeting, 1965

Solution SBR and BR Formulary

The silica surface areas indicated in the following compounds are N_2SA (BET) surface areas. A listing of commercially available precipitated silica products by surface area is provided in Appendix A. The common abbreviations used in these compounds are provided in Appendix E.

BR 1

Elastomer: BR/NR Durometer: 45
Application: Abrasion; Zinc Free

BR 1220	70	ODPA	1
SMR (1’ mill)	30	Sulfur	2.5
180 m^2/g Silica	45	TBBS	1.8
Naphthenic Oil	40		
Titanium Dioxide	2	Specific Gravity	1.06

MDR Cure Rate, T_{50} minutes	16
Mooney Viscosity, ML_4100	75
20 minute cure, 150°C:	
Durometer	45
M300, MPa	2.5
Tensile, MPa	13
Elongation, %	815
PICO Abrasion Index	92
MG Trouser Tear, kN/m	7.1
Pendulum Rebound (Z), 23°C	58
100°C	58

BR 2

Elastomer: BR/NR	Durometer: 59
Application: Tear; Abrasion	

Banbury 1			Banbury 2	
0’	BR 1220	50	Zinc Oxide	3
	220 m^2/g Silica	55	Zinc Dimethacrylate	1
	100C Resin	15	Sulfur	2
0.5’	SMR CV60	50	TBBS	2
1.5’	SAF N121	5	HMT	2
	Aromatic Oil	10		
	HPPD	2		
	TMQ	1		
4’	Dump, 200°C		Specific Gravity	1.14

MDR Cure Rate, 150°C, T$_{50}$ minutes	13
T$_{90}$ minutes	24
Mooney Scorch, 121°C, T$_5$ minutes	30+
Mooney Viscosity, ML$_4$100	56
Durometer, 23°C	59
100°C	53

	Original	700 hrs, 100°C
M300, MPa	3.4	
Tensile, MPa	20	9.7
Elongation, %	875	145

MG Trouser Tear, kN/m, 23°C	34
70°C	29
PICO Abrasion Index	94

Goodrich Flexometer: 100°C; 2.5%; 1 MPa	
Permanent Set, %	37
Heat Build-Up, °C	53
Pendulum Rebound (Z), %, 23°C	43
100°C	54
Compression Set, %, 70 hrs, 100°C	81

BR 3

Elastomer: SSBR/NR Durometer: 62
Application: Tear strength; LT tread; Black

Banbury 1		Banbury 2	
SSBR 750	75	Zinc Oxide	2.5
SMR 5	25	Sulfur	1.3
N220, ISAF	48	TBBS	1
Ciptane I	12	DCBS	0.5
Aromatic Oil	7		
HPPD	1		
Stearic Acid	1		
MC Wax	2	Specific Gravity	1.15

Cure Rate 160°C, T_{90} minutes	8.5
Mooney Scorch, 130°C minutes	23
Viscosity, $ML_4$100	67
15 minute cure, 160°C:	
Durometer	62
M300, MPa	7.5
Tensile, MPa	20
Elongation, %	630
MG Trouser Tear, kN/m	15.8
PICO Abrasion Index	111
25 minute cure, 160°C:	
Pendulum Rebound (Z), %, 23°C	38
100°C	57
Goodrich Flexometer: 100°C; 17.5%; 1 MPa	
Static Compression, %	24
Dynamic Compression, %	16
Drift, %	13
Set, %	15
Heat Build-Up, °C	49
DMA Tan Delta, 60°C, 1 Hz	0.249

BR 4

Elastomer: BR/NR Durometer: 62
Application: Abrasion; Tear; Zinc-free; Non-silane

BR 1220	70	Sulfur	2
SMR CV60	30	TBBS	1.5
Vestenamer 8012	10		
160 m^2/g Silica	45		
100C Resin	10		
ODPA	1	Specific gravity	1.10

MDR Cure Rate, 150°C T_{50} minutes	20	
Mooney Scorch 121°C T_5 minutes		
Original	12	
Shelf Aged 45 days	11	
Mooney Viscosity, ML_4100		
Original	110	
Shelf Aged 45 days	105	
Durometer, 23°C	62	
100°C	57	
DIN Abrasion Loss, ml	65	
PICO Abrasion Index	204	
MG Trouser Tear, kN/m, 23°C	22	
70°C	15	
	Original	700 hrs, 80°C
M300, MPa	4.1	--
Tensile, MPa	17	5.1
Elongation, %	810	160
Pendulum Rebound (Z), 23°C	54	
100°C	52	

Goodrich Flexometer; 100°C; 22.5% 1 MPa		
Permanent Set, %	45	
Heat Build-Up, °C	51	
DMA Dynamic Modulus; 1 Hz	-40°C	+60°C
E’, MPa	242	4.66
E”	27.0	0.49
Tangent Delta	0.111	0.105

BR 5

Elastomer: BR/SSBR/IR Durometer: 62
Application: Abrasion; Footwear; Zinc-free; Non-Silane

BR 1220	60	Zinc Oxide	1
SSBR 715	25	Sulfur	2
IR 2200	15	TBBS	2
160 m^2/g Silica	50	HMT	2
Vestenamer 8012	10		
Naphthenic Oil	17		
ODPA	1	Specific gravity	1.09

ODR Cure Rate, 150°C, T_{50} minutes	9.2
Mooney Scorch 121°C, T_5 minutes	17
Viscosity, ML_4100	68

25 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer, 23°C	62	81
100°C	57	
M300, MPa	4.2	
Tensile, MPa	13	6.8
Elongation, %	695	135

MG Trouser Tear, kN/m	14

Abrasion Indices: PICO	140
NBS	11000

DMA Dynamic Modulus; 1 Hz; 15%	0°C	60°C
E', MPa	4.3	3.0
E"	0.52	0.31
Tangent Delta	0.122	0.105

Pendulum Rebound (Z), %, 23°C	53
100°C	52
Kinetic Coefficient of Friction, Wet	1.07

BR 6

Elastomer: BR Durometer: 63
Application: Tear strength

Addition: Banbury 1			Banbury 2	
0”	BR 1220	50	Zinc Oxide	3
	220 m^2/g Silica	55	Zinc Dimethacrylate	1
	100C Resin	15	Sulfur	2
0.5’	SMR CV60	50	TBBS	2
1.5’	N121	5	HMT	2
	Aromatic Oil	10		
	HPPD	2		
	TMQ	1		
4’	Dump, 200°C		Specific Gravity	1.14

Cure Rate MDR 150°C,	T50 minutes	11
	T_{90} minutes	20
Mooney Scorch 121°C,	T_5 minutes	30+
Mooney Viscosity, ML_4100		73
Durometer, 23°C		63
100°C		56

Stress/Strain	Original	700 hrs, 100°C
M300, MPa	3.4	
Tensile, MPa	19	9.5
Elongation, %	875	110

MG Trouser Tear, kN/m, 23°C	35
70°C	31
PICO Abrasion Index	97

Goodrich Flexometer: 100°C; 22.5%; 1 MPa

Permanent Set, %	38
Heat Build-Up, °C	48
Pendulum Rebound (Z), %, 23°C	45
100°C	54

Compression Set, %, 70 hrs, 100°C	87

BR 7

Elastomer: BR/NR Durometer: 64
Application: Wear resistance, Zinc-free

BR 1220	70	Sulfur	2.7
SMR CV60	30	MBTS	2
Vestenamer 8012	15	DPTH	0.5
160 m^2/g Silica	45		
100C Resin	10		
ODPA	1	Specific gravity	1.10

MDR Cure Rate 150°C, T_{50} minutes	11
Mooney Scorch 121°C, T_5 minutes	27
Mooney Viscosity, ML_4100	91
10/15 minute cure, 150°C	
Durometer, 23°C	64
100°C	61
DIN Abrasion Loss, ml	63
PICO Abrasion Index	158
MG Trouser Tear, kN/m	15
M300, MPa	4.7
Tensile, MPa	16
Elongation, %	765
Pendulum Rebound (Z), %, 23°C	60
100°C	61
Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent Set, %	36
Heat Build-Up, °C	43
Compression Set, %, 70 hours, 100°C	85

BR 8

Elastomer: BR/NR Durometer: 65
Application: Non-silane, Zinc-free; Footwear

BR 1220	70	ODPA	1
SMR CV60	30	Zinc Oxide	1
Vestenamer 8012	10	Sulfur	2
160 m^2/g Silica	45	ZBzDC*	2
100C Resin	10		
*Arazate		Specific Gravity	1.09

MDR Cure Rate, 150°C, T_{50} minutes	6.5
Mooney Scorch, 121°C, T_5 minutes	16
Mooney Viscosity, ML_4100	105
10 minute cure, 150°C:	
Durometer, 23°C	65
100°C	59
M300, MPa	4.4
Tensile, MPa	17
Elongation, %	855
PICO Abrasion Index	165
DIN Abrasion Loss, ml	69
Pendulum Rebound (Z), %, 23°C	58
100°C	56

BR 9

Elastomer: BR/NR Durometer: 64
Application: Abrasion; Zinc-free; Low ML_4100

BR1220	70	Zinc Oxide	1
SMR 60CV	30	Sulfur	2
220 m^2/g Silica	45	TBBS	2
Silane SI69	3.5	HMT	2
Cl 100C Resin	10		
C1 25C Resin	10		
ODPA	1	Specific Gravity	1.11

Cure Rate, 150°C, T_{90} minutes	8.2
Mooney Scorch, 130°C, T_5 minutes	15
Mooney Viscosity, ML_4100	67

10 minute cure, 150°C:	Original	700 hrs, 90°C
Durometer	64	
M300, MPa	5.5	
Tensile, MPa	23	11
Elongation, %	780	180

MG Trouser Tear, kN/m	11
PICO Abrasion Index	166
Compression Set, %, 70 hrs, 100°C	78

Pendulum Rebound (Z), %, 23°C	54
100°C	64
DeMattia Cut Growth, kc to 500%	9
Goodrich Flexometer, 100°C; 22.5%; 1 MPa:	
Permanent Set, %	15
Heat Build-Up, °C	29

DMA Dynamic Modulus; 1 Hz, 15% Deflection

	0°C	30°C	60°C
E’, MPa	14	12	10
E”	1.6	1.4	1.2
Tangent Delta	0.120	0.115	0.117

BR 10

Elastomer: BR/IR Durometer: 65-70
Application: Translucence; Peroxide cure; Silica content

BR 1220	70	SR 206	0.5
IR 2200	30	DBPH	0.8
220 m^2/g Silica	as noted	Silane A174	1
Irgonox 1010	0.5		
Tinuvin 770	0.3		
Tinuvin P	0.3		

220 m^2/g Silica, phr:	30	50
Cure Rate, MDR 160°C , T_{50} minutes	14	10
Mooney Scorch, 121°C, T_5 minutes	18	15
Mooney Viscosity, ML_4100	84	103
10/15 minute cure, 160°C:		
Durometer (Avg.)	65	72
M100, MPa	3.4	4.1
Tensile, MPa	6.4	8.9
Elongation, %	170	200
Aged 700 hours, 60°C		
Durometer	67	73
Tensile, MPa	6.8	9.2
Elongation, %	180	200
Light Transmittance %	55	57
Haze, %	87	88
Dynamic Coefficient of Friction, Wet aluminum	1.93	1.38
MG Trouser Tear, kN/m	3.3	2.8
PICO Abrasion Index	84	110
NBS Abrasion Index	4600	4600
DIN Abrasion, ml	70	80
Pendulum Rebound (Z), %, 23°C	59	58
100°C	59	58

BR 11

Elastomer: BR/NR Durometer: 66
Application: Extrusion; Tear; Abrasion; Zinc-free

BR 1220	50	Zinc Oxide	3
SMR CV60	50	Sulfur	2
180 m^2/g Silica	50	TBBS	2
100C Resin	15	HMT	2
Naphthenic Oil	5	Zn Dimethacrylate	0.3
ODPA	2		
TMQ	1	Specific Gravity	1.12

MDR Cure Rate, 150°C, T_{50} minutes	8.5
T_{90} minutes	23
Mooney Scorch, 121°C, T_5 minutes	30+
Mooney Viscosity, ML_4100	75
Garvey Extrusion, 105°C	
Edge-Surface Rating	10A
% Swell	18
Durometer, 23°C	66
100°C	61

15 minute cure, 150°C	Original	700 hrs, 100°C
Durometer	70	86
M300, MPa	4.3	
Tensile, MPa	21	13
Elongation, %	870	230

MG Trouser Tear, kN/m	24
PICO Abrasion Index	136
DIN Abrasion Loss, ml	126

Compression Set, %, 70 hrs, 100°C	84
Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent Set	27
Heat Build-Up, °C	35
Pendulum Rebound (Z), %, 23°C	55
100°C	59

BR 12

Elastomer: BR/SBR/IR Durometer: 67
Application:Fast cure rate; Zinc-free

BR 1220	65	Zinc Oxide	1
SBR 1502	25	Sulfur	3
IR 2200	10	TBBS	2
Vestenamer 8012	10	MBTS	1
Ciptane 255 LD	52	TMTU	1
Naphthenic Oil	10		
ODPA	1	Specific Gravity	1.12

MDR Cure Rate 150°C, T_{50} minutes	2.5
T_{90} minutes	4.0
Mooney Scorch, 121°C, T_5 minutes	13
Mooney Viscosity, ML_4100	75
Durometer, 23°C	66
100°C	63

6 minute cure, 150°C	Original	700 hrs, 90°C
M100, MPa	3.2	
Tensile, MPa	6.7	5.0
Elongation, %	190	70

PICO Abrasion Index	105
DIN Abrasion Loss, ml	51
Dynamic Friction Coefficient, Wet aluminum	1.08
Light Transmittance, %	34
Compression Set, %, 70 hrs, 100°C	65
Pendulum Rebound (Z), %, 23°C	59
100°C	60

Goodrich Flexometer: 100°C; 22.5%; 1 MPa

Heat Build-Up, °C	32

BR 13

Elastomer: BR/SBR/IR Durometer: 67
Application: Soling; Zinc-free; Abrasion

BR 1220	65	Zinc Oxide	1
SBR 1502	25	Sulfur	2
IR 2200	10	TBBS	2
Ciptane 255 TLD*	52	HMT	2
Vestenamer 8012	10		
Naphthenic Oil 510	10		
ODPA	1	Specific gravity	1.12

*160 m^2/g Silica + 2.5% Silane A189

Cure Rate MDR 150°C, T_{50} minutes	6.8
T_{90} minutes	10
Mooney Scorch 121°C T_5 minutes	30+
Mooney Viscosity, ML_4100	80
Durometer (button)	67 (61 at 100°C)

12 minute cure, 150°C:	Original	700 hrs, 90°C
M300, MPa	8.6	
Tensile, MPa	12	6.2
Elongation, %	385	120

PICO Abrasion Index, 23°C	114
100°C	66
DIN Abrasion Loss, ml	50
NBS Abrasion Index	520
MG Trouser Tear, kN/m	5.2
Light Transmittance, %	46
Ross Cut Growth, Aged, kc to 500%	90
Kinetic Friction Coefficient	
Wet aluminum	0.66

DMA Dynamic Modulus, 1 Hz; 4%	-80°C	-40°C	0°C	30°C
E”, MPa	54	19	1.9	0.86
E’	168	56	15	5.9
Tangent Delta	0.131	0.146		

Pendulum Rebound (Z), %, 23°C	59
100°C	59

BR 14

Elastomer: BR/IR Durometer: 67
Application; Translucent outsole; Peroxide cure

BR 1220	65	Silane A174	1
IR 2200	35	SR 206	0.5
Vestenamer 8012	15	DMBPH 101	0.5
190 m^2/g Silica	45		
WW 371 Oil	10	Specific Gravity	1.08

Cure Rate 160°C, T_{50} minutes	6.4
Mooney Scorch, 121°C, T_5 minutes	23
Mooney Viscosity, ML_4100	99
Durometer (button), 23°C	74
100°C	67
Light Transmittance, (2 mm), %	56
Haze, %	83
DIN Abrasion Loss, ml	82
PICO Abrasion Index, 23°C	191
70°C	99

Ross Flex Cut Growth:	Thickness	kc to 500%
	2.5 mm	100+
	7 mm	2

Durometer	67
M300, MPa	9.9
Tensile, MPa	12
Elongation, %	355
Pendulum Rebound (Z), %, 23°C	66
100°C	61

BR 15

Elastomer: BR/SBR/NR Durometer: 68
Application: Abrasion resistance; Footwear; Zinc-free

BR 1220	50	Zinc Oxide	1
SBR 715	30	Sulfur	2
NR	20	MBTS	2
160 m^2/g Silica	42	HMT	2
100C Resin (6100)	10		
Phenolic AO	1	Specific Gravity	1.12

Cure Rate 150°C, T_{50} minutes	5.1
T_{90} minutes	24
Mooney Scorch 121°C, T_5 minutes	22
Viscosity, ML_4100	82
Garvey Extrusion, 105°C	
% Swell	28
Edge-surface rating	10A

15 minute cure, 150°C	Original	700 hrs, 90°C
Durometer	68	77
M300, MPa	4.1	
Tensile, MPa	19	16
Elongation, %	785	400

Abrasion Indices:	
PICO	119
NBS	225
Pendulum Rebound Z, %, 23°C	55
100°C	59

Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent Set, %	23
Heat Build-up, °C	40

Dynamic Mechanical Analysis; 1 Hz, 30°C; 20% flexural strain	
E’, MPa	15
E”	1.49
Tan Delta	0.103

BR16

Elastomer: BR/NR Durometer: 70
Application: Tear strength; Abrasion; Zinc-free vs SAF

BR 1220	50	Zinc Oxide	3
SMR CV60	50	Sulfur	2
Filler	50	TBBS	2
100C Arom. Resin	15	HMT	2
Naphthenic Oil	5	Zinc Methacrylate	0.3
TMQ	1		
ODPA	2	Specific Gravity	1.13

	150 m^2/g Silica	SAF N121 Black
MDR Cure Rate, 150°C, T_{50} minutes	7.7	10
T_{90} minutes	18	13
Mooney Scorch, 121°C, T_5 minutes	30+	30+
Mooney Viscosity, $ML_4$100	72	54
Garvey Die Extrusion Rating	10A	-
Durometer, 23°C	69	63
100°C	64	54
MG Trouser Tear, kN/m, 23°C	33	18
70°C	20	10
PICO Abrasion Index	121	166
DIN Abrasion Loss, ml	110	76
Goodrich Flexometer Heat Build-up, °C	35	63
Original Stress/Strain		
M300, MPa	4.3	7.6
Tensile, MPa	21	21
Elongation, %	845	640
700 hours, 100°C		
Durometer	85	80
Tensile, MPa	13	9
Elongation, %	235	190
Strip Adhesion to		
RFL Polyester Fabric, kN/m	95	54
Pendulum Rebound (Z), %, 100°C	59	47

BR 17

Elastomer: BR/SBR/IR Durometer: 70
Application: Abrasion; Footwear; Zinc-free

BR 1220	65	Zinc Oxide	1
SSBR 303	25	Sulfur	2
IR 2200	10	TBBS	2
Ciptane 255LD	42	HMT	2
Naphthenic Oil	5		
ODPA	1	Specific Gravity	1.12

Cure Rate, MDR 150°C, T_{50} minutes	4.6
Mooney Scorch 121°C, T_5 minutes	18
Mooney Viscosity, ML_4100	68
Durometer (button)	70
M300, MPa	7.5
Tensile, MPa	17
Elongation, %	590
PICO Abrasion Index	205
DIN Abrasion Loss, ml	65
Dynamic Friction Coefficient	
Wet aluminum	0.80
Light Transmittance, %	45
Pendulum Rebound (Z), %, 23°C	55
100°C	59

BR 18

Elastomer: BR/NR Durometer: 70
Application: Abrasion resistance; Tear strength; Zinc-free; Silane

BR 1220	70	Sulfur	2
NR	30	TBBS	2
150 m^2/g Silica	50	HMT	2
100C Arom. Resin	10	Zinc Oxide	1
Hindered bisphenol	2		
Silane SI69	3		
Titanium Dioxide	3	Specific Gravity	1.13

Cure Rate 150°C, T_{90} minutes	9.9
Mooney Scorch 130°C, T_5 minutes	20
Viscosity ML_4100	84

12 minute cure, 150°C	Original	700 hrs, 90°C
Durometer	70	80
M300, MPa	6.4	
Tensile, MPa	20	8.8
Elongation, %	715	130

MG Trouser Tear, kN/m	18K
PICO Abrasion Index, 23°C	155
70°C	100

Dynamic Mechanical Analysis	0°C	30°C	60°C
Storage Modulus E', MPa	27	22	19
Loss Modulus E"	3.1	2.3	1.9
Tan Delta	0.116	0.103	0.100

Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent Set, %	38
Heat Build-Up, °C	31

DeMattia Cut Growth, %, kc to 500%	10
Compression Set, %, 72 hrs, 100°C	85

BR 19

Elastomer: SSBR Durometer: 70
Application: Low rebound and Tan delta; control for BR 16, BR 18

Banbury 1		Banbury	2
SSBR	100	Zinc Oxide	3
150 m^2/g Silica	50	PEG 3350	2
100C Arom. Resin	10	Sulfur	2
ODPA	1	TBBS	4
Stearic Acid	2	Specific Gravity	1.17

Cure Rate 160°C, T_{70} minutes	18
Mooney Scorch 130°C, T_5 minutes	30+
Viscosity, ML_4100	89
40 minute cure, 160°C	
Durometer	70
M300, MPa	4.5
Tensile	12.3
Elongation, %	530
PICO Abrasion Index, 23°C	60
70°C	54
Pendulum Rebound (Z), %, 23°C	24
100°C	65

Goodrich Flexometer: 100°C, 22.5%; 1 MPa

Static Compression, %	18
Dynamic Compression, %	7.5
Drift, %	3.6
Set, %	9.3
Heat Build-Up, °C	33

DMA: 1 Hz; 10% Strain	E', MPa	E", MPa	Tan Delta
0°C	59	32	0.540
30°C	21	-	-
60°C	17	1.6	0.106
90°C	14	-	-

BR 20

Elastomer: BR/SBR/NR Durometer: 70
Application: HP tread; SAF control

SSBR 756	56	Zinc Oxide	1
BR 1220	50	Sulfur	2
SMR CV60	10	TBBS	2
Filler	75	HMT	2
Vestenamer 8012	10	HPPD	2
MC Wax	1	TMQ	1
Amide Wax	1	Specific Gravity	1.14

220 m^2/g Silica	25	0
SAF N121 Black	50	75
Naphthenic Oil	10	17
Cure Rate, 160°C, T_{50} minutes	4.8	3.4
Mooney Scorch, 121°C, T_5 minutes	30+	30+
Mooney Viscosity, $ML_4$100	68	51
Cure: 10/15 minute cure, 160°C		
Durometer, 23°C	70	71
100°C	61	64
Original		
M300, MPa	9.1	14.5
Tensile, MPa	19	18
Elongation, %	540	365
700 hours, 90°C		
Durometer	84	88
Tensile, MPa	15	14
Elongation, %	130	70
PICO Abrasion Index, 23°C/100°C	162/103	143/103
MG Trouser Tear, kN/m, 23°C/100°C	15/7.7	6.9/2.2
Flexometer Heat Build-Up, °C	48	42

Dynamic Modulus, DMA, 1 Hz; 15%

	0°C	60°C	0°C	60°C
E', MPa	26	15	23	15
E"	7.2	3.8	5.3	3.3
Tangent Delta	0.279	0.254	0.251	0.221

BR 21

Elastomer: BR/ NR Durometer: 71
Application: Tear strength; Abrasion; Silane effects

BR 1220	70	Zinc Oxide	1
SMR CV60	30	Sulfur	2
150 m^2/g Silica	50	TBBS	2
100C Arom. Resin	13	HMT	2
ODPA	1	Specific Gravity	1.13

	Non-Coupled	Silane-Coupled 1.5 phr A189
MDR Cure Rate, 150°C, T_{50} minutes	6.0	3.9
T_{90} minutes	10	5.0
Mooney Scorch 121°C, T_5 minutes	30+	10
Viscosity, ML_4100	100	62
Garvey Die Rating	5A	
Cure at 150°C, minutes	15/25	8/15
Durometer, 23°C	71	71
100°C	69	69
M300, MPa	5.0	11
Tensile, MPa	20	23
Elongation, %	780	585
Aged 700 hours at 90°C		
Durometer	85	79
Tensile, MPa	12	10
Elongation, %	210	185
MG Trouser Tear, kN/m	26	5.4
Abrasion Indices: PICO	96	178
NBS	-	650
Compression Set, %, 70 hrs, 100°C	90	76
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Permanent Set, %	-	11
Heat Build-Up, °C	-	28
DeMattia Cut Growth, 500% kc	8	5
Pendulum Rebound (Z), %, 23°C	56	59
100°C	60	65

BR 22

Elastomer: BR/ NR Durometer: 72
Application: Abrasion resistance; Tear strength; Zinc-free

Banbury 1		Banbury 2	
BR 1220	70	Sulfur	2
SMR 5	30	TBBS	2
150 m^2/g Silica	50	HMT	2
Aromatic 100Resin	10	Zinc Oxide	1
ODPA	1		
Titanium Dioxide	3	Specific Gravity	1.14

Cure Rate 150°C, T_{90} minutes	4.3
Mooney Scorch, 130°C, T_5 minutes	15
Viscosity, ML_4100	108

10 minute cure, 150°C	Original	170 hrs, 110°C
Durometer	72	82
M300, MPa	4.8	
Tensile, MPa	22	21
Elongation, %	815	555

MG Trouser Tear, kN/n	18K
PICO Abrasion Index	135
Compression Set, %, 3D 100°C	88
Pendulum Rebound (Z), %, 23°C	56
100°C	61
DeMattia Cut Growth, kc to 500%	40

BR 23

Elastomer: BR/SBR/ NR Durometer: 73
Application: Tear strength; Zinc-free; silane

SSBR 715	50	Sulfur	2
BR 1220	40	TBBS	2
NR	10	HMT	2
150 m^2/g Silica	50	Zinc Oxide	1
100C HC Resin	13		
ODPA	1	Specific Gravity	1.13

	Non-Coupled	Silane-Coupled 1.5 phr A189
MDR Cure Rate, 150°C, T_{50} minutes	8.7	4.3
T_{90} minutes	15	6.5
Mooney Scorch 121°C, T_5 minutes	30+	12
Viscosity, ML_4100	91	67
Cure at 150°C, minutes:	15/25	10/15
Durometer, 23°C	73	73
100°C	68	69
M300, MPa	4.4	10
Tensile, MPa	13	19
Elongation, %	725	480
Aged 700 hours, 90°C		
Durometer	84	79
Tensile, MPa	13	12
Elongation, %	200	195
MG Trouser Tear, kN/m	28	7.4
Abrasion Indices: PICO	78	111
NBS	125	215
Compression Set, 70 hrs, 100°C, %	89	79
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Permanent Set, %	22	14
Heat Build-Up, °C	28	32
DeMattia Cut Growth, 500%, kc	11	4
Pendulum Rebound (Z), %, 23°C	51	45
100°C	59	62
DMA: 1 Hz; 15%; 30°C		
E', MPa	25	12
Tangent Delta	0.111	0.115

BR 24

Elastomer: BR/SBR/IR Durometer: 74
Application: Translucent; Peroxide cure

BR 1220	65	WW Naphthenic Oil 371	10
SBR 303	25	DBPDIB 14-40	1.1
IR 2200	10		
Vestenamer 8012	15		
Silica	45	Specific Gravity	1.07

Silica	190 m^2/g	180 m^2/g
MDR Cure Rate 160°C, T_{50} minutes	8.4	11
Mooney Scorch 121°C, T_5 minutes	20	29
Mooney Viscosity, ML_4100	91	63
Durometer, 23°C	74	74
100°C	66	66
Light Transmittance, %	70.5	68.7
Haze	86	87
Yellow Index	38	38
DIN Abrasion Loss, ml	118	154
PICO Abrasion Index	118	118
Stress/Strain Original		
M300, MPa	7.4	8.7
Tensile, MPa	12	11
Elongation, %	455	350
Aged 700 hours, 60°C		
Durometer	81	79
Tensile	10	9.7
Elongation	355	290
MG Trouser Tear, kN/m	5.7	2.5
Ross Cut Growth, kc to 500%		
Specimen thickness 2.5mm	100+	100+
7 mm	3	0.5
Pendulum Rebound (Z), %, 23°C	59	61
100°C	64	67

BR 25

Elastomer: BR/SSBR/NR Durometer: 75
Application: Abrasion resistance; Zinc-Free

Banbury 1		Banbury 2	
SSBR 1215	60	Sulfur	2
BR1220	30	TBBS	2
NR (Milled)	10	HMT	2
Ciptane I	52	Zinc Oxide	0.5
100C Arom. Resin	10		
Antioxidant PC	1	Specific Gravity	1.12

Cure Rate 160°C, T_{50} minutes	3.2	
T_{90} minutes	18	
Mooney Scorch 130°C, T_5 minutes	12	
Viscosity, ML_4100	96	
Garvey Extrusion (B) 120°C, 65 rpm		
Die Swell,%	5	
Edge-Surface Rating	7A	
25 minute cure, 160°C	Original	170 hrs, 110°C
Durometer	75 (74/100°C)	83
M300, MPa	9.8	-
Tensile, MPa	20	8.4
Elongation, %	515	115
MG Trouser Tear, kN/m	7.9	
PICO Abrasion Index, 23°C	145	
100°C	100	
Compression Set, %, 70 hrs, 100°C	56	
Dynamic Properties Cure: 35 minutes, 160°C		
Pendulum Rebound (Z), %, 23°C	49	
100°C	63	
DMA: 30°C; 1 Hz; 20% Strain		
E', MPa	19	
Tan Delta	0.123	

BR 26

Elastomer: BR/SBR/NR Durometer: 80
Application: Abrasion; Footwear; Silane

SSBR 715	50	Zinc Oxide	1		
BR 1220	40	Sulfur	2		
NR	10	TBBS	1.5		
150 m^2/g Silica	60	MBTS	1		
100C Resin	10	HMT	2		
ODPA	1				
Silane SI69	2	Specific Gravity		1.16	

Cure Rate 150°C, T_{50} minutes	7	
Mooney Scorch 121°C, T_5 minutes	22	
Mooney Viscosity, ML_4100	126	
Garvey Extrusion Rating	5A	
10 minute cure, 150°C		
Durometer, 23°C	80	
100°C	74	
13 minute cure, 150°C	Original	700 hrs, 90°C
Durometer	76	86
M300, MPa	10	
Tensile, MPa	19	12
Elongation, %	475	150
Abrasion Indices: PICO, 23°C	155	
PICO, 100°C	102	
NBS	201	
DIN Loss, ml	120	
MG Trouser Tear, kN/m	13	
Ross Flex, kc to 500%	50	
Dynamic Coefficient of Friction,		
Wet Aluminum	0.77	
DMA Dynamic Modulus: 1 Hz; 15%		
E” at 0°C, MPa	3.1	
Tangent Delta at 0°C	0.160	
E’ at 30°C	13	
Pendulum Rebound (Z), %, 23°C	48	
100°C	59	

BR 27

Elastomer: SBR Durometer: 80
Application: Low Tan Delta; Zinc oxide omitted

Banbury 1		Banbury 2	
SSBR 1215	100	Sulfur	2
Silica (Ciptane)	50 (51.5)	TBBS	2
Arom. 100C Resin	10		
ODPA	1		
Stearic Acid	0.7	Specific Gravity	1.15

	150 m^2/g Silica	Ciptane I
Cure Rate, 160°C, T_{70} minutes	10	14
T_{90} minutes	29	22
Mooney Scorch 130°C, T_5 minutes	9.5	9.0
Viscosity, ML_4100	108	113
160°C cure, minutes	40	30
Durometer	80	75
M20, MPa	1.33	1.23
M300, MPa	8.9	14.3
Tensile, MPa	19.2	14.3
Elongation, %	530	290
PICO Abrasion Index, 23°C	80	110
70°C	70	93
Dynamic Properties		
Pendulum Rebound (Z), %, 23°C	31	32
100°C	67	71
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Static Compression, %	15	10
Dynamic Compression, %	3.7	-1.1
Drift, %	3.4	1.3
Set, %	7.3	3.6
Heat Build-Up, °C	24	22
DMA: 1 Hz; 10% Strain		
E; MPa, 0°C	79	61
30°C	29	20
90°C	23	14
E”, MPa, 0°C	33	28
Tan Delta, 0°C	0.420	0.460
60°C	0.067	0.080

BR 28

Elastomer: BR/SBR/NR Durometer: 85
Application: Soling; Zinc-free

BR 1220	40	Sulfur	2
SSBR 303	40	TBBS	1.5
SMR CV60	20	MBTS	1
160 m^2/g Silica	60	HMT	2
Silane 1289	1	Zinc Oxide	1
100C Resin	10		
ODPA	1	Specific Gravity	1.15

MDR Cure Rate, 160°C, T$_{50}$ minutes	3.8	
T$_{90}$ minutes	6.0	
Mooney Scorch, 121°C T$_5$ minutes	30+	
Mooney Viscosity, ML$_4$100	80	
12/20 minute cure, 160°C		
Durometer (button), 23°C	84	
100°C	75	
	Original	700 hrs, 70°C
Durometer	85	88
M300, MPa	8.9	
Tensile, MPa	24	20
Elongation, %	675	430
MG Trouser Tear, kN/m	26	
Abrasion Indices:		
PICO	128	
NBS	164	
DIN Loss, ml	85	
Optical Properties:		
Transmittance, %	9	
Haze	75	
Dynamic Coefficient of Friction,		
Wet aluminum	0.79	
Pendulum Rebound (Z), %, 23°C	32	
100°C	45	
Ross Flex Cut Growth, kc to 500%	100+ (6 mm)	

BR 29

Elastomer: BR/SBR/NR Durometer: 85
Application: Tear and Abrasion Resistant Soling

Banbury 1		Banbury 2	
NR	27	PEG	1
High Styrene Resin	27	Sulfur	2
BR 1220	40	MBTS	1.8
SBR 1502	33	MDB	1
150 m^2/g Silica	50	DPG	0.5
Arom. Resin 100C	10		
Antioxidant	1		
Stearic Acid	1		
Zinc Oxide	5	Specific Gravity	1.10

Cure Rate, 160°C, T_{90} minutes	16
Mooney Scorch, 135°C, T_5 minutes	25
Viscosity, $ML_4$100	71
Durometer	85
M300, MPa	6.2
Tensile, MPa	16.5
Elongation, %	590
MG Trouser Tear, kN/m	21
NBS Abrasion Index	335
Ross Flex Crack Growth, kc	100+ (8 mm)

BR 30

Elastomer: BR/EVA Durometer: 85
Application: Translucent; Peroxide cure

BR 1220	70	Irgonox 1010	0.5
RB 820	30	Perkadox 14	0.4
EVA 150	23		
160 m^2/g Silica	50	Specific Gravity	1.10

MDR Cure Rate, 160°C, T_{50} minutes	10
Mooney Scorch, 121°C, T_5 minutes	30+
Mooney Viscosity, ML_4100	99
Durometer, 23°C	84
100°C	70
Light Transmittance, %	42
Haze, %	89
DIN Abrasion Loss, ml	151
PICO Abrasion Index	140
Stress/Strain	
Durometer	85
M300, MPa	10
Tensile, MPa	14
Elongation, %	385
Pendulum Rebound (Z), %, 23°C	44
100°C	63

BR 31

Elastomer: BR/SBR/NR Durometer: 87
Application : Low cost; Mold flow; Zinc-free

SSBR 715	55	ODPA	1
BR 1220	35	Zinc Oxide	1
SMR CV60	10	Sulfur	3
SBR 1904	20	TBBS	2
Silica	30	HMT	2
Hard Clay	50		
Platy Talc	50		
CI 25 DLC	10	Specific gravity	1.39

	150 m^2/g Silica	Ciptane I
Cure Rate, 150°C, T_{50} minutes	8.1	7.4
Mooney Scorch, 121°C, T_5 minutes	30+	30+
Mooney Viscosity, ML_4100	103	86
Flow in Spider Mold, mm	13	19
Durometer, 23°C	87	86
100°C	77	75
NBS Abrasion Index	43	44
Compression Set, %, 72 hours, 70°C	60	49
Original Stress/Strain		
M20, MPa	2.8	3.2
M300, MPa	10	15
Tensile, MPa	14	15
Elongation, %	425	310
700 hours, 90°C		
Durometer	95	88
Tensile, MPa	13	15
Elongation, %	45	60
DeMattia Cut Growth, kc to 500%	4	1

BR 32

Elastomer: BR/SBR/NR Durometer: 90
Application: Floor tile

Polymer	100	Sulfur	3
High Styrene Resin	15	TBBS	2
150 m^2/g Silica	30	HMT	2
Hard Clay	100	Variables	
25C Resin	9		
Stearic Acid	2	Specific Gravity	1.38

	Emulsion	Solution: Zinc-Free
Polymer	SBR 1502	SBR 715 – 60 BR 1220 – 30 NR – 10
Zinc Oxide	5	0
PEG 3350	2	-
TMTM	0.5	-
Cure Rate, 150°C, T_{50} minutes	4.9	6.7
Mooney Scorch, 121°C, T_5 minutes	21	22
Viscosity, ML_4100	76	100
20 minute cure, 150°C		
Durometer, 23°C	88	90
100°C	69	74
M20, MPa	3.1	3.0
M300, MPa	10.4	11.3
Tensile, MPa	17	13
Elongation, %	470	380
Compression Set, Method A, constant force		
Deflection, initial, mm	1.22	0.51
Permanent Set, % final deflection	54.1	77.0
Creep, % final deflection	51.0	69.0
Taber Abrasion, H22, 1000 rev.; mg lost	142	105
DeMattia Cut Growth, kc to 500%	0.5	3
Pendulum Rebound (Z), %, 23°C	28	38
100°C	44	74

CHAPTER 5

COMPOUNDING PRECIPITATED SILICA IN EPDM

5.1 INTRODUCTION

The successful use of fine and medium particle size silicas in EPDM elastomers is based, as it is with other polymers, on a thorough study of curing systems and the relationships of sulfur, accelerators and activators to processing and vulcanizate properties. Suitably designed formulas will achieve the improvements in heat resistance, tear strength and adhesion normally associated with silica reinforcement.

In EPDM compounding, medium particle size silicas, BET surface area from 35 to 75 m^2/g, are of particular importance due to their ability to provide smooth extruded and calendered surfaces with low shrinkage. These processing improvements are evident in both black and non-black compounds. Unlike the compounding discussions in previous chapters, a large part of the material on EPDM will be based on formulas which contain medium particle size semi-reinforcing silica. A comparison of two low surface area silicas with a 150 m^2/g N_2SA silica, HAF black, a silane treated clay and a platy talc appears in Table 5.12. As can be seen in the tear and abrasion data, low surface area "semi reinforcing" silicas and non-black fillers have little reinforcing contribution, and contribute nothing to adhesion. They do, however, make a superior contribution to heat aging resistance and low hysteresis.

5.2 SILICA AND CARBON BLACK

In Table 5.1, the comparison of semi-reinforcing silica and GPF black is made on the basis of equal filler content, a procedure which leads to a slightly higher durometer in the black compound. The most important divergence between silica and black compounds appears in heat aging resistance. Accelerated aging tests also included 700 hours at 160°C and 70 hours at 190°C, but the silica margin of superiority is somewhat less for these conditions. Complete data are listed in Formulary compound EPDM 15 for a similar compound, with and without silane.

A similar comparison (not shown) between 65m^2/g N_2SA Silica (+2% mercapto silane) and N660, made in oil extended EPDM 5875, produced no significant difference in any property except one, although the aging temperature in this case was only 125°C. The single exception occurred in the compression set test conducted at constant stress (method A) where the silica compound is considerably more resistant to both initial and final creep. Both silica and black produce the same performance in terms of durometer, stress/strain, resilience, flexometer heat build-up, aging at 125°C and dynamic modulus and tan delta.

Table 5.1 Silica and Carbon Black

	65m^2/g N_2SA Silica	**N660 Carbon Black**
Filler Content, phr	60	60
ODR cure, 160°C, T_{90} minutes	15	13
ODR crosslinks, dN-m	45	48
Durometer hardness	61	66
700 hours, 165°C:		
Durometer	72	72
Tensile, MPa	7.7	4.7
Elongation, %	155	70
Compression set, 70 hrs, 150°C, %	85	73

Further comparisons of silica and carbon black involve a reinforcing grade, 220 m^2/g N_2SA, and HAF N330 black in which the silica is also modified by 3% of mercaptosilane A189. Outstanding differences are listed in Table 5.2.

The lower oil content in the silica compounds was intended, somewhat unsuccessfully, to maintain comparable hardness. Excepting abrasion index, the only useful function of silane coupling is to produce 300% modulus equal to that of HAF. Perhaps the most significant property contrast here is the resilience improvement (100°C rebound) in the slightly harder silica compounds. As this margin is attained with a relatively high surface area (small primary particle) silica, a compound based on a silica with particle size more comparable to that of HAF would presumably provide an even greater dynamic advantage. The significance of hot rebound has been discussed previously in respect to its relation to dynamic modulus and low rolling resistance tire treads.

A silica-black comparison in a peroxide cure system involves compounding difficulties in arriving at an equal hardness comparison. The fillers in this case are the same as those in the preceding paragraph. In order to match durometers, it is necessary to add oil and low Mooney EPDM to the silica compound, thereby producing unwanted changes in several other properties. Notwithstanding this, significant silica advantages remain in respect to tear strength and low heat build-up.

Table 5.2 Reinforcing Silica and HAF Black in EPDM

Filler, 50 phr	**220 m^2/g N$_2$SA Silica**	**220 m^2/g N$_2$SA Silica**	**HAF N330 Black**
Silane A189	0	1.5	0
Paraffinic oil	15	15	20
Specific gravity	1.13	1.13	1.09
MDR cure rate 160°C, T_{90} mins	5.0	3.5	4.8
MDR crosslinks,dN-m	17	14	19
Mooney scorch 121°C, T_5 mins	27	19	9
Mooney viscosity, ML_4100	78	53	47
Press cure, 160°C, min/min	12/22	12/22	15/25
Durometer: 23°C	71	73	68
100°C	68	72	65
Original Stress/Strain			
M300 modulus, MPa	3.0	8.5	7.6
Tensile, MPa	23	24	13
Elongation, %	660	570	460
Aged 700 hours at 150°C			
Durometer	85	84	82
Tensile, MPa	13	14	12
Elongation, %	155	160	110
Compression set, %, 70 hrs, 100°C	89	87	73
PICO abrasion index	68	105	63
MG Trouser tear, kN/m	13	9.0	6.2
Pendulum rebound (Z), %: 23°C	52	55	53
100°C	59	60	50
Goodrich flexometer: 100°C; 2.5%; 1 MPa			
Permanent set, %	26	17	11
Heat build-up, °C	39	38	35
DeMattia cut growth, KC to 500%	<0.5	1.0	<0.5
Strip adhesion to RFL nylon, N/25mm	99	106	72
Water immersion, 90°C, % swell			
24 hours	7.9	7.2	6.2
72 hours	7.5	8.5	6.3
170 hours	8.4	11	7.4
Other ingredients: EPDM346-100; ZMTI-1.5; ODPA-1.5; DesicalP-5; Zinc Oxide-1; PEG-0.5; Stearic acid-2; Sulfur-0.4; ZBDC-2; DTDM-2; MBTS-1.5			

Further insight into the silica-black relationship involves the examination of compounds based on filler blends. At what ratio of silica to black do the distinguishing features of silica reinforcement appear? Some answers appear in Table 5.3, based on the formula and fillers of Table 5.2.

Table 5.3 Blends of Silica and Black

220 m^2/g N_2SA Silica	0	15	30	50
HAF N330 Carbon Black	50	35	20	0
Paraffinic oil	20	17	15	15
Mooney scorch 121°C, T_5 mins	9	15	22	27
Durometer hardness	68	65	70	71
M300 modulus, MPa	7.6	6.0	4.4	3.0
PICO abrasion index	63	60	73	68
MG trouser tear, kN/m	6.2	5.5	7.8	13
100°C pendulum rebound, %	50	57	56	59
Static adhesion, RFL nylon (kN/25mm)	72	76	103	99

Significant improvement in tear strength appears only at 50 phr silica. However, 30 phr are sufficient to influence peel adhesion to RFL treated nylon fabric, and at 15 phr there is a rapid increase in hot rebound. Of great practical interest is the sizable increase in scorch safety at high silica-black ratios, probably due to the relatively high surface area of the silica used here. Unfavorable losses in modulus, compression and flexometer set (not shown) can usually be corrected, at some sacrifice in tear strength, by the addition of 3% mercaptosilane.

5.3 ACCELERATION SYSTEMS

The need for powerful acceleration in most EPDM compounds is especially important where precipitated silica is the reinforcing filler. This requirement, together with accelerator solubility limitations, leads to the use of three different accelerator types in a typical cure system. Zinc dibutyldithiocarbamate (ZBDC) is generally the accelerator of choice from both speed and solublity standpoints. Solubility evaluations in the form of bloom measurements indicate that TBBS is slightly more soluble than ZBDC in normal sulfur systems, and slightly less so in zinc-free systems. Both these accelerators are far superior to MBTS and TMTD in solubility.

Additional curing activity in a three part system is obtained from a thiazole or sulfenamide (e.g., TBBS, MBS, MBTS). The third component is selected from the group of sulfur donors, usually for use in low sulfur systems, or, in the case of dipentamethylenethiuramhexasulfide (DPTH), to increase the proportion of monosulfide crosslinks. Sulfur donors such as DTDM or MDB are also useful for moderating scorching tendencies. Among other accelerators, TMTM offers little activity and is inferior in retaining aged tensile; MBT is unduly scorchy. In contrast, MBTS is safe processing, active, and provides improved heat resistance, as shown in Formulary compound EPDM 15.

5.4 LOW SULFUR SYSTEMS WITH DONORS

The basic heat resistance qualities of EPDM are further enhanced by the design of low sulfur cure systems. An excellent definition of "low" sulfur is seen in Figure 5.1 where sulfur content is plotted against aged tensile and elongation.

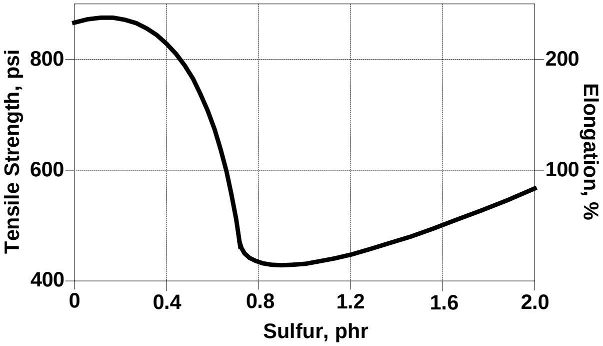

Figure 5.1 Effect of Sulfur Concentration on Tensile and Elongation

For best retention of both aged tensile and aged elongation, 0.4 phr sulfur is a maximum. However, properties such as compression set and cure rate are only slightly changed over a sulfur range of 0 to 2 phr. Zinc oxide plays an equally important role is attaining the best aging qualities, as illustrated in Figure 5.2. In this case, 10 phr is the minimum needed for optimum heat resistance.

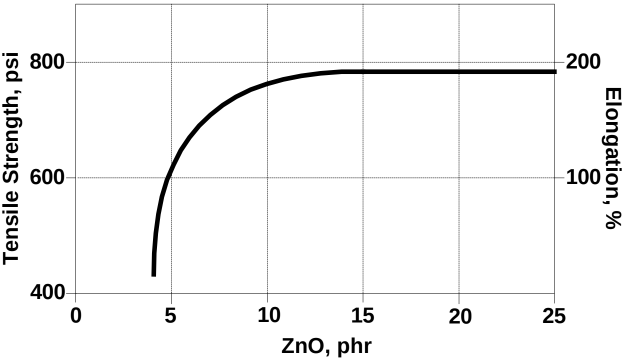

Figure 5.2. Effect of ZnO Concentration on Tensile and Elongation

Low sulfur content requires a sulfur donor. Figures 5.3a through 5.3e are a trend line evaluation of four common donors. DPTH and TMTD combine sulfur donation with crosslinking activity; DTDM and MDB are solely sulfur donors. For both good aging and low set, DPTH appears to be the best choice, accompanied with an inevitable sacrifice in trouser tear, cut growth resistance and scorch safety. For flex resistance combined with heat resistance DPTH can be replaced, in whole or in part, by MDB, as seen in Table 5.4.

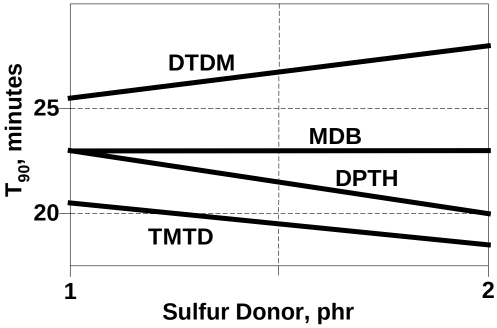

Figure 5.3a Sulfur Donor Concentration vs ODR 90% Cure at 154°C

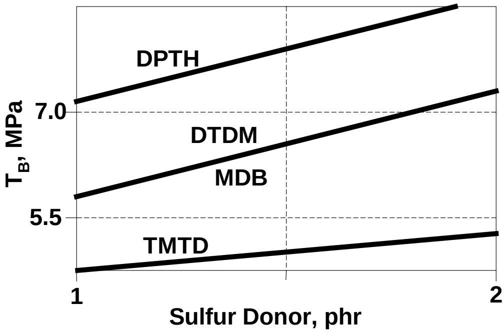

Figure 5.3b Sulfur Donor Concentration vs Tensile (T_B), 70 Hours at 175°C

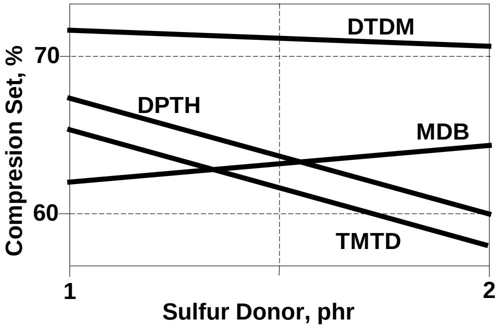

Figure 5.3c Sulfur Donor Concentration vs Compression Set

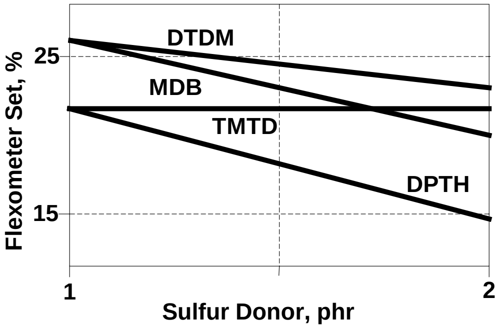

Figure 5.3d Sulfur Donor Concentration vs Flexometer Set

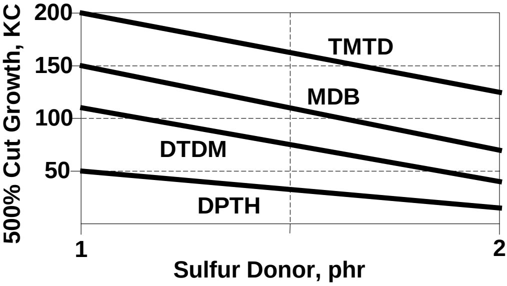

Figure 5.3e Sulfur Donor Concentration vs DeMattia Cut Growth

Formulary examples of heat resistant compounds with MDB include compounds EPDM 14, 15, 20, 25. Attaining superior heat resistance, set and dynamic properties through these accelerator systems can often be impeded by the presence of tackifying resins. Compression set, in particular, will benefit from omission of resin softeners.

Table 5.4 Cure Systems for Heat and Flex Resistance

Cure Systems	Heat resistance	Flex resistance
Sulfur	.04	0.4
MBTS	1.5	1.5
ZBDC	2.0	2.0
DPTH	2.0	--
MDB	--	2.0

5.5 ACTIVATION: OXIDES AND GLYCOLS

The role of zinc oxide in heat resistant formulas has been discussed above. In a normal, soluble zinc cure system for general purpose applications, adequate stress/strain and set properties generally require a minimum of 3 phr. Although magnesium oxide benefits heat resistance in other polymers, the effect is not apparent in EPDM. Aging at either 150°C or 175°C is not improved and both static and dynamic set are substantially increased by a 5 phr addition of magnesia. The effects of glycol activation must be related to the type of cure system and EPDM polymer. In a normal, soluble zinc system at sulfur levels of 1 to 2 phr, the addition of polyethylene glycol improves cure rate and reduces set. In ENB polymers, tensile strength is frequently increased. Perhaps the most unusual effect is a simultaneous increase in both cure rate and scorch safety. In heat resistant low sulfur systems, PEG has little effect except for a considerable loss in flex fatigue and cut growth resistance .

5.6 ANTIOXIDANTS: HEAT RESISTANCE

EPDM elastomers are the most heat resistant of general purpose polymers. In much of the work described below, heat resistance has been evaluated over the same 700 hour period used for other elastomer compounds, but at higher temperatures, the most severe being 165°C. Naturally, this temperature is usually reserved for those EPDM grades with the lowest unsaturation. Heat resistance evaluations are also made at 175°C for 70 hours. In addition to polymer unsaturation, sulfur content and acceleration systems, as well as antioxidants, all have a role in developing superior heat resistance. Cure systems effects have been described above. All accelerated aging tests for temperatures greater than 120°C are conducted in ventilated tubes in an aluminum block heater.

Antioxidant studies which involve NBC (nickel dibutyldithiocarbamate) were first undertaken to exploit the UV resistant properties of NBC (e.g., Formulary compound EPDM 17). However, it became apparent that this material is also effective in combating oxidation as well as UV degradation. Many of the compounds designed for heat resistance in these studies contain a total antioxidant content of 6 phr, divided among three different antioxidants, of which NBC is frequently the predominant member. In Table 5.5 the aging performance of two such compounds, which differ only in NBC content, indicate that NBC at 3.5 phr contributes to a remarkable retention of tensile and elongation after 700 hours at 165°C.

Complete formula and data are listed in Formulary compound EPDM 15. Black N550 controls evaluated in the same series with NBC at 3.5 phr have the same 5 point durometer increase, but elongation after 700 hours of aging is only 400%.

Table 5.5 Superior Aging Antioxidant Blends

NBC	3.5	2.0
TMQ	1.0	2.0
ZMTI	1.5	2.0
Durometer: Original	65	61
700 hrs, 165°C	70	76
Tensile, MPa: Original	13	12
700 hrs, 165°C	15	7.7
Elongation, %: Original	680	670
700 hrs, 165°C	495	155

5.7 ZINC-FREE CURE SYSTEMS

The objective of improving abrasion resistance through the removal of soluble zinc stearate from the silica surface is successfully accomplished in EPDM, as in other solution polymers, by eliminating stearic or other fatty acids from the compound. This process and its attending compound property changes are described in Table 5.6. Compound A is a normal zinc oxide activated cure system; B is a typical zinc-free system with zinc oxide reduced to 1 phr and stearic acid omitted; compounds C, D and E reflect accelerator activity. Success of the zinc-free system in raising abrasion resistance is apparent from the increase in index from 46 to 79. Complete elimination of zinc oxide produces a further increase, but the accompanying crosslink density and modulus losses, together with accelerator blooming, indicate the need for a minimum zinc presence. Excessive durometer losses at 100°C illustrate a further role for zinc in maintaining heat stability. However, the zinc concentration of 1 phr used in the zinc-free system is not adequate to match the retention of tensile and elongation during accelerated aging of the normal zinc control. It can be concluded that the role of soluble zinc in providing age resistance is comparable to that of antioxidants.

Rheometer crosslink losses are reflected in significant loss in 300% modulus in the zinc-free compounds, which is not adequately countered by improved silica-polymer bonding. One remedy to this typical zinc-free shortcoming is the addition of silane coupling. The sulfur cured compound in Table 5.7 is a good example. Here the mercaptosilane coupled zinc-free compound D has partially closed the crosslink gap and attained vastly superior modulus and abrasion resistance compared to that of the normal soluble zinc control B (notwithstanding minor formula changes). An alternative remedy involves the use of the sulfur donor thiuram, DPTH. This material is possibly the most effective accelerator in zinc-free systems, its use limited only by scorch considerations.

Table 5.6 Zinc-Free Cure Systems for EPDM

Cure System:	**A**	**B**	**C**	**D**	**E**
Sulfur	1.5	1.5	1.5	1.5	1.5
TBBS	2	2	2	2	2
ZBDC	2	2	2	2	-
DPTH	2	2	2	-	-
Zinc oxide	5	1	-	-	-
Stearic acid	2	-	-	-	-
MDR cure rate 160°C: T_{50} min	3.9	2.6	2.6	3.1	5.2
T_{90} min	14	3.9	3.3	4.2	17
MDR crosslinks, dN-m	45	25	15	14	10
Reversion at 25’, dN-m	+	1	6	2	+
Mooney scorch 121°C, T_5 min	18	16	17	21	30+
Mooney viscosity $ML_4$100	44	56	59	57	67
Bloom, 40 days	None	None	Much	Mod.	Mod.
Durometer: 23°C	68	64	62	63	63
100°C	70	66	50	50	50
Original Stress/ Strain					
Cure time, 160°C, minutes	20	6	6	6	20
M300, MPa	4.5	3.6	2.0	1.6	1.3
Tensile, MPa	5.3	26	18	10	2.7
Elongation, %	340	725	925	1100	1200
Aged 70 hours, 175°C					
Durometer	81	82	81	82	81
Tensile, MPa	6.5	4.5	4.9	3.3	3.9
Elongation, %	75	30	45	15	35
PICO abrasion index	46	79	109	96	33
Pendulum rebound, %: 23°C	63	61	57	59	61
100°C	68	66	49	51	47

Ingredients: EPDM 346-100; 150 m^2/g N_2SA silica-40; 2280 oil-15;TMQ-1; stearic acid-varied. Banbury 2: Zinc oxide- varied; Sulfur-1.5; TBBS-2; Accelerators-varied

Of interest in respect to factory production is the significant increase in cure rate (particularly lower T_{90}) in the zinc-free compounds. Faster cure rate is somewhat mitigated by an accompanying decrease in rheometer crosslink density, indicating a significant reduction in all types of sulfur crosslinks.

The success of hexamethylenetetramine (HMT or hexa) in effecting favorable changes in the rheometer curves of zinc-free BR compounds leads to similar expectations in EPDM. Unfortunately, the addition of 1.5 phr to compound B in Table 5.6 produces, excepting a 2 minute increase in scorch safety, none of the desirable cure and viscosity changes that occur in solutions BR and SBR. This failure may be partially related to the dilution effects of the relatively large oil content in this and other EPDM formulas.

Table 5.7 Normal and Zinc-free Cure Systems with Silanes

	A	**B**	**C**	**D**
Cure System:	Peroxide	Sulfur	Peroxide	Sulfur
Stearic Acid	2	2	0	0
DCP	2.8	-	-	-
BPDIB	-	-	2.8	-
Sulfur	-	0.4	-	1.5
Zinc oxide	15	15	1	3
Zinc dimethacrylate	-	-	3	5
EGMA	5	-	-	-
Silane A174	-	-	1.5	-
Silane A189	-	-	-	1.8
ODR cure rate 155°C, T_{90} min	20	20	-	-
MDR cure rate 160°C, T_{50} min	-	-	8.2	10
Rheometer crosslinks, dN-m	69	68	41	46
Durometer hardness, 23°C	78	75	78	79
Compression set, %, 70 hrs, 100°C	35	80	44	82
Original stress/strain				
M300 modulus, MPa	3.3	1.9	9.8	9.8
Tensile, MPa	14	14	23	25
Elongation, %	690	710	505	475
Original S/S at 100°C				
M300, MPa	2.3	1.6	-	-
Tensile, MPa	6.7	4.0	-	-
Elongation, %	980	970	-	-
Aged 700 hours at:	150°C	150°C	140°C	140°C
Durometer	88	88	-	-
Tensile, MPa	10.3	10.9	17	14
Elongation, %	220	130	255	110
PICO abrasion index	84	67	137	166
MG trouser tear, kN/m	105	85	14	13
Pendulum rebound (Z), %: 23°C	51	50	57	58
100°C	53	56	58	60
DeMattia cut growth, kc to 500%	9	2	1	2
Ross flex cut growth, aged, to 500%	100+	4	-	-

A,B: EPDM346-100; 150 m^2/g N_2SA silica-55; oil-20; TMQ-2; PEG-1;
B:MDB-2; MBTS-1.5; ZBDC-1
C,D: EPDM346-100; 160 m^2/g N_2SA silica -60; oil-20; TMQ-2, PEG-1;
D:ZBDC-2; TBBS-1; DPTH-1

Accelerator bloom is a frequently encountered problem in EPDM compounds, which usually contain larger than normal amounts of curatives. A legitimate question for zinc-free systems, in which crosslinking chemistry is drastically altered, concerns the changes which may occur in accelerator solubility. A modest study of the blooming activity of TBBS, MBTS, TMETD, and ZBDC in both zinc-free and stearic acid activated systems produced the somewhat unexpected results noted in Table 5.8. After 7 days of shelf aging of the cured stock, only MBTS and TMETD show a significant tendency to bloom, and this occurs only in the soluble zinc (stearic acid) compounds. After 40 days there is little to choose between zinc free and normal zinc systems based on these two accelerators. The most bloom resistant compound is the zinc-free version based on ZBDC. It should be noted that, to promote blooming in these experiments, accelerators are added to the first Banbury stage and mixed to 160°C.

Table 5.8 Blooming Tendencies in the Zinc-free System

	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
Stearic acid	2	0	2	0	2	0	2	0
Accelerator, 2 phr	TBBS		MBTS		TMED		ZBDC	
Bloom rating*								
Shelf aged (cured): 7 d	0.2	0.2	1	0	1	0	0.2	0
40 d	0.3	1	4	3	4	4	1	0.2
MDR, 150°C, T_{50} min	9.5	4.5	14	13	11	10	9	4
MDR Xlinks dN-m, 60min	21	15	17	13	12	5	20	14
Scorch,121°C, T_5 min	30+	18	30+	30+	7	-	30+	17
Mooney visc, ML_4 100	56	64	58	71	68	72	58	68
Durometer hardness:								
23°C	54	53	50	54	52	53	52	55
100°C	54	50	48	49	48	43	51	51
M300 modulus, MPa	2.0	2.6	1.7	1.6	1.9	1.7	2.2	3.1
Tensile, MPa	14	15	13	13	11	2.8	16	16
Elongation, %	840	950	920	945	1000	665	840	920
Compression set, %, 70 hrs, 100°C:	83	91	90	92	95	00	88	95
Pendulum Rebnd (Z), %:								
23°C	64	64	62	63	65	67	65	64
100°C	71	62	65	69	59	53	68	61

*0 to 5 scale; surface completely covered at 5

Ingredients: EPDM 4969-66; EDPM 40A-67; SBR 1620- 1; 65 m^2/g N_2SA silica-57; 150 m^2/g N_2SA silica-13; 410 oil-16; ZNO-2; sulfur-2(2nd stage); ZBDC-1; (TBBS-1 in G & H); variables added in Banbury 1

Formulary compound examples of zinc-free systems include EPDM 7, 9, 21, 31, 34, 36, 37, and 38. The benefits of zinc-free systems for adhesion to galvanized metal are discussed in later sections.

5.8 SILANE COUPLING

Mercaptosilane coupling agents on high surface area silicas are effective in producing an improved state of cure and enhanced reinforcement in both normal zinc activated and zinc-free cure systems, as demonstrated in Tables 5.9 and 5.10. The major effects of MPTS at 3% silica basis include substantial increases in cure rate, 300% modulus, abrasion index and DeMattia cut growth resistance, together with a reduction in viscosity. Relatively unaffected are durometer, tensile, elongation, heat resistance, resilience, compression set and flexometer heat build-up. However, with low surface area semi-reinforcing silicas, the usual desirable changes in abrasion index and set are in a more moderate range (e.g., Formulary compound EPDM 15), similar to those seen in natural rubber and considerably below those obtained in SBR and BR. Heat aging performance is not significantly improved.

Silica surface area effects are discussed in detail in the next section. Silane effects in various compounds are seen in Formulary compounds EPDM 2, 4, 5, 12, 13, 15, 18, 20, and 31. Formulary compound EPDM 31 illustrates the role of silane in improving the low cure state produced by an unmodified high surface area silica in a 74 durometer compound. The performance of silane treated silica in 80 durometer EPDM is seen in Formulary compound EPDM 34.

An interesting, but unfavorable, result of silane modification of silica - polymer bonding and silica structure appears in EPDM brake cup compounding. The undesirable leaching of plasticizing oil by brake fluid is greatly increased in compounds which contain mercaptosilane, an action which returns the silica compound to the same level of behavior seen in black reinforced compounds. Silane interference with the normal leaching of soluble salts (and reduced compound swelling) during water immersion has been discussed in earlier chapters.

How much silane is required, is there an optimum concentration, and does it depend on silica surface area? Answers to these and other questions appear in Tables 5.9 and 5.10 where mercaptosilane (MPTS) concentrations are varied from 2 to 8% for two high surface area silicas in normal and zinc-free formulas. The principal reason for using silane with silica is to increase abrasion resistance. Unfortunately, the zinc-free system has already raised abrasion indices to the point where any silane influence is obscured. This conflict is also apparent in 300% modulus, compression set and resilience.

Table 5.9 Silane Concentration, Silica Surface Area in Zinc-free EPDM

	150 m^2/g N$_2$SA Silica			220 m^2/g N$_2$SA Silica			
	A	**B**	**C**	**D**	**E**	**F**	**G**
Mercaptosilane, phr	1.2	2.4	4.8	0	1.2	2.4	4.8
Silica basis, %	2	4	8	0	2	4	8
MDR, 160°C, T_{90}	16	11	5.4	15	17	20	12
MDR Xlinks dN-m	22	25	14	10	12	16	12
Scorch,121°C, T_5	14	9	7	14	17	19	9
Visc, ML_4 100	48	46	55	80	68	58	56
Original stress/strain:							
Durometer	75	74	73	77	78	76	71
M300, MPa	7.6	8.4	7.8	3.0	5.6	7.2	7.6
Tensile, MPa	21	20	20	18	21	22	21
Elongation, %	635	580	635	900	800	720	625
Aged 700 hrs, 150°C	- All brittle -						
PICO abr. index	143	149	129	142	136	160	157
MG tr tear, kN/m	11	10	14	51	25	18	14
Compression set, %, 70 hrs, 100°C:							
	83	90	92	96	96	88	91
Rebound resilience, %:							
23°C	56	57	57	58	58	58	58
100°C	60	59	60	55	55	59	59
DMA dynamic modulus, 1 Hz, 60°C:							
E”, MPa	1.57	1.35	1.09	1.34	1.20	1.21	0.91
E’, MPa	13.2	11.0	7.4	11.6	12.5	11.4	6.7
Tangent delta	0.119	0.123	0.146	0.116	0.095	0.107	0.136
Dynamic coefficient of friction, wet aluminum:							
	0.96	1.09	1.04	0.94	1.04	1.00	1.05
100°C H_2O immersion, % swell:							
24 hours	6.3	7.9	4.8	9.9	4.5	3.0	3.7
48 hours	11	11	9.2	11	6.3	6.2	6.2
170 hours	23	23	18	14	8.7	9.6	10

Ingredients: EPDM 346-100; silica-60; 510 oil-15; 2280 oil-10 (12 with 220 m^2/g silica); ODPA-1 ZMTI-1; Zn methacrylate-2; sulfur-2; TBBS-1.5; ZDBC-1.5; DPTH-1.5

The situation becomes even more complicated in respect to rheometer data. With low BET surface area silicas, cure rate increases in concert with silane concentration; with high surface area (150 to 250 m^2/g) silicas no such increase occurs until silane is increased to 8%. This response only at 8% is reflected in the dynamic modulus tests where both loss and storage moduli undergo a precipitous drop at the 8% concentration.

Table 5.10 Silane Concentration, Silica Surface Area in Sulfur Cured EPDM

	150 m^2/g N_2SA Silica			220 m^2/g N_2SA Silica			
	A	**B**	**C**	**D**	**E**	**F**	**G**
Mercaptosilane MPTS	1.2	2.4	4.8	0	1.2	2.4	4.8
% silane, silica basis	2	3	8	0	2	4	8
MDR cure, 160°C, T_{50} min	5.9	5.2	2.7	6.2	5.9	6.2	4.5
T_{90} min	14	15	16	-	-	-	-
MDR Xlinks, 15 min dN-m	20	22	23	15	16	15	19
Scorch 121°C, T_5 min	20	14	5.5	26	30+	30+	9
Mooney visc, ML_4 100	42	44	48	84	68	54	50
Durometer: 23°C	73	71	67	74	72	70	67
100°C	72	69	65	71	72	68	64
M300 modulus, MPa	8.2	9.6	10.4	2.7	6.3	6.5	6.5
Tensile, MPa	16	18	20	22	25	25	24
Elongation, %	495	475	470	810	735	745	720
Din Abrasion loss, ml	150	139	117	171	134	117	118
PICO abrasion index:							
23°C	97	115	126	85	110	126	136
100°C	65	72	81	57	72	82	94
Comp set, 70 hrs, 100°C, %	51.6	49.5	43.2	76.4	69.1	66.7	61.1
DMA dyn mod, 30°C, 1 Hz							
E”, MPa	1.20	1.27	0.63	1.10	1.02	1.12	0.80
E’, MPa	11.2	9.8	5.3	12.9	11.0	9.7	5.9
Tangent delta	0.107	0.129	0.120	0.086	0.093	0.115	0.135
Goodrich flex, 100°C; 22.5%; 1 MPa:							
Dynamic Compression %	2.3	2.4	3.9	6.9	4.3	5.2	8.2
Permanent set, %	11	10	8.6	blow	blow	21	blow
Heat build-up, °C	39	34	32			39	

Ingredients: EPDM 346-100; silica-60; 510 oil-15; stearic acid-2, ZMTI-1; ODPA-1
Banbury 2: Zinc oxide-10; PEG-0.5; sulfur-0.5; MBTS-1.5; DTDM-2, 1.5,1.0

It might be predicted that this silica structure de-agglomeration phenomenon would also be seen in the uncured state in a significant reduction in viscosity. That this did not occur is probable evidence of the strength of the silica network structure in a green zinc-free compound environment. The importance of silane coupling in providing extended compression fatigue life is discussed in a later section.

5.9 SILICA SURFACE AREA

In general, silicas of higher surface area produce compounds with increased reinforcement and higher uncured viscosity. Major changes occur between the easy processing areas of 35 to 65 m^2/g and the reinforcing areas of 125 to 250 m^2/g. An equal hardness comparison of surface area effects in a normal zinc activated formula is seen in Table 5.11.

Table 5.11 Silica Surface Area Effects

Silica m^2/g N_2SA	65	150	180	220
Paraffinic oil	18	25	25	25
MDR cure rate, 160°C, T_{90} minutes	15	10	14	15
MDR crosslinks, dN-m	25	19	19	19
Mooney viscosity, ML_4100	26	48	54	71
Durometer hardness	67	70	69	70
Tensile, MPa: Original	9.4	19	21	21
700 hrs, 155°C	13	11	7.4	8.2
Elongation, %: Original	555	680	710	720
700 hrs, 155°C	90	85	25	45
PICO abrasion index	31	52	54	59
MG trouser tear, kN/m	5.1	19	20	26
Compression set, %	66	80	84	89
Ingredients: EPDM346-100; Silica-60; Oil-var; ODPA-1.5; ZMTI-1.5; Stearic acid-2; ZnO-10; PEG 0.5; Sulfur-0.4; ZBDC-2; DTDM-2; MBTS-1.5				

Once the reinforcing surface area of 150 m^2/g is reached , there is little to choose between 150 and 220 m^2/g. The low surface silica (65 m^2/g) has an obvious advantage in heat resistance and low viscosity to add to its previously noted extrusion and calendering superiorities. However, low surface area silicas cannot be expected to match the tensile, abrasion, and tear properties of reinforcing silicas in the 150 to 250 m^2/g range. Among the reinforcing grades, aging performance declines with increasing surface area. Explanation of the improved crosslink density with low surface areas involves their reduced sequestering of soluble zinc, thus leaving more available for its cure activating function. This activating function includes production of a greater proportion of monosulfide crosslinks. Interestingly, the crosslinking increase is not reflected in the essentially unchanged 300% modulus values where reduced reinforcement from the large primary particle size overcomes the crosslinking component (not shown).

Table 5.12 combines a silica surface area evaluation with that of two non-black semi-reinforcing fillers as well as HAF N330 black. The silane treated clay and the untreated platy talc, while equal in reinforcement, differ completely in resistance to accelerated aging. In this respect, the talc compares favorably with the low surface area silicas. However, the heat resistance advantages of low surface area fillers do not extend to adhesion evaluations where 150 m^2/g appears to be a minimum surface area for good bonding. Reduced volume swell during water immersion also favors the higher surface area silica, although the very low talc and HAF values are best. Easy processing Formulary compounds based on low surface area silicas include EPDM 1 through 6, 10, 14, 18, 20, 22, 25, 26, and 29.

Table 5.12 Silica Surface Area Effects vs Clay, Talc and Carbon Black

Filler (60 phr)	Silica			Clay[1]	Talc[2]	N330
N_2SA, m^2/g	150	65	35	25	18	82
ODR cure, 154°C, T_{90} min	31	32	21	19	20	16
Scorch 121°C, T_5 min	30	30	22	13	13	9
Mooney visc, $ML_4$100	58	33	32	22	22	53
Stress / Strain (Cure 35 min/154°C):						
Durometer hardness	71	70	63	63	64	75
M300 modulus, MPa	2.3	2.1	1.7	2.1	2.1	8.0
Tensile, MPa	17	11	11	16	13	20
Elongation, %	780	660	600	600	620	540
Aged 700 hours, 160°C:						
Durometer	93	85	78	93	78	93
Tensile, MPa	4.8	9.0	12	1.4	8.3	7.6
Elongation, %	20	80	120	10	100	10
180° bend	Bk	Flx	Flx	Bk	Flx	Bk
MG trouser tear, kN/m	15	4.9	2.5	2.6	3.3	7.6
PICO abrasion index	76	40	24	33	34	92
DeMattia cut growth, kc to 500% growth	50	2	0.3	2	1	2
Goodrich flexometer, 100°C; 22.5%; 1MPa:						
Durometer	67	67	62	62	62	79
Dynamic Comp %	8.4	6.5	5.0	7.5	9.3	1.4
Drift, %	28	17	11	6.5	19	10
Permanent set	33	17	9.7	10	19	8.2
Heat build-up, °C	56	45	36	33	56	49
Strip adhesion to RFL nylon fabric, kN/m:	14	6.0	2.1	2.3	1.8	5.1
water immersion, 70 °C, % vol increase: 24 hours	3.2	4.4	1.7	1.5	0.9	1.5
168 hours	6.9	15	12	3.5	2.3	2.2
340 hours	9.4	18	14	11	3.4	2.8

[1] Nucap, silane treated kaolin; [2] Mistron, platy talc

Ingredients: Epcar 346-100; filler-60, oil-20; TMQ-2; stearic acid-2; zinc oxide-10; PEG3350-0.5; Sulfur-0.4;ZBDC-1.5; MDB-1.5

A Formulary example of a blend of a low surface area clay with a very high surface area silica appears in Formulary compound EPDM 21. Here the non-reinforcing nature of the clay is overcome, in respect to both tear and abrasion, by the silica content of 70 phr.

Surface area comparisons with a peroxide curing system reveal remarkably few differences in both static and dynamic properties. Exceptions include the outstanding age resistance of a 130 m^2/g CTAB silica. This behavior, anomalous in respect to surface area, may well be related to this product's carbon dioxide precipitation and post acidification with hydrochloric acid, procedures which are unique among commercial silicas.

5.10 PEROXIDE CURE SYSTEMS

Silica reinforced EPDM cured with peroxides and co-agents exhibits the improvements in set and heat resistance which are normally obtained with this system in black reinforced compounds. Low surface area silicas are preferred for lowest set. The presence of sulfur acts to increase cure rate at the expense of age resistance. Glycols produce an anomalous combination of reduced cure state (low modulus), low set and improved heat resistance. Limited evaluations of peroxide types indicate that dicumyl peroxide (DCP) provides better retention of aged stress/strain properties than does butylperoxydiisopropylbenzene (BPDIB). Concentrations greater than 3 phr may reduce aging and cut growth resistance. Examples of peroxide compounds include Formulary compounds EPDM 9, 10, 12, 17, 24, 30, 32, 33, 35 and 39.

Comparisons between peroxide and sulfur cure systems are made both with and without added stearic acid, that is, with both normal and zinc-free sulfur cured compounds, as in Table 5.7. The comparable hardness objective is easily attained in all four compounds but the relatively high (20 phr) oil content in the stearic acid pair leads to slightly high elongation values. In the case of zinc-free compounds (C and D), the lack of zinc interference with polymer bonding together with the presence of silane coupling produces vulcanizates of lower elongation and much higher reinforcement, with little change in cure rate, crosslinking, and stress/strain properties. In both compound pairs the customary low compression set contribution of peroxide crosslinking is evident. A peroxide advantage in heat aging resistance, however, is seen only in the pair without stearic acid (C and D). PICO abrasion indices and trouser tear values indicate that peroxide systems have little to offer in respect to these properties in the zinc-free system, and only a slight superiority in comparison to a normal sulfur cure compound (A and B).

Peroxide EPDM compounds also benefit from silane coupling. In this case, their coupling requires the presence of unsaturated functionality on one end of the silane molecule. A methacryloxy type (A174) is typical. Effects of note include an increase in PICO abrasion index, and reductions in trouser tear and set. Crosslinking, viscosity, durometer, stress/strain and dynamic properties are unchanged by coupling.

Peroxide cured EPDM has a prominent role in the production of transparent compounds, for footwear and other applications. Typical compounds, based on a blend of EPDM 1660 and EVA, are described in Formulary compound EPDM 30.

5.11 PROCESSING

The contribution of coarse and medium particle size silicas in producing exceptionally smooth extruded and calendered products of low shrinkage cannot be overemphasized. Semi-reinforcing silica contents of 50 to 180 phr are generally required to achieve these effects. Formulary compounds EPDM 1, 2, 4, 5, 10, 14, 15, 18, 20, 22, 25, and 29 are all noted for their excellent processing properties.

Inadequate building tack has frequently been a characteristic production problem for EPDM compounds. To the extent that semi-reinforcing silicas produce low viscosity, they offer significant help in overcoming this problem. Other methods to improve tack involve partial replacement of the original EPDM polymer with low molecular weight grades, or the addition of well broken down natural rubber. Table 5.13 is based on a 30/40 phr blend of 65 m^2/g N_2SA silica and N550 black in BPDIB peroxide cured EPDM. Tack is measured by separating hand stitched uncured strips after shelf aging of 24 and 120 hours.

Table 5.13 Tack Improvement in EPDM

Royalene® 580HT	60	100	--
Keltan® 1446A	40	--	--
Epcar® 346	--	--	100
Natural rubber, milled	--	--	30
Mooney viscosity ML_4100	53	75	43
Autotack, avg.N/25mm: 24 hours	11	7	19
120 hours	21	6	23
Ingredients: Formulary compound EPDM 39			

It is apparent that tack separation values are closely related to viscosity reduction. Other than a reduction in elongation from 655% to 535% in EPDM 580HT, curing and vulcanizate properties were not significantly altered by the polymer substitution and addition changes in these compounds. An increase in silica content from 30 to 70 phr in the EPDM 346 formula does not change tack values, but produces a 100% increase in cured adhesion to RFL fabric.

Viscosity reduction without hardness loss in peroxide systems is most efficiently obtained through the use of a maleinized liquid polybutadiene (Ricobond® 1731). The relationship between viscosity and durometer, as shown in Table 5.14, is a feature of this material which sets it apart from paraffinic oil and low molecular weight EPDM.

Table 5.14 Liquid Polybutadiene: Hardness and Low Viscosity

Ricobond® 1731	15	--	--
EPDM 1446A	--	15	--
2280 oil	--	--	15
Mooney.viscosity,$ML_4$100	75	100	76
Durometer	92	81	78
Ingredients: Formulary compound EPDM 39			

Banbury mixing temperatures can have important effects on both processing and physical properties. For example an increase in stock temperature from 140°C to 185°C has produced major changes in viscosity reduction, improved scorch safety, lower set, reduced durometer and increased tensile strength. These benefits are probably related to silica free water loss at high mixing temperatures, a surface modification which reduces the strength of the silica network structure and improves silica - EPDM bonding. These temperature mixing effects can vary among EPDM types and silica grades and content. Improved processing is obtained only with semi-reinforcing silicas, e.g., 35 m^2/g N_2SA, at contents of 100 phr or more. The presence of large amounts of oil or extender fillers mitigates the temperature effect. Normal contents (60 phr) of reinforcing silicas generally respond to high mixing temperatures only in terms of vulcanizate property improvement, for both normal and zinc-free systems. Hot mixing of certain EPDM grades degrades reinforcement.

The use of crosslinking promoters during hot mixing is also productive for improved processing and vulcanizate properties. Dithiodimorpholine (DTDM) has been effective in producing improved cure state and tensile with reduced viscosity in EPDM 1165 with 180 phr of 35 m^2/g N_2SA silica.

Mixing order of EPDM compounds frequently includes the upside down procedure in which silica and oil are preblended in the Banbury prior to polymer addition. Unlike carbon blacks, silicas do not suffer dispersion degradation from concurrent addition of large amounts of oil.

5.12 ADHESION TO BRASS

Early work on the bonding of silica reinforced EPDM to brass relied chiefly on the static peel separation of press cured laminates of compound and brass sheet [1]. The brass composition in this work was 71/29. As in all adhesion evaluations, test procedures have a profound influence on results, particularly in the case of static versus dynamic (cyclic) deformation. Dynamic procedures reveal differences among compounds and metal surfaces which are not apparent from static peel testing; in some cases the reverse is true. Static procedures, however, are quite adequate to establish some of the basic requirements for bonding EPDM to brass.

Precipitated silicas appear to be unique in providing a wettable or compatible compound surface which affords intimate contact between rubber and metal. The positive influence of silica content in blends with SRF black is seen in a comparison between a 65 m^2/g N_2SA silica and N770 black in Table 5.15.

Table 5.15 Brass Adhesion: Silica and Carbon Black

65 m^2/g N_2SA Silica	40	80	120
SRF N770 Carbon black	80	40	0
Static Peel Adhesion to brass strip, kN/m	1.0	>11	>16

When silica comprises the minor part of the filler blend, no bonding occurs. Reversal of the ratio of silica to black produces a substantial bond, which is further enhanced as silica becomes the sole filler. The > sign indicates tearing in the compound rather than a clean metal surface separation. For silicas of 150 m^2/g area and more, smaller minimum contents (55 phr) are both practical (in a processing sense) and preferred to attain the high bond values noted above.

As we have previously found for bonding natural rubber to brass, variables such as sulfur and zinc oxide content, together with the addition of magnesium oxide, are important to successful bond formation. Zinc oxide and sulfur effects, within a narrow range, are summarized in Table 5.16.

Table 5.16 Brass Adhesion: Zinc Oxide and Sulfur Effects

Zinc oxide	5	5	15	15
Sulfur	1.5	3.0	1.5	3.0
Static brass strip adhesion, N/m				
Cure: 20 min/155°C	8.8	9.7	13	19
35 min /155°C	5.3	11	7.0	>18
60 min /155°C	6.2	1.7	8.0	2.7

Higher levels of both variables produce the highest adhesion values, but 3 phr sulfur leads to a complete loss at long cure times. When zinc oxide is added in the second stage of a Banbury sequence, adhesion is lost even at 35 minutes. Unfortunately, these interesting sulfur/cure relationships could not be verified in wire pull-out testing.

The vulnerability of the brass bond to over-curing is best demonstrated in a plot of sulfur content and static bond strength at a cure of 70 minutes at 155°C, in Figure 5.4.

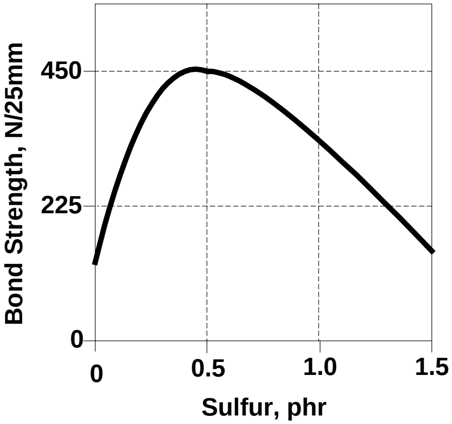

Figure 5.4. EPDM-Brass Adhesion at Overcure

A sulfur concentration of 0.5 phr is an obvious optimum to avoid adhesion loss at long cure times. In this case, brass bond strength of the low sulfur compound remained at 19 kN/m over the entire curing range. Acceleration in this compound includes ZBDC, 2; MBS, 1.5; DPTH, 1; stearic acid, 4; ZnO, 10.

The appearance of the separated compound surface after adhesion testing supplies a clue to the mechanism of over-cured bond failures. Many over-cured specimens in which static adhesion values fall to 5 to 10 kN/m have a metallic coating residue on the separated EPDM compound surface. Analysis of this coating shows a predominance of copper. The conclusion is that over-cured bond failure is not interfacial, but occurs in the surface of the brass. When these compounds are bonded to brass-coated steel wire, the pull-out values of over-cured specimens show no evidence of adhesion degradation.

An alternative remedy to the over-cure problem with brass sheeting is a partial replacement of zinc oxide by magnesium oxide. With sulfur at 1.5 phr, a 5 phr replacement produces a compound with no significant adhesion loss over the entire cure time range, up to 90 minutes at 155°C. Another possible remedy is the use of resorcinol-hexa resin combinations, which have been a more or less standard component of many natural rubber brass skim compounds. In EPDM they have proved to be less than effective. Additions of as little as 2.5 resorcinol and 1.5 HMT produce adhesion losses in both static and dynamic test modes.

Cure temperatures can also influence brass adhesion. A minimum of 155°C is recommended. Another important factor in evaluating brass adhesion is the age of the uncured compound. Bonded specimens prepared with freshly mixed stock are often found to produce over-cured adhesion losses which do not occur with compounds aged one or two days between milling and curing. The relatively high stearic acid and zinc oxide concentrations in many of the brass adhesion formulas reflects their importance in untreated nylon adhesion and heat resistance.

Although accelerator type has a great influence in bonding natural rubber to brass, in EPDM concentration appears to be of more importance than type. In a system based on 0.8 sulfur and 2 ZBDC, a dynamic evaluation of MBS, MBT, MBTS, MDB and DPTH accelerated compounds finds a severe loss in bond fatigue life at the 2 phr level, but none at 1 phr.

The result of combining these compounding factors in a single brass adhesion formula can be seen in Formulary compound EPDM 3.

5.13 FABRIC ADHESION

Although much of the work on bonding EPDM compounds to fabrics has been carried out by the usual static strip adhesion procedures, a more complete picture can be obtained only when dynamic behavior (bond fatigue life) is included. A typical example of the relationship between static and dynamic procedures for two compounds which differ only in silica/black ratio appears in Table 5.17.

Table 5.17 Static and Dynamic Fabric Adhesion

	Silica/Carbon Black	
Adhesion to untreated nylon:	120/0	80/40
Static at 23°C, kN/m	5.2	3.9
Dynamic at 116°C, separation time, min	4.6	0.3

Although the static procedure indicates a moderate adhesion loss when silica (65 m^2/g) is partially replaced by SRF black, the dynamic procedure reveals an almost complete deterioration of bond life. In some cases, the static relationship can even be reversed by dynamic testing. In exploring the kinetic aspects of fabric bonding, described below, static adhesion data are used.

The two most important compounding variables in EPDM bonding are the ratio of silica to black and the use of bonding additives, chiefly resorcinol and its derivatives. When *RFL treated fabrics* are involved, only the silica content is a determining factor. An example is seen in Table 5.18, where a decrease in silica content of 20 phr produces a sizable loss of adhesion. Added resorcinol/hexa is ineffective, except in cure rate.

Table 5.18 EPDM Adhesion to RFL Treated Fabric; Silica Effects

150 m^2/g N_2SA Silica	60	40	40
65 m^2/g N_2SA Silica	20	30	30
Paraffinic oil	30	20	20
Resorcinol	0	0	3
HMT	0	0	3
Durometer hardness	64	63	64
Static Strip Adhesion, kN/m			
RFL treated nylon fabric	550	290	310
MG trouser tear, kN/m	20	8.0	8.6
PICO abrasion index	56	49	48
M300 modulus, MPa	2.4	2.1	3.4
Tensile, MPa	18	16	15
Elongation, %	795	750	675
Compression set, 70 hrs, 100°C, %	91	81	79
Pendulum Rebound (Zwick),%: 23°C	47	50	52
100°C	55	61	59
MDR cure rate 155°C, T_{50} minutes	10	12	4.5
MDR crosslinks dN-m	20	27	30
Mooney viscosity, ML_4 100	38	36	35
Ingredients: EPDM 346-100; EPDM 1446A-20; ZMTI-1.5; ODPA1.5; ZnO-10; Stearic acid-3; PEG-0.5;Sulfur1; MOR-1.5; ZBDC-1.5; TBBS-1.5			

Bonding EPDM to *untreated fabrics* provides the most revealing data on the development and strength of adhesive bonds. A lengthy series of experiments in which variables included silica/SRF black ratio (120 phr total), oil content, zinc oxide content, stearic acid content, and resorcinol content forms the basis for the observations below and the curves in Figure 5.5 [1]. Acceleration of these compounds remained unchanged with sulfur-1.5; ZBDC-1.8; MBS-1; TMTD-0.8; the EPDM is Nordel 1070.

Figure 5.5 illustrates the kinetic adhesion behavior of compounds based on this formula with silica/black ratios of 120/0, 80/40, and 40/80. Not only does the all-silica compound attain the highest bond strength, it does so at the fastest reaction rate. In reference to reaction rate, it should be noted that rate of adhesive bond development bears little relationship to rates of crosslinking development; cure rates are almost always faster. The data in this plot includes averages of several different ENB and HD EPDM compounds. These compounds all include higher levels of zinc oxide and stearic acid and intermediate resorcinol/hexa concentrations.

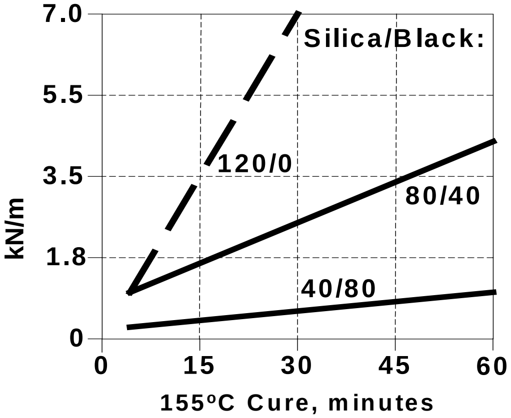

Figure 5.5 Silica: Black Ratio vs EPDM Adhesion to Untreated Nylon Fabric

Dotted lines indicate that the separation occurred in the compound rather than at the interface. Large amounts of adhering compound indicate that tear strength is a greater influence than actual adhesive strength on the 'adhesion' values. Interfacial separation which leaves a relatively clean fabric surface is a highly important feature of these test procedures. With 'clean' separations, it is safe to assume that evaluations are in terms of adhesion rather than compound cohesion.

In addition to the ratio effects described above, studies of the dilution of the silica filler by the addition of extender fillers (e.g., 40 phr hard clay) show that such dilution has a disastrous effect on adhesion.

Polyester cord in contact with EPDM compounds suffers tensile degradation during exposure to high temperatures. Investigation of this problem in respect to silica reinforced EPDM indicates that silica type, curatives and adhesion additives all have some influence on cord degradation. Conditioning compound-encased cord specimens for 4 hours at 175°C or 5 days at 150°C reduces cord tensile by 35% for both 150 and 65 m^2/g silicas with a sulfur donor cure system. A 35 m^2/g silica with a pH of 9 caused a loss of 60%. Resorcinol-HMT resins showed no additional adverse effects. A dicumyl peroxide cure reduced tensile loss to 10%, but BPDIB gave little improvement over the sulfur donor system (35%).

Formulary examples of EPDM fabric adhesion include compounds

EPDM 10, 11, 16, 19, 23, 27, 28, 29, 36, and 38.

5.14 ADHESION TO ZINC (GALVANIZED) COATINGS

Traditional compounding technology to achieve adhesion between EPDM compounds and galvanized (zinc-coated) surfaces required the presence of 1 to 10 phr litharge (PbO). Since environmental regulations have precluded the use of lead, the work discussed below is based on formulas without litharge or other lead compounds. There are, of course, other materials which can improve galvanized bonding. These include magnesium oxide, cobalt naphthenate, zinc oxide and resorcinol-hexa resins. These are present in most of the sulfur cured compounds described here. For the most part, these materials have not been successful in matching the static pull-out values achieved with litharge. In the case of peroxide systems, which generally provide higher static pull-out values, these additives appear to have little influence on bond strength.

As in all adhesion evaluations, test procedure is a critical factor. Most of the literature relies on static peel or pull-out procedures and data. Unfortunately, these are often at odds with data obtained from dynamic procedures which measure bond fatigue life, a property which has more predictive value for dynamic applications. In these discussions percent rubber cover is reported with the static separation value. The objective here is to distinguish between true interfacial adhesion (zero cover) and cohesive strength of the compound (50 to 100% cover). High percent cover does not necessarily predict high static bond strength.

Comparisons between silica and carbon black must be based on comparable cure systems. With sulfur crosslinking there is little to choose between the two fillers. With peroxide crosslinking, the superior wetting function of silica results in favorable margins in respect to both cable pull-out and percent rubber cover, as seen in Table 5.19.

Peroxide formulas do not contain stearic acid or additives such as magnesium oxide, cobalt naphthenate, and resorcinol which contribute to zinc bonding in sulfur based compounds. High pH silicas have not been evaluated in peroxide systems.

Among silica properties, surface area and pH are both important influences on adhesion. Unfortunately, the lower surface area, semi-reinforcing silicas are available only at somewhat higher pH values than those of the reinforcing grades. It is thus not possible to separate completely the effect of these two properties on zinc adhesion. Silicas of surface area greater than 150 m^2/g produce 50 to 100% rubber cover, but with no increase in pull-out values.

Table 5.19 Adhesion to Galvanized Metal: Silica and Black

150m2/g N2SA Silica	20	50
FEF N550 Black	65	35
2280 Oil		
MDR crosslinking, dN-m	43	37
Durometer	77	76
Adhesion to galvanized cable, 1.9mm diam.		
Pull-out, N/25mm	585	765
% cover	0	50
Other ingredients: EODM346-100; ZnO-1; OPDA-1; ZMTI-1.5; ZDMZ634-5; DCP40-7		

Cable pull-out adhesion data from a sulfur cured formula in which silica is the sole filler are noted in Table 5.20.

Table 5.20 Adhesion to Galvanized Metal: Silica Surface Area and HAF Carbon Black Effects

Filler	Silica	Silica	Silica	HAF N330
Silica N_2SA, m^2/g	35	65	150	-
Filler pH	9.8	8.5	7.0	6.5
Filler Content, phr	75	70	60	70
MDR cure rate 160°C, T50 min	11	8.0	5.3	4.8
MDR crosslinks, dN-m	19	12	10	28
Adhesion to galvanized cable, 1.9mm dia, cure 60 min/160°C				
Pull-out, avg. N/25mm	700	500	290	295
% cover	5	0	0	0
Other ingredients: EPDM346-100; 510 oil-20; OPDA-1; MgO-6; ZnO-3; Resorcinol-2.4; HMT-2; Cobalt Naphthenate-2; Sulfur-2; ZBDC-2; DPG-2				

Although pull-out data are notoriously dependent on modulus and hardness, the silica compounds here are all at 70 durometer and their adhesion differences are taken to be related to pH and, possibly, surface area. Highest pull-out together with slight evidence of zinc reaction is attained with the high pH silica (35 m^2/g N_2SA). Similar results have been obtained with a 45 phr/ 30 phr blend of 150 m^2/g and 65 m^2/g silica.

The reversal of the usual cure rate and surface area relationship indicates that pH is also a factor in the reduced cure rate of the low surface area silica. Further evaluation of the 9.8 pH silica at all-silica contents of 75, 110, and 145 phr gave, unexpectedly, *reduced* pull-out adhesion values. Other studies confirm that both cobalt and resorcinol are still required to maintain adhesion with high pH silica. Although the HAF compound is 11 durometer points higher, it appears to share the same lack of adhesion as found with the 150 m^2/g silica.

Most of the formulas designed for zinc adhesion are those in which stearic acid has been omitted. This is the basis for the zinc-free compounding techniques described in previous chapters on solution polymers. EPDM is no exception, particularly in respect to galvanized adhesion, in benefiting from a zinc-free environment. Addition of 2 phr stearic acid to a formula based on a filler content of 30/30 150 m^2/g silica /N351 reduced pull-out adhesion from 750 to 400 N/25mm. The explanation, as in similar compounding situations, involves the preservation of the silanol surface free from soluble zinc contamination and the resulting loss of reactivity with the galvanized surface.

Accelerator type can have a significant effect on adhesion. The combination of ZBDC and DPG has consistently produced higher pull-out values. The base formula in the Table 5.21 accelerator comparison is the same as that in the preceding table.

Table 5.21 Adhesion to Galvanized Metal: Accelerators

Sulfur	2	2	2	2
ZBDC	2	2	-	2
DPG	2	-	2	-
MBTS	-	-	2	-
DTDM	-	-	-	2
MDR cure rate 160°C, T_{50} min	8.3	20	6.0	21
MDR crosslinks, dN-m	19	27	25	32
Durometer hardness	71	73	70	74
Adhesion to galvanized cable				
Pull-out, N/25mm	490	300	185	340
% cover	0	0	0	70

Two items deserve mention: MBTS has an unexpected degrading influence, and the use of a sulfur donor, DTDM, changes the nature of the interfacial separation from adhesion to compound cohesion. The wide variation in cure rate and crosslink density appears to be unrelated to adhesion. A Formulary recommendation for peroxide cured EPDM adhesion to galvanized cable is compound EPDM 32.

5.15 COMPRESSION FATIGUE LIFE

Compression fatigue resistance at elevated temperatures is a property particularly well suited to the capabilities of EPDM compounds.

Applications such as automotive motor mounts have made good use of the heat and fatigue resistance provided by certain EPDM grades. Since durometers in the 40 to 45 range define a popular motor mount hardness, compounds are often based on oil extended, high molecular weight, high unsaturation and high ethylene EPDM grades. Of grades 4969, 645, and 5459, number 4969 provides significantly lower heat build-up and longer fatigue life. Silica and black fillers are selected from semi-reinforcing grades, which maintain low heat build-up performance. Heat resistance is aided by 8 phr of zinc oxide. The base formula, with variables noted, contains: EPDM-175 to 200; Filler-65; ZMTI-2; TMQ-2; Zinc Oxide-8; stearic acid-1-2; PEG3350-1; ZBDC-1.5; MDB-2; sulfur-variable; silane-variable. Some guidance to selecting optimum amounts of sulfur and silane coupling agent is found in the data of Tables 5.22 and 5.22a and the contour curves of Figure 5.6.

Table 5.22 Compression Fatigue Life; Silane and Sulfur Effects

Mercaptosilane A189	-	-	0.3	0.3	0.3
Sulfur	0.5	2.0	0.5	1.0	2.0
MDR cure rate 160°C, T_{50} min	5.3	4.0	4.5	4.0	3.6
MDR crosslinks MH-ML, 20 min, dN-m	7	8	7	7	8
Mooney scorch 121°C, T_5 min	30+	21	22	20	17
Durometer hardness, cured 20 min, 160°C					
23°C	49	45	42	43	46
100°C	39	44	40	43	45
Goodrich flexometer fatigue: 100°C; 22.5%; 1MPa; 2 mm slit					
Weibull life, minutes	15	60	39	120	140
Failure, °C	105	107	108	106	104
DeMattia cut growth, KC to 500%	7	3	12	8	3
Pendulum rebound (Z), 100°C, %	73	78	73	76	77
Compression set, 70 hrs, 100°C, %	58	72	54	62	70
DMA dynamic modulus, 1 Hz; 60°C					
E", MPa	0.26	0.25	0.27	0.25	0.25
Tan delta	0.24	0.20	0.22	0.21	0.19
Original S/S cured 15 min, 160°C:					
M300, MPa	1.8	2.5	2.6	2.8	2.9
Tensile, MPa	17	16	18	19	19
Elongation, %	880	740	850	795	805
Aged 700 hrs, 150°C:					
Durometer	60	74	62	67	75
Tensile, MPa	6.7	6.8	7.3	6.4	7.4
Elongation, %	130	65	110	90	70

Other ingredients: EPDM 645-175; 65 m^2/g N_2SA silica-65; 2280 oil-25; ZMTI-2; TMQ-2; ZnO-8; PEG 3350-1; Stearic acid-1 MDB-2; ZBDC- 1.1-1.5

Table 5.22a Compression Fatigue Life; Silane and Sulfur Effects

Mercaptosilane (MPTS)	0.8	0.8	0.8	2	2
Sulfur	0.5	1.0	1.6	0.5	1.3
MDR cure rate 160°C, T_{50} min	4.0	3.3	3.1	2.7	2.3
MDR crosslinks MH-ML, 20 min, dN-m	7	8	8	7	9
Mooney scorch 121°C, T_5 min	18	14	13	9.4	8.1
Durometer hardness, buttons cured 20 min, 160°C					
23°C	42	44	45	41	43
100°C	41	43	45	40	44
Goodrich flexometer fatigue: 100°C; 22.5%; 1MPa; 2 mm slit,					
Weibull life, minutes	80	250	230	80	290
Failure, °C	107	103	103	108	102
DeMattia cut growth, KC to 500%	18	10	5	30	8
Pendulum rebound (Z), 100°C, %	73	76	77	74	76
Compression set, 70 hrs, 100°C, %	54	56	61	51	56
DMA dynamic modulus, 1 Hz; 60°C					
E”, MPa	0.26	0.24	0.24	0.26	0.24
Tan delta	0.24	0.20	0.18	0.26	0.22
Original S/S cured 15 min, 160°C					
M300 MPa	3.0	3.3	3.7	3.6	4.4
Tensile, MPa	19	20	20	22	18
Elongation, %	730	680	710	840	710
Aged 700 hrs, 150°C:					
Durometer	61	66	71	58	65
Tensile, MPa	7.6	7.0	6.5	7.3	6.6
Elongation, %	130	90	65	145	85

Other ingredients: EPDM 645-175; 65 m^2/g N_2SA silica-65; 2280 oil-25; ZMTI-2; TMQ-2; ZnO-8; PEG 3350-1; Stearic acid-1 MDB-2; ZBDC- 1.1-1.5

The contour plot follows the compression fatigue life (Weibull characteristic life) of compounds in which sulfur varies from 0.5 to 2.0 phr and mercaptosilane A189 (MPTS) from 0.3 to 2 phr. Minimum acceptable amounts for both sulfur and silane are 1 phr. A maximum for sulfur would be determined by aging behavior and durometer limits; for silane by silica surface saturation and cost considerations.

This study provides a classic example of the relative influence of crosslink density and silica-polymer bonding on a particular property. In this case compression fatigue life is equally dependent on both mechanisms. Crosslink density (increased sulfur content) and silica-EPDM bonding (increased silane content) are equally vital to achieving extended fatigue life. In the data of Tables 5.22 and 5.22a it is interesting to note a lack of linear correlation between fatigue life and any other vulcanizate property. This is in large part due to the conflicting influence of the variables, sulfur and silane, on properties which include durometer, cut growth, rebound, set, tensile and, surprisingly, dynamic modulus. Static high extension (M300) modulus is probably closest to predicting fatigue life, but only at the extremes. Vulcanizate aging (4 days at 155°C) before testing reduced fatigue life. Uncured stock aging (6 weeks at 23°C) is even more vitiating, with fatigue life reductions to 1 hour. The importance of these aging effects can hardly be overestimated, particularly for factory opreations.

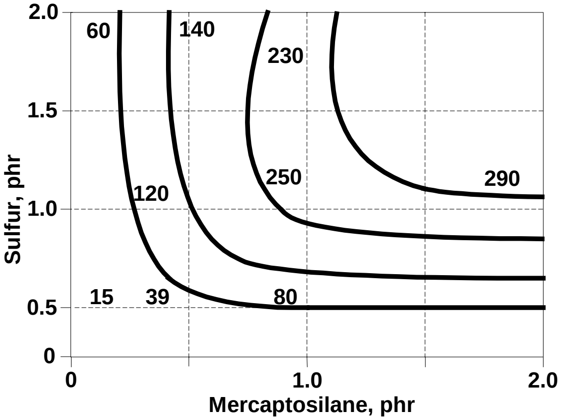

Figure 5.6 Sulfur and Silane Concentration: Weibull Fatigue Life (Mins.)

Unfortunately, curing properties offer a more problematic story. The compound with the best fatigue life is also the most scorchy, certainly not suitable for factory operations. A possible remedy (a T_5 value of over 30 minutes) has been achieved through use of EPDM 4969, reduction of ZBDC to 0.5, addition of TBBS at 1 phr and substitution of silane SI69 for A189 (2 for 1 phr). Performance of this compound is described in Table 5.23. To the extent that crosslink density and silica-polymer bonding are not compromised, many alterations similar to those above are feasible.

For the fatigue test in these studies, the Goodrich Flexometer is operated for extended periods at 100°C or 125°C and 1 or 1.6 MPa.. Definition of failure life is based on examination of the failed specimen. The normal blow-out condition of failed Flexometer specimens is not considered acceptable evidence of fatigue failure; data from such specimens are discarded. True fatigue failure is characterized by sample disintegration, with no evidence of blow-out cavities.

Table 5.23 Flexometer Compression Fatigue: Silica and Carbon Black

	A	B	C
65 m^2/g N_2SA Silica	65	65	-
GPF N660 Black	-	-	65
Mercaptosilane A189 (MPTS)	1	-	-
Mercaptosilane SI69 (TESPT)	-	2	-
MDR cure rate 160°C, T_{50} min	4.9	7.0	4.7
MDR crosslinks dN-m	11	12	13
Mooney scorch 121, T_5 min	23	30	19
Mooney viscosity, ML_4 100C	57	56	56
Values in () for stock shelf aged 7 days at 40°C before curing:			
Durometer: 23°C	42 (42)	42 (42)	44 (44)
100°C	45 (44)	44 (45)	46 (46)
Pendulum rebound (Z), %: 23°C	65 (75)	66 (73)	67(75)
100°C	72 (82)	72(80)	75 (82)
DMA dynamic modulus, 60°C 1 Hz;			
E”, MPa	0.24(.23)	0.23(.22)	0.23(.22)
E’, MPa	1.52	1.42	1.42
Tan delta	0.16	0.16	0.16
DeMattia cut growth, KC	7 (9)	7 (7)	2 (3).
Compression set, 70 hrs, 100°C, %	50 (46)	61 (62)	50(46)
Original Stress / Strain; cure 20 min/160°C			
M300 modulus, Mpa	3.0 (4.1)	2.8 (3.6)	3.3 (4.0)
Tensile, Mpa	21 (19)	20 (21)	18 (18)
Elongation, %	815 (740)	815 (860)	705 (705)
Aged 700 hrs, 150°C			
Durometer	70	79	75
Tensile, Mpa	4.5	5.6	3.0
Elongation, %	55	40	30
Other ingredients: EPDM 4969-200; ZnO-8; Stearic acid-1; ZMTI-2; TMQ-2; PEG 3350-1; Sulfur(mill)-1; MDB-1; TBBS1; ZBDC-0.5 [Mixed in Banbury to 122°C (stock temperature)]			

A comparison between silica and black has been made in the base formula noted above with EPDM 4969 (in place of 645 with no added oil) and sulfur at 1.0 phr, with details in Tables 5.23 and 5.23a. The flexometer conditions here are at the most severe level and the test was terminated at 24 hours with no fatigue failures for compounds B and C, as seen in Table 5.23a. At this point, the N660 compound has a 3ºC lower temperature margin versus the silica with SI69, a difference which is offset by the slightly poorer aging performance of the black compound.

Table 5.23a Compression Fatigue: Silica and Black

	A	B	C
65 m^2/g N_2SA Silica	65	65	-
GPF N660 Black	-	-	65
Mercaptosilane A189 (MPTS)	1	-	-
Mercaptosilane SI69 (TESPT)	-	2	-
Flexometer.compression fatigue, 125°C; 22.5%; 1.6 Mpa:			
Failure, hours	18	24+	24+
Temperature, ºC	141	139	136
Aged 700 hrs, 150°C			
Durometer	70	79	75
Tensile, Mpa	4.5	5.6	3.0
Elongation, %	55	40	30

Despite the slight margin in aging resistance, the silica-TESPT compound cannot be promoted as significantly superior to the GPF control. However, in situations where color is a requirement, the choice is obvious. More extensive compression fatigue testing would certainly be helpful in resolving the silica-black comparison. Exploration of increased silane contents may alter silica performance here, but the added material costs are not attractive.

References

1. N.L.Hewitt and M.P.Wagner, “The Role of Silica in EPDM Adhesion”, Adhesives Age, October, 1974

2. N.L.Hewitt, “Adhesive Systems for Belts and Hose”, paper ACS Rubber Division meeting, Chicago IL, April 1999

EPDM
Formulary

The silica surface areas indicated in the following compounds are N_2SA (BET) surface areas. A listing of commercially available precipitated silica products by surface area is provided in Appendix A. The common abbreviations used in these compounds are provided in Appendix E.

EPDM 1

Elastomer: EPDM Durometer: 34
Application: Low specific gravity

EPDM N597	200	Sulfur	0.4
35 m^2/g Silica	70	ZBDC	2
Paraffinic oil	20	MBTS	2
Zinc oxide	10	DBTH	1.5
Stearic acid	2		
PEG 3350	2	Specific gravity	1.05

ODR cure rate, 154°C, T_{90} minutes	17
Mooney scorch 121°C, T_5 minutes	15
T_{35} minutes	30+
Mooney viscosity, ML_4100	55

10 minute cure, 154°C:	Original	700 hrs, 90°C
Durometer	34	65
M300, MPa	0.7	
Tensile, MPa	14	5.8
Elongation, %	780	140

EPDM 2

Elastomer: EPDM Durometer: 42
Application:Heat resistance; Silane

Banbury 1		Banbury 2	
EPDM 1560	60	Zinc oxide	5
EPDM 1440	40	Sulfur	1
35 m^2/g Silica	70	ZBDC	2
Paraffinic Oil	60	TMDS	1
Naphthenic Oil	30	MBTS	0.6
Stearic Acid	1		
PEG 3350	2	Specific Gravity	1.04

Silane A189:	0	1.0
Cure Rate, 160°C, T_{90} minutes	11.5	10.0
Mooney Scorch, 121°C, T_5 minutes	88	17
Viscosity, ML_4100	22	20
Garvey Extrusion (Royale) Edge-Surface Rating	8D	9C

15 minute cure, 160°C:	Original	Aged*	Original	Aged*
Durometer	42	50	45	49
M300, MPa	0.8	-	1.7	-
Tensile, MPa	10.6	8.1	11.3	9.7
Elongation, %	890	700	900	700

*Aged 170 Hrs, 121°C

Compression Set B, %		
22 Hours, 70°C	17	18
70 Hours, 100°C	65	61

Trouser Tear, Cut Groove, Kn/m		
Original	5.6	6.3
170 hrs, 121°C	3.3	3.7

EPDM 3

Elastomer: EPDM Durometer: 42
Application: Metal adhesion; Heat resistance

Nordel 1440	100	Stearic acid	4
150 m^2/g Silica	25	Sulfur	0.4
65 m^2/g Silica	35	ZBDC	2
Zinc Oxide	12	DBTH	1.5
Magnesia	5	MBS	1
		Specific gravity	1.09

ODR Cure Rate, 154°C, T_{90} minutes	22
Mooney Scorch , 121°C, T_5 minutes	22
Viscosity, ML_4100	37

30 minute cure, 154°C:	Original	72 hrs, 150°C
Durometer	42	57
M300, MPa	1.0	
Tensile, MPa	10	9.7
Elongation, %	840	640

Goodrich Flexometer, 100°C; 22.5%; 1 MPa	
Set, %	22
Heat Build-up, °C	50
Dynamic Brass Strip Adhesion, 116°C	
30 minutes, 300 cpm*	no separation

*modified DeMattia: 8 lb. Dead weight on 1” wide strip

Static Steel Strip Adhesion (D429B with adhesion)	
40 minutes, 154°C, 1 kN/m	9.0 (cement – stock separation)

EPDM 4

Elastomer: EPDM Durometer: 45
Application: Motor mount; Black control

EPDM 5876	200	Zinc oxide	8
Filler	65	Sulfur	0.5
Silane A189	1.3	TBBS	2
ZMTI	1	ZBDC	1.5
TMQ	2	Vultac 710	1
Stearic acid	1		
PEG 3350	1	Specific gravity	0.97

Filler:	65 m^2/g Silica	N660 Black
Cure Rate, 155°C, T_{90} minutes	6.6	6.3
Mooney Scorch, 121°C, T_5 minutes	8.0	13
Viscosity, $ML_4$100	59	52
10 minute cure, 155°C:		
Durometer	45	43
M300, MPa	3.7	3.2
Tensile, MPa	19	21
Elongation, %	745	696
Aged 700 Hours, 124°C:		
Durometer	51	50
Tensile, MPa	8.0	7.7
Elongation, %	255	230
Compression Set, 72 hrs, 125°C, Method A, % of final deflection:		
Set	48	48
Creep	37	41
Deflection, % of original thickness	10	10

Pendulum Rebound, %	23°C	100°C	23°C	100°C
Original	69	76	70	75
72 hours, 125°C	74	80	73	79

Goodrich Flexometer, 100°C; 22.5%; 1 MPa:		
Drift, %	0	0.5
Set	2.8	3.1
Heat Build-up, °C	10	10

Dynamic Mechanical Modulus, 1 Hz; 20% strain:

Temperature:	0°C	100°C	DMA of black compound not available
E”, MPa	0.62	0.50	
E’, MPa	5.2	2.5	
Tan delta	0.119	0.200	

EPDM 5

Elastomer: EPDM　　Durometer: 46
Application: Motor mount

Epcar 6875	200	PEG 3350	1
65 m^2/g Silica	60	Stearic acid	0.5
Silane A189	1.2	Sulfur	0.5
ZMTI	2	MDB(Morfax)	2
TMQ	2	ZBDC	1.5
Zinc oxide	8	Specific gravity	1.03

Cure rate, 150°C, T_{50} minutes		9.6	
T_{90} minutes		19	
Mooney Scorch, 121°C, T_5 minutes		21	
Viscosity, ML_4100		70	
25 minute cure, 150°C:	<u>Original</u>	<u>170 hrs, 125°C</u>	<u>700 hrs, 150°C</u>
Durometer, 23°C	46	52	80
100°C	46		
M300, MPa	3.2		
Tensile, MPa	11	5.4	6.5
Elongation, %	685	220	55
Compression set, 72 hrs, 100°C, %			
Method B		50	
Method A (0.8 MPa):			
Set, %		52	
Creep, %		38	
Deflection, %		9	
Pendulum rebound, %, 23°C		68	
100°C		77	
Goodrich flexometer, 100°C; 22.5%; 1 MPa			
Dynamic Comp.		15	
Drift		0	
Set, %		1.3	
Heat build-up, °C		6	

DMA; 1 Hz; 20% strain	E’	E”	Tan delta
0°C	6.7	1.3	0.192
30°C	2.4	0.4	0.169
60°C	2.0	0.3	0.168
100°C	2.1	0.3	0.151

EPDM 6

Elastomer: EPDM Durometer: 45
Application: Low set; Tear strength

EPDM	Variable	Zinc oxide	8
220 m^2/g Silica	30	Sulfur	0.5
65 m^2/g Silica	35	TBBS	2
TMQ	2	ZBDC	1.5
ZMTI	2	MDB	2
Stearic acid	1		
PEG 3350	1	Specific gravity	0.97

	Low Set	Tear Strength
EPDM	5875:200 phr	637P: 175 phr
Paraffinic oil, phr	0	25
Cure Rate, 160°C, T_{50} minutes	5.7	7.4
T_{90} minutes	16	13
Mooney Scorch, 121°C, T_5 minutes	26	30+
Viscosity, $ML_4$100	58	52
160°C cure, 15/20 minutes:		
Durometer, 23°C/100°C	46/47	47/41
Original		
M300, MPa	4.0	2.3
Tensile, MPa	21	20
Elongation, %	665	805
Aged 170 hrs, 125°C		
Durometer	49	52
Tensile, MPa	13	20
Elongation, %	450	620
Compression Set, Method B, %		
70 hrs, 100°C	54.1	70.7
70 hrs, 125°C	64.4	75.2
Tear Strength, kN/m		
Die C	24	30
MG Trouser	7.3	15.0
Pendulum Rebound (Z), %, 23°C	68	63
100°C	76	71
Goodrich Flexometer; 100°C, 22.5%, 1 MPa		
Dynamic Drift, %	0	5.0
Permanent Set, %	3.4	19
Heat Build-up, °C	8	22

EPDM 7

Elastomer: EPDM Durometer: 48
Application: Tear strength; Zinc-free compared

EPDM 5857	66	Sulfur	2
EPDM 1040	67	ZBDC	1.8
Ciptane 255LD	42	MBS (MOR)	1(2)*
Naphthenic oil	16	TMTD	0.8(0.0)*
Zinc oxide	3(1)*		
Stearic acid	2(0)*	*Zinc-free acceleration	

Acceleration	Normal	Zinc-free
Zinc oxide	3	1
Stearic acid	2	0
MDR cure rate, 160°C, T_{50} minutes	6.7	2.7
Mooney Scorch 121°C, T_5 minutes	21	16
Mooney Viscosity, ML_4100	59	58
20/30 minute cure, 160°C:		
Durometer, 23°C	48	48
100°C	45	42
M300, MPa	2.3	2.4
Tensile, MPa	16	11
Elongation, %	785	745
MG Trouser tear, kN/m	21.4	14.4
Abrasion Indices		
PICO	53	69
NBS	114	151
Compression set, 70 hrs, 100°C, %	76	86
Pendulum rebound (Z), %, 23°C	61	61
100°C	63	57

EPDM 8

Elastomer: EPDM Durometer: 55
Application: Abrasion; Peroxide cure

EPDM	200	Zinc oxide	1
220 m^2/g Silica	75	SR 350	5
Silane A174	1.5	BPDIB	2.8
ZMTI	2		
ODPA	2	Specific gravity	1.05

MDR Cure Rate, 165°C, T_{50} minutes	4.5
T_{90} minutes	12
Mooney Scorch, 121°C, T_5 minutes	30+
Mooney Viscosity, ML_4100	84
Durometer, 23°C	55
100°C	51

	Original	170 hrs, 170°C
M300, MPa	3.5	Brittle*
Tensile, MPa	15	
Elongation, %	620	

*Requires addition of zinc dimethacrylate

MG Trouser Tear, kN/m	19
100°C	4.5
PICO Abrasion Index, 23°C	560
100°C	210
Compression Set, 70 hrs, 100°C, %	24
Pendulum Rebound (Z), %, 23°C	57
100°C	62
Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Static Compression, %	38
Dynamic Compression, %	26
Drift	0
Permanent Set, %	11
Heat Build-up, °C	30
DeMattia Cut Growth, kc to 500%	15

EPDM 9

Elastomer: EPDM Durometer: 55
Application: Zinc-free, Low Mooney

Banbury 1		Banbury 2		
EPDM 346	100	Sulfur	1.5	
150 m^2/g Silica	30	TBBS	2.0	
Paraffinic Oil	28	ZBDC	1.5	
TMQ	1	DPTH	1.5	
		Zinc Oxide	1.0	
		Specific gravity		1.01

Cure Rate, 160°C, T_{90} minutes	5.4
Mooney Scorch 121°C, T_5 minutes	29
Viscosity, ML_4100	30

10 minute cure, 160°C:	Original	70 hrs, 175°C
Durometer	55	-
M20, MPa	0.70	1.1
M300, MPa	1.6	-
Tensile, MPa	16	2.0
Elongation, %	635	65
20 minute cure, 160°C:		
PICO Abrasion Index	41	
Pendulum Rebound (Z), %,		
23°C	63	
100°C	71	

Compression Set, %, 70 hrs, 100°C	92

EPDM 10

Elastomer: EPDM	Durometer: 55
Application: Peroxide Cure	

EPDM 1440	100	Stearic Acid	2
65 m^2/g Silica	75	PEG 3350	2
Paraffinic oil	35	Ethylene Dimethacrylate	5
TMQ	2	DCP 40C	10
		Specific gravity	1.17

ODR Cure Rate, 125°C, T_{90} minutes	17
Mooney Scorch, 121°C; T_5 minutes	12
T_{35} minutes	>30
Viscosity, ML_4100	47

20 minute cure, 165°C:	Original	72 hrs, 175°C
Durometer	56	72
M300, MPa	2.5	
Tensile, MPa	9.7	7.7
Elongation, %	740	380

30 minute cure, 165°C, Compression Set, %	
1 day, 150°C	20
3 days, 121°C	25

Adhesion to RFL Nylon fabric, kN/m	
30 minutes, 160°C	18+
45 minutes, 160°C	16+

EPDM 11

Elastomer: EPDM Durometer: 58/59
Application: Adhesion

EPDM 1070	100	PEG 3350	0.5
150 m^2/g Silica	60	Stearic acid	3.0
65 m^2/g Silica	20	TBBS	1.5
Paraffinic oil	30	ZBDC	1.5
Titanium dioxide	5	MDB (Morfax)	1.5
Zinc oxide	10	Sulfur	1.0
ZMTI	1.5		
ODPA	1.5	Specific gravity	1.15

Resorcinol	0	3
HMT	0	3
MDR cure rate, 155°C, T_{50} minutes	12	7
Mooney scorch, 121°C, T_5 minutes	30+	14
Mooney viscosity, ML_4100	91	72
15/25 minute cure, 155°C:		
Durometer, 23°C	59	58
100°C	55	55
Strip adhesion to RFL polyester belt fabric:		
Low pressure press cured (100 psi), 155°C, N/25 mm		
30 minutes	105	115
60 minutes	125	130
15 minute cure, 155°C:		
M300, MPa	1.7	2.3
Tensile, MPa	13	14
Elongation, %	870	840
Aged (Al Block) 700 hrs, 150°C		
Durometer	83	80
Tensile	9.5	9.1
Elongation, %	155	155
PICO Abrasion Index, 23°C	44	37
100°C	29	28
Compression Set, 70 Hrs, 100°C, %	82	80
DeMattia cut growth, kc to 500%	4	6

EPDM 12

Elastomer: EPDM Durometer: 60
Application: Tear strength; MRG; Peroxide; Silane effects

EPDM 4969 (5875)	200	Zinc oxide	1
220 m^2/g Silica	75	BPIPB 40	7
ZMTI	2	SR 350	6
ODPA	2	Specific gravity	1.06

Silane A174	0		3	
MDR Cure Rate, 165°C, T_{50} minutes	4.9		4.0	
Mooney Scorch, 121°C, T_5 minutes	30+		23	
Mooney Viscosity, ML_4100	92		75	
Durometer, 23°C	60		63	
100°C	56		61	
MG Trouser Tear, kN/m	27		21	
PICO Abrasion Index	54		58	
NBS Abrasion Index	500+		500+	
Compression Set, %, 70 hrs, 100°C	30		26	
Goodrich Flexometer, 100°C; 22.5%; 1MPa				
Permanent Set, %	7.7		6.1	
Heat Build-up, °C	27		26	
Original				
M300, MPa	3.6		4.5	
Tensile, MPa	17		15	
Elongation, %	695		540	
Aged hrs/°C:	70/170	700/130	70/170	700/130
Durometer	70	70	70	72
Tensile, MPa	3.6	4.4	3.7	5.1
Elongation, %	160	160	150	185
DeMattia Cut Growth, 500%, KC	20		9	
Pendulum Rebound (Z), %, 23°C	58		58	
100°C	63		63	

EPDM 13

Elastomer: EPDM Durometer: 61
Application: Abrasion; Tear strength; Traction

EPDM 346	100	Sulfur	1.5
Ciptane 255 LD	50	ZBDC	1.5
Paraffinic oil	35	TBBS	1.5
Stearic acid	2	DPTH	1.0
Zinc Oxide	3		

MDR Cure Rate, 160°C, T_{50} minutes	6
T_{90} minutes	30
Mooney Scorch, 121°C, T_5 minutes	21
Mooney Viscosity, ML_4100	47
15/20 minute cure, 160°C:	
Durometer, 23°C	61
100°C	59
M300, MPa	4.1
Tensile, MPa	26
Elongation, %	835
MG Trouser Tear, kN/m	15
PICO Abrasion Index	100
Dynamic Coefficient of Friction	
Wet Aluminum	1.23
Wet Varnished Wood	1.52
Compression Set, % , 72 hours, 100°C	90
Pendulum Rebound (Z), %, 23°C	62
100°C	65

EPDM 14

Elastomer: EPDM Durometer: 63
Application: Low set; Heat resistance

Banbury 1		Banbury 2	
EPDM 55	100	Sulfur	0.4
65 m^2/g Silica	60	ZBDC	2
Paraffinic Oil	10	MDB	2
ZMTI	1	MBTS	1.5
TMQ	1		
NBC	4		
Stearic Acid	2		
PEG 3350	1		
Zinc Oxide	10	Specific gravity	1.16

Cure Rate, 160°C, T_{90} minutes	13
Mooney Scorch, 121°C, T_5 minutes	14
T_{35} minutes	24
Viscosity, ML_4100	78

17 minute cure, 160°C:	Original	70 hrs, 175°C	550 hrs, 160°C
Durometer	63	73	80
M300, MPa	4.3		
Tensile, MPa	10.3	14.5	17.3
Elongation, %	510	335	155

Compression Set, %	
72 hrs, 100°C	40
72 hrs, 150°C	67

EPDM 15

Elastomer: EPDM Durometer: 65
Application: Heat resistance; Silane effects

Banbury 1		Banbury 2	
EPDM 5206	100	Sulfur	0.4
65 m^2/g Silica	60	ZBDC	2
Paraffinic Oil	12 (20 with Silane)	MDB	2
ZMTI	1.5	MBTS	1.2
TMQ	1		
NBC	3.5		
Stearic Acid	2		
PEG 3350	1		
Zinc Oxide	10	Specific gravity	1.16

Silane A189:	0	1.2
Cure Rate, 154°C, T_{90} minutes	27	21
Mooney Scorch, 121°C, T_5 minutes	25	21
Viscosity, ML_4100	85	78
30 minute cure, 154°C:		
Durometer		
Original	65	62
7 Days, 190°C	71	64
28 Days, 165°C	70	65
Tensile, MPa		
Original	12.6	14.8
7 Days, 190°C	4.9	4.4
28 Days, 165°C	14.7	15.6
Elongation, %		
Original	680	700
7 Days, 190°C	190	150
28 Days, 165°C	495	475
Compression Set B, %		
3 Days, 100°C	62.1	54.0
3 Days, 150°C	82.0	74.3
Monsanto Fatigue, 100% Extension		
Kilocycles, Avg.	90	215

EPDM 16

Elastomer: EPDM Durometer: 65
Application: Textile adhesion; Direct bonding

EPDM 346	100	Sulfur	0.4
150 m^2/g Silica	60	ZBDC	2
Zinc Oxide	10	NDB	2
Resorcinol	3	MBTS	1.5
Stearic Acid	6	HMT*	2
TMQ	1	*micronized	
Paraffinic Oil	25	Specific Gravity	1.15

Cure Rate, 154°C, T_{90} minutes	18
Mooney Scorch, 121°C, T_5 minutes	17
T_{35} minutes	29
Viscosity, ML_4100	27

30 minute cure, 154°C:	Original	72 hrs, 175°C
Durometer	65	79
M300, MPa	270	
T_B	1730	1700
E_B	700	230
Trouser Tear, Grooved; kN/m		
Original	11	
7 Days, 100°C	7.9	
Compression Set, %, 3 Days, 100°C	63	

Adhesion to Untreated Fabrics, kN/m		
Nylon	Original	70 hrs, 175°C
40 minutes, 154°C	11	7.0
60 minutes, 154°C	8.8	
Activated Polyester		
40 minutes, 154°C	5.2	11
60 minutes, 154°C	6.1	11

Polyester Cord Degradation in Stock, Cord Tensile, N*	
Original	155
4 hrs, 175°C	87
96 hrs, 150°C	87

*Tensile loss similar without R/H or with peroxide cure

EPDM 17

Elastomer: EPDM Durometer: 65
Application: Hose; Hot tear strength

EPDM 4969	200	Zinc oxide	3
220 m^2/g Silica	70	Stearic acid	2
Mistron Vapor Talc	100	ZDMA 634	5
Paraffinic oil	10	BPDIB 40	7
ZMTI	1.5		
ODPA	1.5	Specific gravity	1.23

MDR Cure Rate, 160°C, T_{50} minutes	4.7
T_{90} minutes	17
Mooney Scorch, 121°C: T_5 minutes	30+
Mooney Viscosity, ML_4100	72
40 minute cure, 160°C:	
Durometer, 23°C	65
100°C	58
MG Trouser Tear, kN/m, 23°C	34
100°C	25
30 minute cure, 160°C:	
M300, MPa	4.8
Tensile, MPa	15
Elongation, %	760
Compression Set, %, 70 hrs, 100°C	54
DIN Abrasion Loss, ml	226
Water Immersion 100°C, % Volume Increase	
24 Hours	0.6
72 Hours	0.6
300 Hours	1.8
Pendulum Rebound (Z), %, 23°C	53
100°C	59

EPDM 18

Elastomer: EPDM Durometer: 66
Application: UV resistance; Roofing

Banbury 1		Banbury 2	
EPDM 5206	100	Sulfur	0.8
65 m^2/g Silica	60	ZBDC	2
Silane A189	1.4	TBBS	3
Paraffinic Oil	12		
Titanium Dioxide	25		
TMQ	1		
NBC	3		
ZMTI	1		
PEG 3350	1		
Stearic Acid	2		
Zinc oxide	10	Specific gravity	1.23

Cure Rate, 160°C, T_{90} minutes	10
Mooney Scorch 121°C, T_5 minutes	19
Viscosity, ML_4100	82
Garvey Extrusion, 125°C	
Swell, %	28
Edge-Surface	9A

20 minute cure, 160°C:	Original	28 Days, 160°C	Weathermeter*
Durometer	66	82	69
M300, MPa	6.0	-	6.0
Tensile, MPa	10.3	5.7	9.6
Elongation, %	535	110	495

*200 hours

Compression Set B, %	
3 Days, 100°C	65
3 Days, 150°C	82

DeMattia Cut Growth, kc to 500%	3

EPDM 19

Elastomer: EPDM Durometer: 67
Application: Adhesion; Direct bonding

Banbury 1		Banbury 2	
EPDM 346	100	Zinc oxide	10
150 m^2/g Silica	60	HMT	2
Paraffinic oil	20	Sulfur	1
TMQ	1	TBBS	1.5
Stearic acid	3	ZBDC	1
Resorcinol 60% MB	5	MDB	2

MDR Cure Rate, 160°C, T_{90} minutes	16	
Mooney Scorch 121°C, T5 minutes	30+	
Mooney Viscosity, ML_4100	37	
Garvey Extrusion:		
% Swell	15	
Edge-Surface	8A	
	Original	70 hrs, 175°C
Durometer, 23°C	67	82
100°C	65	
M300, MPa	4.8	
Tensile, MPa	14	10
Elongation, %	565	105
PICO abrasion index	52	
Pendulum rebound (Z), %, 23°C	55	
100°C	63	

Strip adhesion to untreated fabrics, N/25m	Nylon	Polyester, activated
60 minutes, 142°C	80	
100 minutes, 142°C	120	
40 minutes, 154°C	140	130(260)*
60 minutes, 154°C	180	
20 minutes, 166°C	185	
40 minutes, 166°C	300	

*70 hrs, 150°C

Polyester cord tensile degradation, N (in contact with compound)	
Original	150
96 hrs, 150°C	110
4 hrs, 175°C	23

EPDM 20

Elastomer: EPDM Durometer: 67
Application: Heat Resistance

Banbury 1		Banbury 2	
EPDM 5206	100	Zinc oxide	10
65 m^2/g Silica	60	Sulfur	0.4
Silane A189	1.2	ZBDC	2
Paraffinic Oil	10	MDB (Morfax)	2
TMQ	1	TMTD	0.5
NBC	4		
Stearic acid	2		
PEG 3350	1	Specific gravity	1.12

Cure Rate, 180°C, T_{90} minutes	4.3
160°C, T_{90} minutes	11
Mooney Scorch, 121°C, T_5 minutes	15
Viscosity, ML_4100	92

10 minute cure, 180°C:	Original	350 hrs, 180°C
Durometer	67	72
M300, MPa	5.0	
Tensile	13.7	7.4
Elongation, %	715	334

Compression Set, %	
3 Days, 100°C	50
3 Days, 150°C	72

Ross Flex Aged 2 Days 180°C No cut growth

EPDM 21

Elastomer: EPDM Durometer: 67
Application: Tear strength; Hose; Zinc-free

EPDM 4969	200	Zinc oxide	1
220 m^2/g Silica	70	Sulfur	1.5
Soft clay	150	TBBS	1.5
Paraffinic oil	15	ZBDC	1.5
ODPA	1	DPTH	1.5
Titanium dioxide	10		
Zn dimethylacrylate 634	2	Specific gravity	1.31

MDR Cure Rate, 160°C, T_{50} minutes	7.9
T_{90} minutes	15
Mooney Scorch, 121°C, T_5 minutes	30+
Mooney Viscosity, $ML_4$100	67
Durometer, 23°C	67
100°C	61
M300, MPa	5.8
Tensile, MPa	14
Elongation, %	615

Embrittled after oven aging 700 hrs, 150°C

MG Trouser Tear, kN/m	33
PICO Abrasion Index	56
DIN Abrasion Loss, ml	308
Compression Set, %, 70 Hours, 100°C	65
Pendulum Rebound (Z), %, 23°C	49
100°C	54

EPDM 22

Elastomer: EPDM Durometer: 69
Application: Tear strength; Low shrinkage

Banbury 1		Banbury 2	
EPDM 40A	100	Sulfur	0.4
35 m^2/g Silica	125	ZBDC	1.5
Paraffinic Oil	40	MDB	1.5
Zinc oxide	5	MBTS	1.5
Stearic acid	2	Specific gravity	1.18

Cure Rate, 160°C, T_{90} minutes	13
Mooney Scorch, 130°C, T_5 minutes	15
Viscosity, $ML_4$100	79
ODR Minimum	7.0
Mill Behavior	Smooth surface; No sticking; Good tack
Garvey Extrusion, 121°C:	
Die Swell, %	3
Edge-Surface Rating	9A
20 minute cure, 160°C:	
Durometer	69
M300, MPa	4.4
Tensile, MPa	6.5
Elongation, %	555
Permanent Set, %	10.4
MG Trouser Tear, kN/m	10.6

Aged (Al Block)	70 hrs, 175°C	550 hrs, 150°C
Durometer	81	81
Tensile, MPa	10.6	11.0
Elongation, %	140	120

30 minute cure, 160°C	
Compression Set, %	
22 hrs,70°C	22.2
70 hrs, 100°C	67.2
Pendulum Rebound (Z), %	50
Water Immersion 70°C, % Volume	
3 Days	1.3
14 Days	6.7

EPDM 23

Elastomer: EPDM Durometer: 69
Application: Hose Wrap

EPDM 346	100	PEG 3350	0.5
150 m^2/g Silica	60	Sulfur	1
65 m^2/g Silica	20	TBBS	1.5
Titanium dioxide	5	MDB	1.5
Paraffinic Oil 2280	30	ZBDC	1.5
ZMTI	1.5	Zinc oxide	10
ODPA	1.5		
Stearic acid	3	Specific gravity	1.16

Banbury 1 mixed 4 minutes, 160°C

MDR Cure Rate, 155°C, T_{50} minutes	9.1
T_{90} minutes	20
Mooney Scorch, 121°C, T_5 minutes	30+
Mooney Viscosity, ML_4100	42
Durometer (button), 23°C	69
100°C	65

10 minute cure, 155°C:	Original	700 hrs, 145°C
Durometer	68	88
M300, MPa	2.9	
Tensile, MPa	15	17
Elongation, %	755	130

MG Trouser Tear, kN/m	18
PICO Abrasion Index	56

Strip Adhesion,RFL belt fabric, N/25mm	535
Dynamic Coefficient of Friction	
Wet aluminum	1.10
Pendulum Rebound (Z), %, 23°C	45
100°C	55
Compression Set, %, 70 hrs, 100°C	89

EPDM 24

Elastomer: EPDM Durometer: 69
Application: Abrasion; Peroxide

EPDM 4969(5875)	200	BPDIB 40	7
220 m^2/g Silica	75	SR 350	12
Silane A189	3	Zinc oxide	1
ZMTI	2		
ODPA	2	Specific gravity	1.06

MDR Cure Rate, 165°C, T_{50} minutes	1.4
Mooney Scorch, 121°C, T_5 minutes	22
Mooney Viscosity, ML_4100	69
Durometer (button), 23°C	69
100°C	66

MG Trouser Tear, kN/m	18
PICO Abrasion Index	76
NBS Abrasion Index	>500
Compression Set, %, 70 hrs, 100°C	25

Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Set, %	5.1
Heat Build-up, °C	26

M300, MPa	6.2
Tensile, MPa	15
Elongation, %	485

DeMattia Cut Growth, kc to 500%	2
Pendulum Rebound (Z), %, 23°C	58
100°C	64

EPDM 25

Elastomer: EPDM Durometer: 70
Application: Tear strength; Extrusion

Banbury 1		Banbury 2	
EPDM 40A	100	Sulfur	0.4
65 m^2/g Silica	125	ZBDC	1.5
Paraffinic Oil	40	MBTS	1.5
Zinc oxide	5	MDB (Morfax)	1.5
Stearic acid	2		
PEG 3350	1	Specific gravity	1.20

Cure Rate, 160°C, T_{90} minutes	13
Mooney Scorch, 130°C, T_5 minutes	26
Viscosity, ML_4100	112
Garvey Extrusion 121°C:	
Swell, %	6
Edge-Surface Rating	10A
20 minute cure, 160°C:	
Durometer	70
M20, MPa (psi)	1.6
M300, MPa	7.1
Tensile, MPa	12.5
Elongation, %	600
MG Trouser Tear, kN/m	14.2

EPDM 26

Elastomer: EPDM Durometer: 70
Application: Hose; Low cost

EPDM 5508	100	Sulfur	0.4
35 m^2/g Silica	70	ZBDC	2
Hard Clay	200	MBTS	2
Zinc Oxide	5	TMETD	1.5
Paraffinic Oil	100		
Stearic acid	2		
PEG 4000	2	Specific gravity	1.34

ODR Cure Rate, 154°C, T_{90} minutes	17
Mooney Scorch, 121°C, T_5 minutes	28
Viscosity; ML_4100	73

30 minute cure, 154°C:	Original	3 days, 175°C	14 days, 150°C
Durometer	68	81	90
M300, MPa	310		
Tensile, MPa	1060	660	1110
Elongation, %	750	70	60

Compression Set, % 70 hrs, 100°C	64

EPDM 27

Elastomer: EPDM Durometer: 70
Application: Static charge dissipation; Fabric adhesion; Black

Banbury 1		Banbury 2	
EPDM 346	100	Hexa 402PD	2
150 m^2/g Silica	60	Sulfur	0.6
XCF N472	45	ZBDC	1.5
Paraffinic Oil	40	MBTS	1.5
TMQ	2	TBBS	3
ZMTI	2		
Stearic acid	3		
Resorcinol 401P	3		
Zinc oxide	10	Specific gravity	1.20

Cure Rate, 150°C, T_{50} minutes	13
T_{90} minutes	26
Mooney Scorch, 121°C, T_5 minutes	30+
Viscosity, ML_4100	51
30 minute cure, 150°C:	
Durometer	70
M300, MPa	4.6
Tensile, MPa	9.6
Elongation, %	625
Adhesion to RFL Fabric, N/25 mm	
30 minute cure, 150°C	280
60 minute cure, 150°C	310
Electrical Properties	
Surface Resistivity	9 E8 ohms/sq.
Volume Resistivity	4 E9

EPDM 28

Elastomer: EPDM Durometer: 71
Application: Fabric adhesion; Fast cure

EPDM 346	100	PEG 3350	0.5
150 m^2/g Silica	60	Sulfur	0.5
Naphthenic oil	15	MBTS	1.5
Titanium dioxide	5	ZBDC	2
ZMTI	1	Zinc oxide	10
ODPA	1		
Stearic acid	2	Specific gravity	1.13

MDR Cure Rate, 160°C, T$_{50}$ minutes	4.9
T$_{90}$ minutes	14
Mooney Scorch, 121°C, T$_5$ minutes	30+
Mooney Viscosity, ML$_4$100	60
30 minute cure, 160°C:	
Durometer, 23°C	71
100°C	62

15 minute cure, 160°C	Original	700 hrs,150°C
Durometer	67	88
M300, MPa	2.7	
Tensile, MPa	20	15
Elongation, %	755	120

Adhesion to RFL polyester, strip, N/25mm	420
MG Trouser Tear, kN/m	16
PICO Abrasion Index, 23°C	67
100°C	41
Compression Set, %, 70 hrs, 100°C	84
Pendulum Rebound (Z), 23°C	52
100°C	58
Goodrich Flexometer: 100°C, 22.5%, 1MPa	
Permanent Set, %	21
Heat Build-up, °C	41
DeMattia Cut Growth, kc to 500%	13

EPDM 29

Elastomer: EPDM Durometer: 73
Application: Textile Adhesion (Direct Bonding)

Royalene 515	100	Sulfur	1.5
65 m^2/g Silica	120	MBS	2.5
Zinc oxide	8	ZDBDC	1.7
Resorcinol	2.5	Tellurac	0.6
Stearic acid	4.5	Hexa (micronized)	1.5
Naphthenic oil	35		

Cure Rate, 154°C, T_{90} minutes	24
Mooney Scorch, 121°C, T_5 minutes	30
Viscosity, ML_4100	43
30 minute cure, 154°C:	
Durometer	73
M300, MPa	2.7
Tensile, MPa	6.1
Elongation, %	280

Adhesion to Untreated Nylon N/25 mm	Press	Hot Air
20 minutes, 154°C	>155	>155
60 minutes, 140°C	>135	>135

EPDM 30

Elastomer: EPDM Durometer: 70-77
Application: Transparency

EPDM 1660	60
EVA 150	40
TAC	0.5
UM Blue	0.003
DMBPH (101)	2

160 m^2/g Silica:	15	25	35
Cure Rate, 160°C, T_{50} minutes	6.5	4.8	4.3
T_{90} minutes	28	24	20
Crosslinks, MH-ML	39	46	50
Mooney Scorch, 130°C: T_5 minutes	21	14	12
T_{35} minutes	30+	27	20
Viscosity, MDR Minimum	2.3	3.8	6.5
ML_4100	63	90	130
Garvey Extrusion (B), 85 rpm, 120°C			
Rate cm/min	78	87	108
% Swell (width)	50	23	20
Edge-Surface	10A	8A	4B
Light Transmittance, 2 mm thickness			
Transparency, %	86.6	84.2	85.4
Haze, %	16.3	18.6	17.2
Color	------Water White----		
25 minute cure, 160°C:			
Durometer, 23°C	69	73	77
70°C	61	67	73
M300, MPa	6.2	7.1	8.5
Tensile, MPa	7.5	10.8	12.9
Elongation, %	340	375	375
Aged 350 hrs, 70°C:			
Durometer	70	76	81
Tensile, MPa	8.9	9.8	13
Elongation, %	355	310	320
Pendulum Rebound (Z), %, 23°C	70.0	67.2	63.4
100°C	70.2	69.8	67.2
PICO Abrasion Index	55	65	73
Specific gravity	0.97	1.01	1.04

EPDM 31

Elastomer: EPDM Durometer: 74
Application: Zinc-free; Tear strength; Abrasion; Silane

EPDM 346	100	Zinc oxide	1
220 m^2/g Silica	60	Sulfur	2
Naphthenic oil	15	TBBS	1.5
Paraffinic oil	12	ZBDC	1.5
ZMTI	1	DPTH	1.5
ODPA	1		
Zinc dimethacrylate	2	Specific gravity	1.13

Silane A189	0	2.4
MDR Cure Rate, 160°C, T_{50} minutes	4.4	5.4
Crosslinks, dN-m	10	16
Mooney Scorch 121°C, T_{50} minutes	14	19
Mooney Viscosity, $ML_4$100	80	58
Durometer, 23°C	74	72
100°C	66	68
PICO Abrasion Index	142	160
MG Trouser Tear, kN/m	51	18
Strip Adhesion to RFL Nylon, N/25 mm	106	95
Stress/Strain:		
Durometer	77	76
M300, MPa	3.0	7.2
Tensile, MPa	18	22
Elongation, %	900	720
Pendulum Rebound (Z), %, 23°C	58	58
100°C	55	59
DMA Dynamic Modulus, 60°C, 1 Hz		
E”, MPa	1.34	1.21
E’, MPa	11.6	11.4
Tangent delta	0.116	0.107
Compression Set, %, 70 hrs, 100°C	96	88
Dynamic Friction Coefficient,		
Wet Aluminum	0.94	1.00

EPDM 32

Elastomer: EPDM Durometer: 76
Application: Adhesion to zinc (galvanized); Peroxide; Black

EPDM 346	100	Zinc oxide	1		
150 m^2/g Silica	50	ZDMA 634	5		
FEF N550	35	BPDIB 40%	7		
Paraffinic oil	30				
ODPA	1				
ZMTI	1.5			Specific gravity	1.14

MDR Cure Rate, 160°C, T_{50} minutes	9.1
MDR Scorch, 160°C, T_{S2} minutes	1.7
Mooney Viscosity, ML_4100	43
30 minute cure, 160°C:	
Durometer, 23°C	76
100°C	71
Adhesion to galvanized cable, press cured 40 minutes, 160°C	
Pull-out, N/12 mm embedment	765
Rubber cover, %	50

Stress/Strain	Original	300 hrs, 155°C
Durometer	76	85
M300, MPa	9.9	
Tensile, MPa	13	11
Elongation, %	435	175

Compression Set, %, 70 hrs, 100°C	40
MG Trouser Tear, kN/m	11
PICO Abrasion Index, 23°C	112
100°C	88
Pendulum Rebound (Z), %, 23°C	51
100°C	53

Note: Reduction in oil content or addition of Armorslip CP at 1 phr may be needed to relieve mill sticking

EPDM 33

Elastomer: EPDM Durometer: 80
Application: Heat resistance; Flex life; Tear strength; Peroxide

Epcar 346	100	Zinc oxide	10
150 m^2/g Silica	55	PEG 4000	1
TMQ	2	SR206	5
Paraffinic oil	20	DICup 40C	7
Stearic acid	2	Specific gravity	1.15

ODR Cure Rate, 154°C, T_{90} minutes		20
Mooney Scorch, 121°C,	T_5 minutes	8
	T_{35} minutes	>30
Viscosity, ML_4100		80

30 minute cure, 154°C:	Original		Aged	
	20°C	100°C	3 days,175°C	28 days, 150°C
Hardness	79	-	87	88
M300, MPa	3.3	2.4	-	-
Tensile, MPa	14	7.5	10	10
Elongation, %	680	550	220	220

Trouser Tear, Grooved, kN/m	
20°C	19
100°C	10
7 Days, 100°C	12

DeMattia Flex, 20°C, kc to 0.6”	10
Monsanto Flex, kc	20
Ross Flex, 7 days, 100°C	
kc to 0.6” cut growth	>100
Aged hardness	80
PICO Abrasion Index	84

EPDM 34

Elastomer: EPDM Durometer: 80
Application: 100°C abrasion; Tear strength; Zinc Free

EPDM 346	100	Zinc Oxide	1
EPDM 1446A	20	Sulfur	1.5
ZDMA 634	5	TBBS	2 (1 in B)
TMQ	2	ZBDC	2
ZMTI	2	DPTH	1.5(1 in B)
		Specific gravity	1.09

	A	B
220 m^2/g Silica	60	-
Ciptane 255TLD	-	65
MDR Cure Rate, 160°C, T$_{50}$ minutes	8.5	10
T$_{90}$ minutes	30	29
Mooney Scorch, 121°C, T$_5$ minutes	11	10
Mooney Viscosity ML$_4$100	76	80
30/40 minute cure, 160°C:		
Durometer, 23°C	81	79
100°C	78	76

Stress/Strain	Original	Aged*	Original	Aged*
Durometer	81	91	79	90
M300, MPa	6.1		9.8	
Tensile MPa	23	14	25	14
Elongation, %	635	100	575	110

*Aged 700 hours, 140°C

	A	B
PICO Abrasion Index, 23°C	123	166
100°C	80	100
MG Trouser Tear, kN/m	16	13
Pendulum Rebound (Z), %, 23°C	59	58
100°C	59	60
Compression Set, %, 70 hrs, 100°C	87	82
Goodrich Flexometer, 100°C; 22.5%; 1 MPa		
Permanent set, %	24	20
Heat Build-up, °C	42	43
DeMattia Cut Growth, kc to 500%	2	2

EPDM 35

Elastomer: EPDM Durometer: 85
Application: Abrasion Resistance; Peroxide

EPDM 1070	20	Zinc oxide	1
EPDM 6520Z	80	BPDIB 40C	7
220 m^2/g Silica	60	ZMTI	2
Silane A174	1.5	ODPA	2
SR 634	3	Specific gravity	1.11

MDR Cure Rate, 165°C, T_{50} minutes	5.7
Mooney Scorch, 121°C, T_5 minutes	21
Mooney Viscosity, ML_4100	152
Durometer, 23°C	87
100°C	82

Stress/Strain	Original	700 hrs, 140°C
Durometer	85	89
M300, MPa	13	
Tensile, MPa	29	18
Elongation, %	485	220

MG Trouser Tear, kN/m	19
PICO Abrasion Index, 23°C	264
100°C	156
Compression Set, %, 70 hrs, 100°C	31

Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Permanent set, %	3.7
Heat Build-up, °C	34
Pendulum Rebound (Z), %, 23°C	62
100°C	61

EPDM 36

Elastomer: EPDM Durometer: 85
Application: Belts

EPDM 346	100	Zinc oxide	1
EPDM 1446	20	Sulfur	1.5
220 m^2/g Silica	60	DPTH	1.5
Zn dimethacrylate*	3	TBBS	2
ZMTI	2	ZMDC	2
TMQ	2	Specific gravity	1.10

*for reduction in viscosity and HBU (cut growth resistance less)

MDR Cure Rate, 160°C, T_{50} minutes	3.8	
T_{90} minutes	15	
M-M, 20 minutes	37	
Mooney Scorch, 121°C, T_5 minutes	11.3	
T_{35} minutes	20	
Mooney Viscosity, ML_4 100	110	
20 minute cure, 160°C:		
Durometer, 23°C/100°C	85/79	
PICO Abrasion Index, 100°C	102	
DIN Abrasion Loss at 23°C, ml	118	
MG Trouser Tear, kN/m, 23°C/70°C	23/11	
15 minute cure, 160°C:	Original	700 hours, 140°C
M300, MPa	5.3	
Tensile, MPa	25	15
Elongation	715	85
Adhesion to RFL fabric, N/25mm	145	
Compression Set, %, 70 hrs, 100°C	92	
Pendulum Rebound (Z), %, 23°C/100°C	59/59	
Goodrich Flexometer: 100°C, 22.5%; 1 MPa		
Static Compression, %	8.4	
Dynamic compression	0	
Drift	34	
Set, %	27	
Heat Build-up, °C	38	
DMA Dynamic Modulus: 1 Hz; 60°C		
E”, MPa	1.72	
E’	14.7	
Tangent delta	0.12	
DeMattia Cut Growth: kc at 500%	4	

EPDM 37

Elastomer: EPDM Durometer: 87
Application: Tear; Abrasion; Zinc-Free

EPDM 2722	75	Zinc oxide	1
EPDM 346	25	Zn dimethylacrylate	5
220 m^2/g Silica	40	DPTH	1.5
65 m^2/g Silica	20	Sulfur	1.5
TiO_2	15	TBBS	2
Paraffinic oil	5	ZBDC	2
ODPA	1.5		
ZMTI	1.5	Specific gravity	1.17

MDR Cure Rate, 150°C, T_{50} minutes	5.0
T_{90} minutes	8.7
Mooney Scorch 121°C T_5 minutes	13
Mooney Viscosity, ML_4100	72
Durometer, 23°C	87
100°C	76
15 minute cure, 150°C:	
M300, MPa	8.2
Tensile, MPa	21
Elongation, %	550
MG Trouser Tear, kN/m	20
PICO Abrasion Index	131
Compression Set, %, 70 hours, 100°C	84
Pendulum Rebound (Z), %, 23°C	50
100°C	59

EPDM 38

Elastomer: EPDM Durometer: 89

Application: Fabric adhesion; Tear strength; Zinc-free

EPDM 2722	50	Zinc oxide	1
EPDM 346	50	Sulfur	1.5
220 m^2/g Silica	60	TBBS	2
65 m^2/g Silica	20	ZBDC	2
Paraffinic oil	5	DPTH	1.5
Titanium dioxide	5		
Zn dimethylacrylate	5		
ZMTI	1.5		
ODPA	1.5	Specific gravity	1.19

Mixed Banbury 1:4’ to 175°C, stock temperature

MDR Cure Rate, 155°C, T_{50} minutes	5.0
T_{90} minutes	14
Mooney Scorch, 121°C, T_5 minutes	18
Mooney Viscosity, ML_4100	88
Durometer, 23°C	89
100°C	81

Stress/Strain	Original	700 hrs, 145°C
Durometer	89	96
M300, MPa	9.1	
Tensile, MPa	16	13
Elongation, %	505	30(Brittle)

MG Trouser Tear, kN/m	25
PICO Abrasion Index	163
Adhesion, RFL Polyester, strip, N/25 mm	390
Compression Set, %, 70 hrs, 100°C	91
Pendulum Rebound (Z), %, 23°C	47
100°C	55
Dynamic Coefficient of Friction, Wet Aluminum	0.59

EPDM 39

Elastomer: EPDM Durometer: 92(78D)
Application: MRG; Peroxide

EPDM 346	100	Zinc oxide	1
220 m^2/g Silica	60	ZDMA 834	3
Silane A174	1.5	BPIPB 40	7
Softener	15		
ZMTI	2		
ODPA	2	Specific gravity	1.12

Softener:	Ricon 1731	Paraffinic 2280 Oil
MDR Cure Rate 165°C, T_{50} minutes	8.4	8.2
Mooney Scorch, 121°C T_5 minutes	30+	30+
Mooney Viscosity, ML_4100	75	76
Durometer, 23°C	92	78
100°C	90	73
MG Trouser Tear, kN/m	12	14
PICO Abrasion Index	161	137
Compression Set, %, 70 hrs, 100°C	43	44
DeMattia Cut Growth, kc to 500%	0.5	1.0
Pendulum Rebound (Z), %, 23°C	55	57
100°C	58	58
Original		
M300, MPa	-	9.8
Tensile, MPa	17	23
Elongation, %	260	505
Aged 700 hrs, 150°C	Br	Br
Pilling (PICO, 100°C)	0	slight

CHAPTER 6

COMPOUNDING PRECIPITATED SILICA IN NEOPRENE

6.1 INTRODUCTION

A rubber chemist is, of course, well aware that there are chloroprene polymers other than neoprene available in the global market. However, most of the work described in this chapter was carried out with various grades of neoprene and the neoprene grade letters will be retained in both text and Formulary compounds.

A principal concern in a description of silica compounding with neoprene is the existence of two separate neoprene types – sulfur modified (SM or G types) and non sulfur modified (NSM or W types). These two types, with the exception of several hybrids, are sufficiently different in their curing and performance properties to require consideration as separate or sub-polymers. Precipitated silica has found use as a reinforcing filler in both types. In NSM neoprene, principal applications include hose, conveyor belts, cable and mechanical goods. In SM neoprene, power transmission belts are a major use. These silica uses are based, as with other elastomers, on contributions to adhesion, heat resistance and tear strength. Although the Formulary compounds are confined to a single polymer, based on hardness, examples of both SM and NSM neoprenes generally appear together at each durometer hardness level. A direct comparison between NSM and SM types, in a formula based on a semi-reinforcing silica, appears in Formulary compound CR 14. The acceleration for the NSM neoprene here is the glycol-thiuram-HMT combination described below.

The basic difference between SM and NSM types is well illustrated in a series of compression set experiments which include both silica and carbon black uncured compounds. The initial objective here was to explore the effect of silane coupling before crosslinking. However, in a serendipitous turn of events, the results reveal the chemical contrast between neoprene types as well as the silica-polymer bonding effect of mercaptosilane. The test compounds, in Table 6.1, contain only 30 phr filler, with and without silane.

These set values, unlike those of cured compounds, represent flow behavior. Resistance to flow under pressure results in low set values. The outstanding number here is the low set value for the coupled silica in NSM neoprene. At 17%, this is well below the values for any other combination of filler and polymer, and indicates a very significant increase in silica-polymer bonding. A modest counterpart occurs in the HAF-silane-SM compounds where the black-sulfur bonding is improved by silane addition.

Table 6.1 Neopenes Types SM and NSM; Silane Coupling

150m2/g N_2SA Silica	30	30	--	--
HAF N330 Carbon Black	--	--	30	30
Mercaptosilane A189	--	0.7	--	0.7
Compression set of uncured neoprene, 24 hrs, 38°C; %:				
SM neoprene	66	65	52	34
NSM neoprene	56	17	48	43

These data predict that silane addition will be considerably more effective in silica reinforced NSM than in SM compounds. Formulary compound examples demonstrate that this is indeed the case. Another prediction suggested by the low uncured set value of the silica-silane compound involves viscosity. The increase in network stability here should result in improved flow resistance and an increase in Mooney viscosity. Formulary compound CR 8, a comparison of skim compounds with and without silane, does indeed show a viscosity increase from 63 to 100 and corresponding reduction in tack in the silane compound. This behavior is in complete contrast to the viscosity reduction which occurs when silane is added to silica reinforced SBR and other non-chlorine elastomers, and indicates the initial formation of coupling bonds at processing temperatures.

6.2 NSM (TYPE W) NEOPRENE: OXIDE CROSSLINKING

Magnesia and zinc oxide are both generally required for effective crosslinking, but not necessarily in the traditional 4 and 5 phr concentrations. Variations in magnesia content produce much wider property fluctuations than do those of zinc oxide. In a base compound highly filled with silica and clay, magnesia variation influences curing properties, as in Table 6.2.

Table 6.2 Magnesium Oxide Effects in NSM Neoprene

Magnesia, phr	0	2	5	10
ODR cure rate, 155°C, dN-m/5 min	16	20	12	7
Mooney scorch 121 °C, T_5 min	15	20	19	30
Compression set, 70 hrs, 100 °C, %	64	50	59	67

The optimum low set value at 2 phr indicates that crosslink stability is highest at this concentration. This concentration also provides the fastest cure rate and the most scorch safety (10 phr excepted). Other properties, including water absorption, are relatively unaffected by magnesia variation, although at 0 phr the resulting high heat build-up and 1000% elongation indicate a prohibitively low state of cure. Second stage addition of magnesia, in contrast to the normal early first stage, slows the cure rate with no corresponding increase in scorch safety; M300 modulus and durometer are reduced.

Zinc oxide variation (magnesia at 2 phr) over the 2 to 8 phr range shows no effect on any property with the exception of aged elongation. Elongation after oven aging at 121°C is significantly reduced at 2 phr.

6.3 NSM NEOPRENE (W): ORGANIC ACCELERATION

The most powerful accelerating agent for the alteration of curing and vulcanizate properties in silica reinforced NSM neoprene is ethylene thiourea (ETU). Diethylthiourea (DETU) shows similar activity but with somewhat less scorch safety. Other thiourea derivatives are less effective, particularly in respect to attaining low compression set. Concentration effects of ETU in a neoprene W compound with a 60 phr blend of low and medium surface area silicas and magnesia at 2 phr are noted in Table 6.3.

Table 6.3 Ethylene Thiourea Effects in Neoprene NSM

ETU, phr	0.2	0.4	0.8
ODR cure rate, 155°C, dN-m/5 minutes	6	11	22
Mooney scorch 121°C, T_5 minutes	25	19	13
30 min cure, 155°C:			
Durometer	48	50	55
M300, MPa	0.7	1.4	2.1
Elongation, %	900	830	700
Compression set, 70 hrs/100C, %	66	50	40

Set and hysteresis properties continue to improve with increasing ETU. Scorch safety is the limiting factor. In one case, a 78 durometer compound with 2 phr ETU achieved a set of 24% with scorch T_5 at 10 minutes. Formulary examples of ETU and other thiourea accelerations include CR 2, 4, 5, 9, 10, 11, 16, 19 and 24. CR 16 contains a comparison of ETU with a sulfur-guanidine system.

An early alternative to ETU which provided improved scorch safety at the expense of compression set and -40°C stiffness included sulfur, TMTM and DOTG. This acceleration also reduced water swell at 70°C. A comparison of these accelerations, with and without silane coupling, appears in Table 6.4.

Table 6.4 Acceleration and Silane Coupling for NSM Neoprene

ETU	0.6	0.6	--	--
Mercaptosilane	0	1	0	1
Sulfur	--	--	1.5	1.5
TMTM	--	--	0.5	0.5
DOTG	--	--	0.5	0.5
ODR cure rate, 150°C, T_{90} minutes	57	34	57	50
ODR MH-ML crosslinks	55	70	56	55
Mooney scorch 121°C, T_5 minutes	13	5.9	30+	28
Mooney viscosity, $ML_4$100	69	85	62	132
Cure: 30 minutes, 160^{o}C				
Durometer	61	65	55	57
Original Stress /Strain:				
M300 modulus, MPa	3.6	13	2.6	8.2
Tensile, MPa	18	21	19	24
Elongation, %	820	470	850	670
Aged 70 hrs, 100°C				
Durometer	65	67	70	68
Tensile, MPa	17	16	19	18
Elongation, %	660	260	610	370
Compression set, 70 hrs, 100°C, %	56	34	82	74
PICO abrasion index	75	115	78	104
NBS abrasion index	80	248	81	172
Goodrich flexometer: 100°C; 22.5%; 1 MPa:				
Permanent set, %	8.0	0.5	12	3.5
Heat build-up, ^{o}C	49	30	49	35
Other ingredients: CR W-95; 150 m^2/g N_2SA silica-40; Oil 790-10; ODPA-2; Stearic acid-0.5; Magnesium oxide-4; Zinc oxide-5				

A sulfurless acceleration of HMT, TMETD and PEG has been successful in reducing compression set to the lowest range and retaining the good aging properties of ETU (0.5 phr). This system is described in Formulary compound CR 22 and compared to an FEF black control in CR 1, and to GRT in CR 14.

6.4 NSM NEOPRENE: GLYCOL ACTIVATION

Polyethylene glycol produces desirable reductions in viscosity and compression set without degradation of stress/strain or curing properties. A 70 durometer compound filled with silica and hard clay benefits from PEG addition, as in Table 6.5. In less highly filled compounds where silica is the only filler, the effects of PEG are relatively minor, but there is still a contribution to improved crosslink density as evidenced by lower flexometer set and reduced DeMattia flex life. As noted above, PEG is a component of the effective accelerator system which includes HMT and TMTM.

Table 6.5 PEG Activation in NSM Neoprene

PEG 3350, phr	0	4
Mooney viscosity, ML_4100	134	93
Durometer (30 min/154°C)	72	75
Compression set, 22 hrs, 100°C, %	59	46

In contrast to PEG, diethylene glycol has a pronounced activation effect on cure and scorch. Notwithstanding the scorch problem, DEG has found considerable use in augmenting the superior water resistance of silica compounds. Addition of 2.5 to 3.5 phr DEG reduces the normal 100°C water swell of silica reinforced NSM neoprene by 40%.

When DEG is accompanied by the addition of 3 phr water, a substantial hardness increase accompanies the reduction in swelling, as seen in Table 6.6. Water addition increases the strength of the agglomerated silica network. This phenomenon is useful is maintaining the hardness stability of compounds exposed to hot water environments. Among other possible activators, triethanolamine and benzoic acid are used to obtain easy processing and smooth extrusion of highly filled compounds, with some sacrifice in scorch safety.

Table 6.6 Glycol and Water Effects in NSM Neoprene

DEG/water, phr	0	3/3
ODR cure rate (slope), dN-m/5 minutes	14	40
Mooney scorch 121°C, T_5 minutes	15	6
Durometer, original	68	79
Water immersion, 170 hrs, 100°C:		
Durometer	74	80
% Swell	11	6

6.5 NSM NEOPRENE: PLASTICIZATION

A comparison among naphthenic oil (LPO), vegetable oil (linseed), and ester plasticizers (DOS) at 15 phr in an NSM formula with 75 phr of 150 m^2/g N_2SA silica reveals little difference in processing or vulcanizate properties. Extensive processing modifications of silica filled neoprene are generally supplied by silica network changes based on agglomeration reduction by silanes, glycols, triethanolamine and benzoic acid. Table 6.7 shows a summary and comparison of these materials. The most effective viscosity reducers are TEA and the castor oil ester, propylene glycol recinoleate (PGR), but both suffer from severe sticking on a laboratory mill. Sticking is relieved with blends of PGR , butyl oleate and brown factice. Mill roll sticking is eliminated by the amide wax, but viscosity is only slightly reduced. All of these materials, except TEA, produce a dramatic loss in hardness and high strain modulus (M300). The sought after combination of complete mill release and low viscosity remains elusive. Perhaps the best compromise is the replacement of 20 phr of neoprene by CSM, together with added PGR. In this case, hardness is retained but M300 modulus is cut in half. Low M300 generally signifies low abrasion resistance.

Table 6.7 Plasticizers and Release Agents for Silica Reinforced NSM Neoprene

Plasticizer						
Type	**phr**	**ML_4100**	**Mill Sticking**	**Duro**	**M300 MPa**	**Tensile MPa**
None	--	160	moderate	78	7.4	9.9
Triethanolamine	4	113	much	80	5.0	9.4
Castor oil ester, PGR	10	82	much	67	2.9	7.4
PGR + Factice	5+10	94	slight	71	3.7	8.0
Butyl oleate	10	105	slight	70	5.0	7.8
Amide wax	5	123	None	71	3.3	7.8
Neoprene Replacement:						
CSM, Hypalon 20	20	132	slight	84	9.3	9.6
CSM + PGR 10phr	20	83	none	80	4.6	6.9
Neoprene FB	25	135	moderate	78	6.0	7.4

Other ingredients: CR W-100; 150 m^2/g N_2SA silica -35; 35 m^2/g N_2SA silica -95; aromatic oil-22

6.6 NSM NEOPRENE: SILICA AND BLACK

Although polar elastomers like neoprene are usually more compatible with the silanol surface of precipitated silica, the silica vulcanizate shortcomings of modulus, set, abrasion resistance, resilience and hysteresis are still apparent in both SM and NSM neoprene compounds. Also still apparent are the usual silica advantages over carbon black in respect to heat resistance, trouser tear strength and fabric adhesion. An equal hardness comparison in Table 6.8 is illustrative. Silane coupling can, of course, change this picture completely. In Formulary compound CR 1, a comparison of a coupled semi-reinforcing silica with FEF black in a motor mount formula demonstrates superior silica performance in set, creep, aging, resilience, heat build-up and dynamic efficiency.

Table 6.8 Silica and Black in NSM Neoprene

220 m^2/g N$_2$SA Silica	-	15	30	45
HAF N330 Carbon Black	60	45	30	15
Mercaptosilane A189	-	-	-	0.3
DOS	10	10	12	15
MDR cure rate, 150°C, T$_{90}$ minutes	17	12	17	21
MDR crosslinks, dN-m	23	28	25	34
Mooney scorch 121°C, T$_5$ minutes	7.5	10	13	11
Mooney viscosity, ML$_4$100	50	44	43	45
Garvey die rating	5B	4B	5A	5A
% swell	10	10	34	40
Cure at 155°C, minutes	15/25	15/25	15/25	20/30
Durometer, 23°C	72	67	67	71
Original Stress/Strain: M300, MPa	20	15	8.4	6.4
Tensile, MPa	19	17	17	16
Elongation, %	270	330	505	685
Aged 170 hrs, 125°C: Durometer	86	89	87	85
Tensile, MPa	18	16	16	17
Elongation, %	110	135	180	230
MG Trouser Tear, kN/m	5.1	6.0	9.4	23
PICO Abrasion index	109	90	83	74
Compression set, 70 hrs, 100°C, %	37	46	64	74
Peel Adhesion to RFL nylon fabric, N/25mm	25	52	115	205
Pendulum Rebound (Z), %: 23°C	45	44	45	45
100°C	64	62	58	54
DeMattia Cut Growth, kc to 500%	0.3	1	3	35
Goodrich Flexometer: 100°C; 22.5%; 1 MPa				
Static compression %	14	17	21	20
Dynamic compression, %	2.3	6.0	11	20
Permanent set, %	3.2	7.3	--	15
Heat build-up, °C	20	22	41(BO)	32
Other ingredients: CR WRT-100; BR 1220-4; MgO- 2; ZnO-4; ODPA-2; Stearic acid-2; PEG 33350-3; TMETD-1.2; HMT-2.2				

A further look at silica-black relationships, with and without silane, taken from the equal hardness study based on a 220 m^2/g N$_2$SA silica and HAF N330 black, is summarized in contour graphs, Figures 6.1 to 6.3 and 6.5. Addition of mercaptosilane appears to have surprisingly little influence on tear, cut growth and aging and only a modest negative one on adhesion (water absorption is discussed below). Positive coupling effects are seen in resilience, hysteresis and dynamic storage modulus (increased flexibility). Cure rate, crosslink density and viscosity are relatively unaffected by either variable.

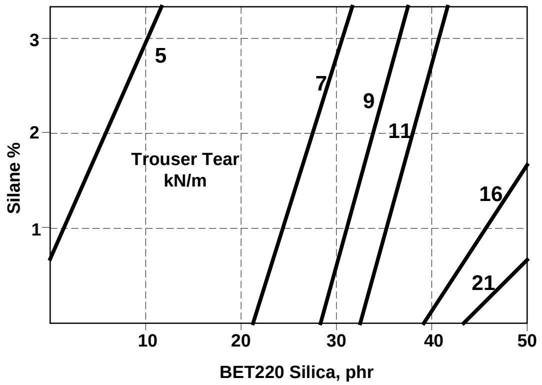

Figure 6.1 Effect of Silica and Silane Concentration on Trouser Tear

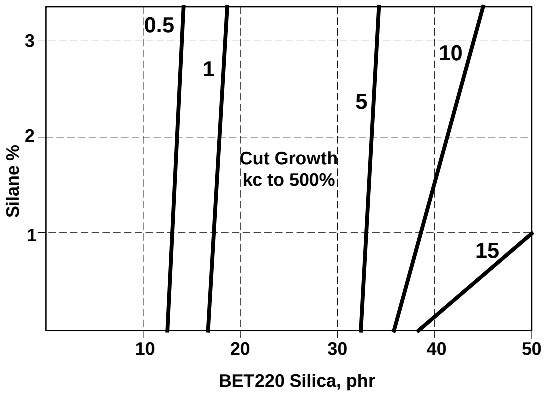

Figure 6.2 Effect of Silica and Silane Concentration on DeMattia Cut Growth

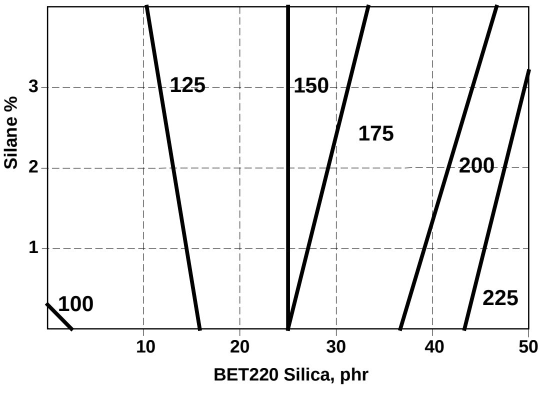

Figure 6.3 Effect of Silica Content and Silane on Aged Elongation

Silica content is the major influence in improving trouser tear, cut growth resistance, age resistance and adhesion to RFL treated nylon. Next in importance is in aging resistance. In all compounds in Table 6.8, the near brittleness of the all-black control is steadily improved as silica content increases. Silica also produces its customary lowering of tangent delta and and degradation of static modulus and compression set.

6.7 SILICA SURFACE AREA

Properties imparted by silicas with a surface area range of 35 to 150 m^2/g are described in Table 6.9. The expected decline of reinforcement with lower surface area includes durometer, modulus and tear strength.

Table 6.9 Silica Surface Area Effects in NSM Neoprene

Silica N_2SA, m^2/g	150	65	35
ODR cure rate (slope), dN-m/5 min.	20	13	11
Mooney scorch 121°C, T_5 minutes	20	16	21
Mooney viscosity, ML_4100	57	50	48
Stress /Strain (Cure: 30 min/154°C)			
Durometer hardness	58	48	49
M300, MPa	2.3	1.7	1.1
Tensile, MPa	13	9	11
Elongation, %	800	780	48
Aged 70 hrs, 121°C			
Durometer hardness	80	67	64
Tensile, MPa	11	11	7.9
Elongation, %	480	420	560
Trouser tear, cut groove, kN/m	33	15	10
Compression set, 70 hrs, 100°C, %	53	40	32
Goodrich flexometer: 100°C; 22.5%; 1 MPa			
Static compression, %	19	23	24
Dynamic compression, %	14	13	13
Permanent set, %	20	13	10
Heat build-up, °C	46	42	37
Water immersion at 70°C, % volume change			
1 day	9	9	6
7 days	13	13	11
14 days	12	11	11
DeMattia cut growth, kc to 500%	20	16	8
Other ingredients: Neoprene W-100; BR 1203; Silica-50; MgO-2; ODPA-1.5; Naphthenic oil-15; Stearic acid-1.5; PEG-3; ZnO-4; ETU-0.4			

For no apparent reason cure rate is fastest (steepest rheometer slope) with the high surface area silica. Best aging resistance is obtained with the lowest surface area. The lower surface area grades perform their usual function of providing smooth, low swell extrusions with low set properties. This processing benefit has led to the use of 65 m^2/g N_2SA silica in many of the formulary recommendations. The lowest surface area grades have the unusual ability, at 70-100 phr, to produce a glossy surface in highly filled, open steam cured NSM neoprene hose compounds. Blending neoprene grades WHV and WB with W also enhances surface gloss.

6.8 NSM NEOPRENE: SILANE COUPLING

Silane coupling of silica in NSM neoprene produces set, modulus and abrasion properties comparable to those of HAF reinforced compounds. Mercapto silanes are by far the most effective. Among several significant changes they provide the most effective solution to the long standing silica problem of excessive compression or dynamic set.

The effectiveness of silane A189 in reducing the flow and set of uncured NSM neoprene has been described above. Its influence on curing and vulcanizate properties in a compound designed for ply adhesion is seen in Formulary section CR 8. Other Formulary examples of compounds which contain mercapto silane or Ciptane include numbers 11, 15, 18 and 24. Perhaps the most impressive example is in CR 1, a comparison between semi-reinforcing silica and FEF black, where the superior qualities of coupled silica in respect to set (both constant force and constant strain), heat resistance, hysteresis, and dynamic loss modulus are quite evident.

Mercaptosilane coupling efficiency is considerably reduced when sulfur is present, either in the cure system or in the polymer. Table 6.10 shows this lowered efficiency in terms of cure rate, crosslink density, modulus, set and hysteresis. Although the silane increases both cure and scorch rates, it does not perform the accelerator functions of ETU in respect to vulcanizate properties. Even a partial reduction of ETU in the silane compounds (not shown) results in a significant loss in modulus together with a substantial increase in set and heat build-up.

The coupling action of silanes is dependent on a ready access to both polymer and the silica silanol surface. Both magnesium and zinc oxides compete with silane for position on the silica surface, and thereby reduce silica-elastomer bonding. As a consequence of this situation, the order in which these ingredients are added during mixing is critical to the coupling reaction. Figure 6.4 illustrates the case for variables magnesium oxide and mercaptosilane (MPS) and their addition in either first or second Banbury stages. Compression set is taken as a measure of coupling efficiency.

Table 6.10 Acceleration and Silane Coupling for NSM Neoprene

ETU	0.6	0.6	-	-
Mercaptosilane A189	0	1	0	1
Sulfur	-	-	1.5	1.5
TMTM	-	-	0.5	0.5
DOTG	-	-	0.5	0.5
ODR cure rate, 150°C, T_{90} minutes	57	34	57	50
ODR MH-ML crosslinks	55	70	56	55
Mooney scorch 121°C, T_5 minutes	13	5.9	30+	28
Mooney viscosity, ML_4100	69	85	62	132
Durometer, 30 min cure, 160°C	61	65	55	57
Original Stress /Strain:				
M300 modulus, MPa	3.6	13	2.6	8.2
Tensile, MPa	18	21	19	24
Elongation, %	820	470	850	670
Aged 70 hrs, 100°C				
Durometer	65	67	70	68
Tensile, MPa	17	16	19	18
Elongation, %	660	260	610	370
Compression set, 70 hrs, 100°C, %	56	34	82	74
PICO abrasion index	75	115	78	104
NBS abrasion index	80	248	81	172
Goodrich flexometer: 100°C; 22.5%; 1 MPa				
Permanent set, %	8.0	0.5	12	3.5
Heat build-up, °C	49	30	49	35
Other ingredients: CR W-95; 150 m^2/g N_2SA silica-40; Oil 790-10; ODPA-2; Stearic acid-0.5; MgO-4; ZnO-5				

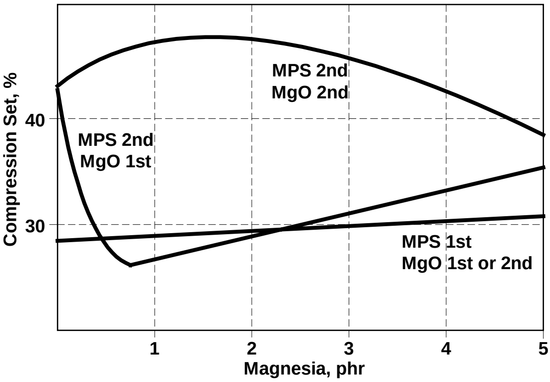

Figure 6.4. Effect of Magnesia, Silane and Mixing on Aged Compression Set

Withholding both magnesia and MPS from the first stage, or complete omission of magnesia, fails to produce any set reduction from coupling. In this case it is important to note the set reduction effect of only 1 phr magnesia. Initial silane addition produces low set values, independent of mixing order or amount of magnesia. The general rule here, and in many similar cases, is to allow unhindered initial mixing contact among silica, elastomer and silane.

6.9 NSM NEOPRENE: FABRIC ADHESION

Previous discussions which compared silica and silane modified silica to carbon black noted the marked improvement in static strip (peel) adhesion to RFL treated nylon fabric in compounds where the ratio of silica to black is highest. Also noted, in Figure 6.5, is the degrading influence of silica modification by mercaptosilane. Since there are no added bonding agents in this formula, the higher bond strength with increased silica content is best ascribed to the superior wetting qualities of silica silanols for the high population of resorcinol hydroxyls on the fabric surface. Any modification of the silanols by silane coupling can be expected to reduce wetting and thus bond strength.

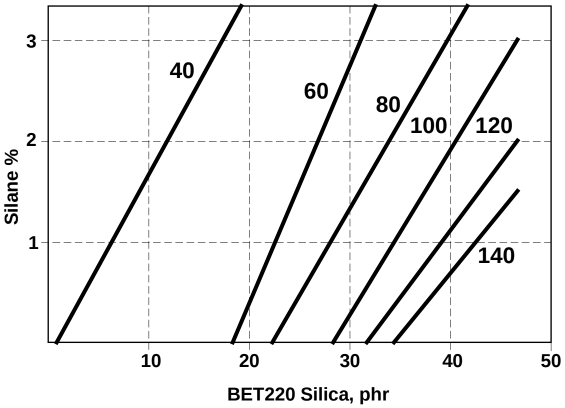

Figure 6.5. Effect of Silica and Silane Concentration on RFL Nylon Adhesion

Of equal importance in high static peel adhesion values are the mechanical aspects of the test procedure. Although this evaluation has been made on an equal hardness basis, high strain modulus and elongation change markedly at higher silica contents. As a result, these compounds will undergo more rapid stress relaxation at the stock-fabric interface and will thus require higher forces to maintain the constant separation rate. As with wetting theory, the effect of silane coupling is negative. Modulus increase and elongation reduction reduce stress relaxation and thus decrease adhesion force values.

Dynamic adhesion procedures frequently offer a more discriminating and prophetic evaluation method than can be obtained from static data. The dynamic procedure used in this and the following examples is the Tension Fatigue test described in Chapter 2 and compound NR 14.

An interesting example of bond fatigue, in Table 6.11, compares SRF black and 150 m^2/g N_2SA silica in NSM neoprene skim compounds at two filler levels. The effect of total filler content is included.

Table 6.11 Dynamic Ply Adhesion by Tension Fatigue: Silica and Black

150 m^2/g N_2SA Silica	0	50	15	50
SRF N774 Black	50	5	75	45
Plasticizer SC	0	0	7	7
TOTAL FILLER	*50*	*55*	*90*	*95*
MDR cure rate 154°C, T_{50} minutes	9.9	14	12	16
MDR crosslinks, MH-ML, dN-m	16	20	25	26
Mooney scorch 121°C, T_5 minutes	30^+	25	24	27
Mooney viscosity, ML_4100	36	56	54	60
Laboratory Mill sticking	none	moderate	none	moderate
Durometer (25 min/154°C)	53	53	62	63
M20 modulus, MPa	0.60	0.70	0.81	0.85
Stress /Strain, Original				
M300 modulus, MPa	9.3	2.8	15	6.0
Tensile, MPa	21	15	16	12
Elongation, %	570	830	335	580
Stress /Strain, 500 hrs, 90°C				
Durometer hardness	64	75	79	85
Tensile, MPa	18	16	15	13
Elongation, %	380	580	195	255
MG Trouser tear, kN/m	8.0	49	7.6	23
DeMattia cut growth, kc at 500%	100+	100+	2	100+
T_g by dynamic modulus (DMA), ^{o}C				
E' MPa, onset	-31	-33	-40	-31
finish	-22	-22	-25	-23
E" MPa peak	-26	-27	-32	-30
Tan delta, peak	-19	-22	-24	-24
Tension Fatigue Bond Separation Rate				
5 Hz; 23°C; 9N tension; (tire cord–skim–tire cord):				
Kilocycle/mm	0.75	33.0	0.07	0.29
Skim thickness, mm	0.34	0.11	0.18	0.12
Other ingredients: CR WRT-100; BR 1203-5; DOS-10; DPPD-2; SDPA-1; MgO-2; ZnO-5;Sulfur-0.5; TMTM-1; DEG (silica only)-2				

The resistance to bond fatigue is measured by the rate of separation of tire cord strips bonded by the ply skim compound under evaluation. The differences in fatigue life of these four compounds is truly astronomical. In the low filler content, equal durometer comparison, replacement of black by silica has produced a 50X increase in separation resistance (KC/mm). This increase in separation rate also takes place in the compounds of higher filler content, but at a 4X ratio. High filler contents degrade bond fatigue life.

What is the effect of specimen geometry and physical properties, other than hardness, on tension fatigue life? Ply skim thickness is significantly greater in the 50 phr black compound of Table 6.11, but it is believed that a thickness reduction would only reduce fatigue life here. The most obvious regression effects appear in 300% modulus, elongation, and tear strength. Low modulus together with high elongation and tear strength are characteristic of all silica reinforced compounds and play a defining role in increasing stress relaxation in dynamic situations. What is not apparent from this and many similar experiments is the relative influence of these instrumental rheological forces and the pure adhesion strength inherent in silica chemistry. Regardless of mechanism, there is little question as to the beneficial effect of black replacement by silica in enhancing bond fatigue life in NSM neoprene.

6.10 NSM NEOPRENE: BRASS ADHESION

Highest bond strengths to brass coatings and brass shim are attained when both sulfur and resorcinol or phenolic bonding agents are present in NSM neoprene compounds. The sulfur requirement evidently relates to the formation of a copper sulfide interfacial layer, similar to that formed in natural rubber to brass bonding. This reaction appears to be quite separate from that of the organic bonding resins. The relative importance of these reactions varies among neoprene types and accelerations. In an NSM neoprene hose cover formula, with or without low surface area silica, the addition of a resorcinol bonding combination produced brass bonding resistant to adhesion loss at longer cure times, as seen in Table 6.12. This effect is independent of the presence of the low surface area silica, which has only a slight positive influence on brass adhesion at the shorter cure. Not noted in the table is the ability of this silica to change the extruded surface of these compounds from dull to glossy.

Many of the studies done on brass adhesion have been based on hydraulic hose formulas that contain both silica and black fillers. A typical formula in which three silicas of varying surface area are compared is described in Table 6.13.

Table 6.12 Bonding Agent Effects on Brass Adhesion of NSM Neoprene

35 m^2/g N_2SA Silica	0	50	0	50
Hard Clay	60	20	60	20
Resorcinol resin SRF 1501	--	--	2	2
HMMM 963	--	--	5	5
Mooney scorch 121°C, T_5 minutes	>30	>30	25	25
Mooney viscosity, MS 121	20	31	22	24
Peel Adhesion to brass shim				
(interior bond), kN/m, 40 min cure /154°C	5.8	8.1	4.4	5.4
60 min cure /154°C	0	0	4.0	5.2
Stress /Strain (30 min cure/154°C)				
Durometer hardness	78	78	NA	*
M300 modulus, MPa	12	8.6	NA	*
Tensile, MPa	14	11	*	*
Elongation, %	350	380	*	*

Other ingredients: CR W-100; GPF-50; Naph. Oil-16; DAPD-1.5; MgO-5; ZnO-5; Sulfur-1; DOTG-1; Stearic acid-2 *not available

Table 6.13 Silica Surface Area Effects on Brass Adhesion

	A	**B**	**C**	**D**
MT N990 Black	100	100	100	--
150 m^2/g N_2SA Silica	50	--	--	--
60 m^2/g N_2SA Silica	--	50	--	--
35 m^2/g N_2SA Silica	--	--	50	50
HMMM 966	3	2	2	2
Resorcinol resin 1501	0.7	1.5	1.5	0.7
ODR 154°C, Cure time at 5.6 N-m, min.	38	39	39	27
Mooney scorch 121°C, T5	15	30+	30+	30+
Mooney viscosity, $ML_4$100	18	13	11	52
Durometer Hardness	63	60	55	60
Peel Adhesion to Brass shim, kN/m				
30 min cure/154°C	18	11	8.8	--
60 min cure /154°C	10	8.8	8.0	19
Stress /Strain, 40 min cure / 154°C				
M300 modulus, MPa	7.6	6.0	5.8	2.4
Tensile, MPa	8.5	8.1	7.7	11
Elongation, %	350	410	390	820

Other ingredients: CR WRT-100; BR 1203-5; MgO-3; LPO-15(12 in D); Ar0. Oil-25(20 in D); ODPA-1; Stearic acid-2; DPG-1; TMTD-1; Sulfur-0.5; ZnO-4

Although the static peel adhesion values here indicate best adhesion from the higher surface area silica, this is possibly a reflection of higher tear strength with a higher surface area silica. Compound D, which produced the highest adhesion value, contains no thermal black and only the lowest surface area silica, and demonstrates the diluting effect of black on brass adhesion. In a similar study where the silica/black ratio was decreased from 50/40 to 50/50, the sensitivity of brass adhesion to silica content is even more apparent. In this case, brass adhesion of the 50/50 compound fell precipitously, with or without the presence of resin bonding agents.

As noted in the processing remarks, scorch safety can be improved by the presence of the thiuram, TMTM. The effect is most apparent in sulfur modified CR (SM) types. However, in SM compounds *without* added sulfur, the presence of TMTM prevents full bond development, as seen in Table 6.14. *With* 0.5 phr sulfur, TMTM provides the highest brass bond values. There is a certain similarity here to the deleterious action of TMTM in the bonding of natural rubber to brass. In that case the thiuram appears to interfere with the copper sulfide bonding layer formation. As noted in the natural rubber chapter, the silica function is to restrain the build-up of the zinc oxide layer at the interface. This reaction may also be a factor with neoprene, but the mechanism is obscure. Bonding resins are required to stabilize the bond during long cure times.

Table 6.14 Brass Adhesion with SM Neoprene

TMTD	1	1	--	--
Sulfur	--	--	0.5	0.5
TMTM	--	1	--	1
Mooney scorch 121°C, T_5 minutes	11	>30	14	18
Static Peel Adhesion, Brass Shim, kN/m				
30 min cure/150°C	27	6.1	19	35
60 min cure/150°C	27	7.0	19	31
Stress /Strain, 40 min cure/150°C				
Durometer Hardness	53	52	55	53
M300 modulus, MPa	5.0	4.3	5.2	5.4
Tensile, MPa	14	14	15	15
Elongation, %	710	760	710	700
Compression set, 22 hrs, 70°C, %	38	39	38	39
Static Peel Adhesion, Untreated Nylon				
Heater cure, kN/m: 30 min cure/150°C	7.0	-	7.0	-
60 min cure/150°C	8.8	-	8.8	-

Other ingredients: CR GN-95; BR 11203-5; MgO-4; 150 m^2/g N_2SA Silica -40; N550-10; ODPA-1; Castor oil ester-5; DOS-12; Oil- 8; Stearic acid-1; HMMM-2.5; Resorcinol resin 1501-0.5; ZnO-4

6.11 NSM NEOPRENE: WATER ABSORPTION

The compounds previously described in the silica/ black and adhesion sections (Table 6.11) are also useful in an examination of the peculiar water absorption characteristics associated with silica reinforced elastomers. The relative influence of silica content and silane modification in terms of percent swell contours is plotted in Figure 6.6. Without silane, water swell is reduced from 30% in the black control to 10% with silica content at 10 phr, with further reduction at higher silica contents. These values were obtained after 14 days immersion in 100°C water.

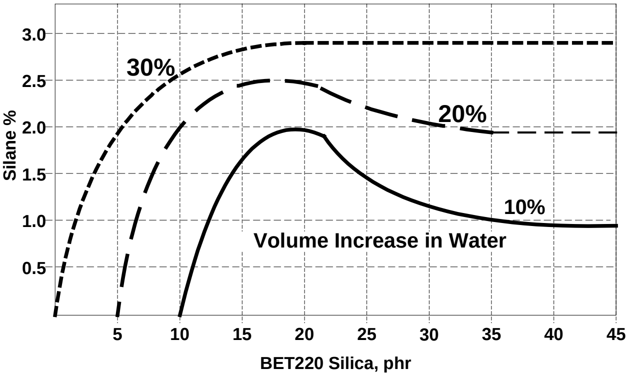

Figure 6.6 Effect of Silica and Silane on Volume Increase in Water

Figure 6.7 provides a picture of absorption rates from 0 to 14 days. At silica contents of either 15 or 30 phr without silane there is complete stability to water take-up in the 1 to 14 day immersion interval. However the presence of 2% silane produces rapid swell which reaches an equilibrium after 7 days of immersion. In the absence of silica the black control continues to imbibe water indefinitely.

An explanation of this behavior rests on two silica characteristics: A residual salt content of 1-2 %, either sodium chloride or sodium sulfate, and channels between silica and polymer which allow leaching of salt solution. Initial swelling during the first hours of immersion is the result of solution of chloride or sulfate salts or other soluble ingredients in the compound through imbibed water. As the salts leach out of the sample, swelling reaches an equilibrium and subsides with continuing immersion. Leaching action is facilitated by the characteristic loose bond between silica and polymer which leads to the formation of channels through which leaching of salt solutions occurs. When this silica-polymer bond is strengthened by the presence of a silane coupling agent, leaching is impeded and swelling continues to a point of higher equilibrium. Water absorption data is available in Formulary compounds CR 9, 10, 14, 22, and 24.

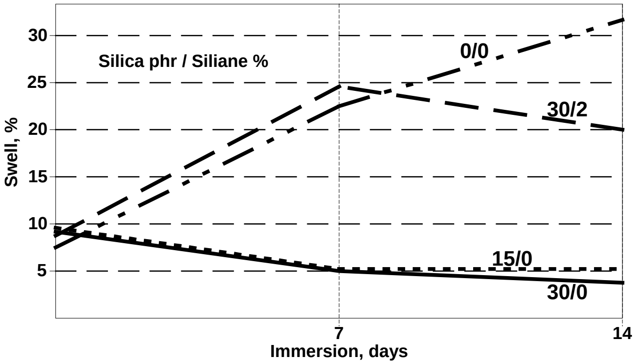

Figure 6.7. Effect of Silica and Silane on Swelling Rate in 100°C Water

6.12 SULFUR MODIFIED (SM) NEOPRENE: CURE SYSTEMS

Zinc oxide and magnesium oxide are the principal crosslinking agents for SM neoprene, and, as such, must be examined in terms of both concentration and interaction with silica. Zinc oxide is the primary crosslinker and adequate curing can be realized with as little as 1.5 phr. However, concentrations below 4 phr fail to provide the full age resistance potential of this polymer. Figure 6.8 shows that rate of cure is remarkably unaffected by changes in zinc oxide concentration .

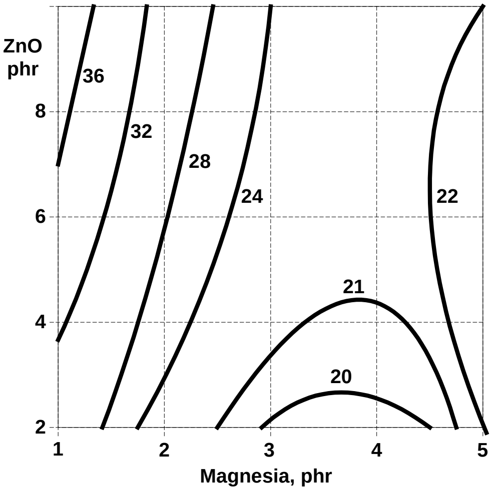

Figure 6.8. Effect of MgO and ZnO on Rheometer Cure Curve Slope; 154°C

Magnesia content is the determining factor for both cure rate and scorch behavior, as seen in Figures 6.9 and 6.10.

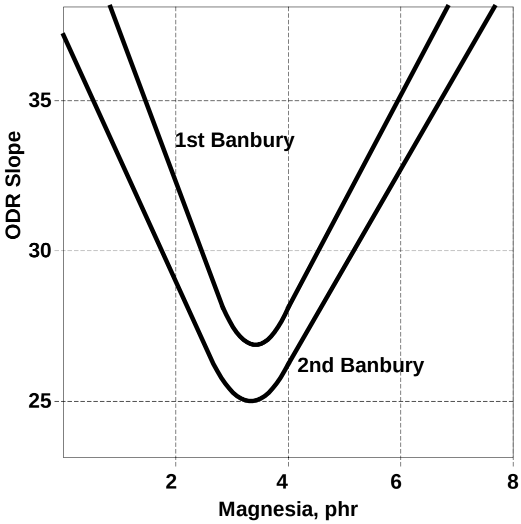

Figure 6.9 Effect of Magnesia Concentration on Cure Rate

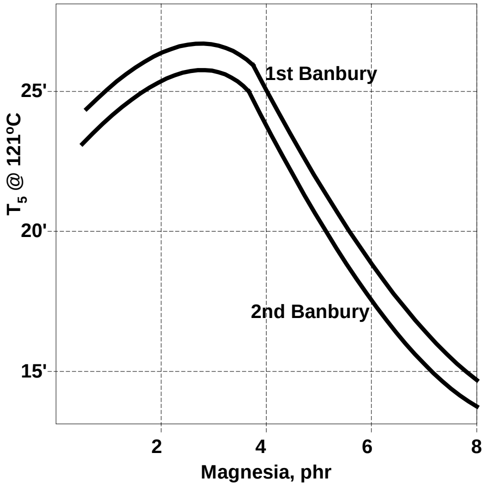

Figure 6.10 Effect of Magnesia Concentration on Scorch

Magnesia produces the lowest cure rates (low rheometer slope) in the 2 to 4 phr range; scorch safety is best at 2 phr. Cure rate is slowed and scorch safety improved when magnesia is added in the second stage Banbury, Thus, for silica reinforced neoprene, the generally recommended 4 phr magnesia should be reduced to 2 phr to provide the best compromise between adequate scorch safety and rapid crosslinking.

As noted in Table 6.15, silica water content may alter the magnesia recommendations for scorch safety somewhat. At a silica water content of 10% (a value reached in some commercial silicas), 4 phr MgO provides more safety than does 1.5 phr. Magnesia effects have been found to vary in corresponding CR grades from different manufacturers. For example, with S-3 grade, in contrast to GNA, an increase in magnesia from 1 to 3 phr produces substantial reductions in viscosity, hardness and modulus.

Table 6.15 Silica Water Content and Magnesia Effects in SM Neoprene

Magnesium oxide	1.5	1.5	1.5	4	4
Silica water content, %	4	7	10	7	10
ODR scorch rate 154°C, T_2 minutes	6.0	5.5	1.5	5.5	9.0
Re-milled	5.5	5.5	3.0	5.0	10
Mooney scorch 121°C, T_5 minutes	17	14	3.5	12	9.0
Re-milled	17	14	5.0	12	10
Mooney viscosity, ML_4 100	65	62	70	74	70
Re-milled	62	57	53	65	64
Durometer hardness, 45 min cure/154°C	65	65	75	67	72
Re-milled	63	60	70	64	70
Trouser Tear, cut groove, kN/m	15	24	NA	19	19
Re-milled	29	29	33	34	30
M300 modulus, MPa	4.2	3.4	3.9	4.2	4.1
Re-milled	4.1	3.5	3.4	3.9	3.5
Goodrich Flexometer: 100°C; 22.5%; 1 MPa					
Dynamic compression, %	6.4	13	9.2	6.6	11
Permanent set, %	14	19	17	BO	19
Heat build-up, °C	53	53	47	-	50
Other ingredients: CR GNA-75; CR W-25; BR 1203-3; 150 m^2/g N_2SA Silica - 40/41/42; FEF-17; OPDA-2; Castor oil ester-5; Aromatic oil-5; Stearic acid-2; Armoslip CP-1; ZnO-10					

Because of the well documented interaction between silica and both zinc and magnesium oxides, concentration alone does not provide a complete determination of compound properties. Mixing order relationships among silica, polymer and oxides must also be considered. In both types of neoprene, scorch safety requires late or second stage addition of zinc oxide. Thus the situation is resolved into a question of pre- or post-silica addition of magnesia. When magnesia is mixed in the second Banbury stage, reductions in both cure rate and scorch safety occur (Figures 6.9, 6.10), admittedly an unusual conjunction. Second stage addition also reduces maximum rheometer torque, although this is not reflected in 300% modulus, which is unchanged.

Perhaps the major result of second stage addition is a marked improvement in cut growth resistance, particularly at 1 phr, due partially, at least, to a slight reduction in durometer. Compression set and abrasion index also improve. Water swell, however, increases 4 to 5%. With both oxides at low concentrations, 1 and 2 phr, second stage addition produces a significant rise in viscosity. Many of the Formulary recommendations contain magnesia at 2 phr.

6.13 SM NEOPRENE: GLYCOL ACTIVATION

Cure activation effects from polyethylene glycol, diethylene glycol or triethanolamine are generally insignificant in silica reinforced SM neoprene. PEG3350 at 3 phr produces scorch and cure rate increases of 4 to 5 minutes with no positive property effects. DEG and TEA are somewhat more reactive than PEG and can be expected to reduce viscosity, with the possibility of mill sticking. These activators increase durometer by 2 to 5 points but modulus and tensile fall. The addition of 3 phr TEA increases low strain modulus (2-10%) to the extent of a very obvious boardy feel in a vulcanized sheet, possibly the result of a very tightly bound silica-TEA network.

6.14 SM NEOPRENE: RETARDING SCORCH

Silica reinforced neoprene, unless handicapped by excessive viscosity, is usually less scorchy than comparable carbon black compounds. Among several additives, TMTM (tetramethylthiuram monosulfide) is by far the most effective scorch retarder. Addition of 0.5-1.0 phr TMTM can supply 5 to 15 minutes added scorch safety (T_5 at 121°C) with little or no sacrifice in rate or state of cure. In contrast to other retarders such as PVI and MBTS, there is little degradation in stress/strain and other properties. The most serious problem associated with TMTM is a possible degrading effect on brass adhesion, a phenomenon discussed at greater length in the brass adhesion sections. Probably the greatest source of neoprene scorching problems is the polymer itself, in respect to both age and grade modification. Data that compares GNA and GRT is illustrative. Cure rate, scorch and viscosity are likely to increase in direct proportion to the age of the product.

6.15 SM NEOPRENE: SILANE COUPLING

The application of silanes, particularly mercaptosilanes, in SM neoprene compounds is more limited in effect than in NSM types. Low compression set values are not attainable. Mercaptopropyltrimethoxysilane (A189, MPS or MPTS) at 1-2% (silica basis) provides an increase in modulus and moderate improvement in abrasion resistance and dynamic properties. Major disadvantages include losses in scorch safety and water resistance.

6.16 SM NEOPRENE: PROCESSING

Although all SM neoprene compounds can suffer in varying degrees from mill and calender sticking, the problem is aggravated by the presence of silica. The most effective remedy is the addition of 3-5 phr of cis-polybutadiene to the neoprene at the start of mixing. Most of the formulas in the Formulary section contain solution polybutadiene for roll release purposes. Other release agents such as stearic acid, metallic stearates, castor oil esters and amide waxes are helpful but usually entail some deterioration in physical properties. Partial replacement of reinforcing silica by semi-reinforcing grades (e.g., 35 m^2/g N_2SA) is quite effective, but reinforcement declines. The effect of mill roll temperature as well as that of the two most effective release agents in a direct bonding 40 phr silica formula is seen in Table 6.16. The absence of roll sticking at 90ºC reflects a physical change in neoprene. Scorch safety considerations frequently preclude processing at this temperature.

Table 6.16 SM Neoprene Processing: Mill Release Agents

BR 1203	--	3	--	3	4
Amide wax (Armoslip CP)	--	--	2	1	2
Mill Temperature	Mill Sticking (0=none; 4= severe)				
40ºC	3	2	2	2	1
60ºC	4	4	4	3	2
90ºC	0	0	0	0	0

The extent to which processing properties depend on the age and type of neoprene is sometimes startling. The data in Table 6.17 is based on compounds reinforced with 40 phr 150 m^2/g N_2SA silica with viscosity and 121°C scorch data recorded before and after re-milling,

Table 6.17 Neoprene Shelf Stability

Neoprene type	GNA		GRT	
Mooney Viscosity/Scorch	ML_4100	T_5 min	ML_4100	T_5 min.
Original	75	10	23	21
Re-milled after: 7 days	64	5	25	19
Re-milled after: 14 days	53	5	20	20

Table 6.18 Filler Effects on Building Tack in SM Neoprene

	Silica			Black
CTAB surface area, m^2/g	135	128	185	42
MDR cure rate, 154°C, T_{50} minutes	5.3	5.9	5.3	2.2
T_{90} minutes	13	15	24	11
Mooney scorch 121°C, T_5 minutes	13	17	6.6	6.0
Mooney viscosity, ML_4100				
Original	57	53	129	59
Shelf aged 10 days	61	56	140	71
Shelf aged 30 days	77	67	*	*
Building Tack, stitched rubber/rubber strips, Separation force (spring gauge), N/25mm:				
Minimum	3	15	--	0
Average	5	13	--	0
Maximum	10	26	--	0
15, 20 min cure/154°C				
Durometer hardness: 23°C	65	64	64	75
100°C	62	60	62	70
Stress/Strain, Original				
M300 modulus, MPa	6.3	5.8	7.2	18
Tensile MPa	18	18	18	20
Elongation, %	730	795	720	315
Stress/Strain, 700 hrs, 100°C				
Durometer hardness	87	87	87	92
Tensile, MPa	16	17	16	21
Elongation, %	150	190	180	135
MG Trouser Tear, kNm	9.8	21	32	4.6
Die C tear, kN/m	53	51	64	50
Din abrasion index	163	150	123	92
PICO Abrasion index	82	78	92	122
Compression set, 70 hrs, 100°C, %	90	91	92	81
Peel Adhesion to RFL nylon fabric, N/25mm				
Original	65	56	38	15
Water immersed, 70 hrs, 50°C	20	90	10	5
Pendulum Rebound (Zwick), %: 23°C	47	47	49	49
100°C	63	64	64	66
				* off chart

Other ingredients: CR GRT-100; BR 1220-5; Silica-40; N550-15(60 in D): LPO oil-10; ODPA-2; DAPD-1; MgO-2; ZnO-10; Stearic acid-2

Cure rates (rheometer slope and T_{90}) remain unchanged after re-milling of either polymer. Although the earlier production date of the GNA accounts in part for higher original viscosity values, the re-milled differences between GNA and GRT and the unacceptably low scorch safety of GNA compounds demonstrate the pitfalls of extrapolating the results of neoprene compounding studies from type to type.

Superior building tack is characteristic of SM neoprene compounds, and is largely responsible for its continuing use in power transmission belting. An illuminating evaluation of silica surface area effects on tack and viscosity is presented in Table 6.18.

Although the FEF N550 control shows a complete lack of building tack, this is likely due to its 5 phr higher filler content and slightly higher viscosity. Viscosity influence is at its greatest in the highest surface area silica compound, which separated immediately after rubber-to-rubber stitching. The lowest viscosity compound provides the best tack-adhesion. Unfortunately, the low scorch safety of the FEF and high CTAB silica compounds compromises both their tack and adhesion values.

6.17 SM NEOPRENE: SILICA SURFACE AREA EFFECTS

A surface area study in which each compound contains 50 phr silica with areas from 35 to 150 m^2/g shows the expected property increases in durometer, viscosity, modulus, tensile, heat build-up, tear strength and abrasion index at higher surface area. However, when filler contents are changed to provide a constant hardness comparison, significant property changes are found in viscosity and elongation but not in other items. In both normal and direct bonding formulas the best static peel adhesion appears with the 60 m^2/g silica. Table 6.19 presents the constant hardness surface area comparison together with data for fumed silica and HAF controls. The fumed silica compound departs from the comparable precipitated silica compound only in higher viscosity, a 6 point durometer increase, and higher modulus. Neither aging resistance, tear strength nor adhesion properties supply a compelling reason to replace precipitated by fumed silica in SM neoprene.

6.18 SM NEOPRENE: SILICA FREE WATER CONTENT

The free water content of silica can be a source of variability in compounding. When the normal range of 5 to 7% is increased to 10%, significant loss in scorch safety and increase in hardness can occur, as was seen in Table 6.15. As water is dissipated during re-milling, these effects disappear. Magnesia content modifies the effect.

Table 6.19 Surface Area Effects in SM Neoprene: Comparable Hardness

60 m^2/g N$_2$SA Silica	55	-	-	-	-
150 m^2/g N$_2$SA Silica	-	40	-	-	-
220 m^2/g N$_2$SA Silica	-	-	40	-	15
200 m^2/g N$_2$SA Fumed Silica M70D	-	-	-	35	--
72 m^2/g HAF N330 Black	-	15	15	20	40
ODR cure rate 155°C, T$_{50}$ min	6.4	5.6	3.9	4.6	5.1
ODR crosslinks, MH-ML, dN-m	26	26	23	26	34
Mooney viscosity, MS 121°C	28	68	150	185	38
Durometer, 25 min cure/155°C: 23°C	66	66	67	73	73
100°C	62	63	64	70	68
Original					
M20, MPa	1.0	1.0	0.9	1.1	1.3
M300 modulus, MPa	4.5	7.5	7.5	11	15
Tensile, MPa	15	19	17	19	21
Elongation, %	865	650	575	490	435
Aged 700 hrs, 90°C					
Durometer	77	81	78	84	90
Tensile, MPa	11	18	19	22	20
Elongation, %	410	300	270	280	190
MG Trouser tear, kN/m	27	22	26	22	7.7
Pendulum rebound (Z), %: 23°C	53	47	49	47	47
100°C	62	67	68	66	66
Flexometer heat build-up, °C	44	51	54/bo	59/bo	45
DeMattia cut growth, kc to 500%	9	17	6	4.5	3
Static peel adhesion to RFL fabric, N/25mm	203	148	107	88	130
Other ingredients: CR GRT-100; BR 1203-3; Naph, oil-10; ODPA-2; MgO-2; ZnO-5; CaO-2; Stearic acid-2					

6.19 SM NEOPRENE: CORD AND FABRIC ADHESION

As noted in Tables 6.11 and 6.20, the mere replacement of carbon black by silicas of varying surface area is sufficient to increase both static peel adhesion and, particularly, bond fatigue life in SM and NSM compounds. However, bonding to *untreated fabrics* requires a different compounding technology. Without the benefit of an RFL surface, the siilica wetting function must be accompanied by a rigid resin system to form the actual adhesive interface. In neoprene, as in other polymers, the latter function is accomplished by either phenolic or resorcinol resin systems. In both cases, the major compounding objective is to avoid scorching at processing temperatures. A fairly reasonable solution to this problem is noted in Formulary compound CR 12. In this example the mutually reacting bonding agents are the partially reacted resorcinol resin (B19s or SRF1501) and hexamethylenemethylmelamine. Scorch (T_5) values are 17 and 10 minutes at 121°C and 135°C.

Table 6.20 Silica Content Effect on Dynamic Cord Adhesion of SM Neoprene

65 m^2/g N_2SA Silica	0	15	30	45
FEF N550 Black	60	45	30	15
Durometer hardness, 30 min cure/154°C	76	73	71	69
Tension Fatigue Life (cord pull-out)				
Treated V-belt cord; 90°C; 4 Hz; 9 N tension;				
Weibull plot Kilocycles to 63% failure	0.001	0.01	0.33	3.50
ODR cure rate 154°C, T_{35} minutes	13	14	16	17
Mooney scorch 121°C, T_5 minutes	11	30+	30+	30+
Mooney viscosity, ML_4100	68	60	58	55
Original				
M300 modulus, MPa	--	14	8.2	4.7
Tensile, MPa	17	14	13	12
Elongation, %	240	330	450	630
Aged 550 hrs, 100°C				
Durometer hardness	91	91	91	90
Tensile, MPa	16	15	13	12
Elongation, %	60	110	120	190
Compression set, 70 hrs, 100°C, %	58	66	71	74
Pendulum rebound (G-H), %: 23°C	60.5	68.4	58.4	59.0
100°C	69.6	69.0	67.8	66.8
DeMattia cut growth, kc to 500%	<0.5	<0.5	2	9
Goodrich flexometer: 100°C; 22.5%; 1 MPa				
Static compression, %	8.6	9.7	11	13
Permanent set, %	3.0	5.9	9.2	BO
Heat build-up, °C	30	40	49	52
Other ingredients: CR GRT-100; BR 1203-3; Naph. Oil-10; ODPA-2; Stearic acid-2; Amide wax-1; MgO-3; ZnO-5				

When the Tension Fatigue dynamic adhesion procedure is adapted to cord, the fatigue life measurement is based on cord pull-out from the compound, rather than the separation rate used for fabric specimens. This procedure is used to evaluate, in Table 6.20, the dynamic adhesion effects of replacing FEF black by a semi-reinforcing silica. Generally, physical property trends here are typical of silica-black relationships, but the hardness differences weaken definite conclusions on adhesion improvement at the higher silica contents. In any case, improvement in cord fatigue life can be realized in several orders of magnitude if an application can accept significant losses in both static and dynamic stiffness as well as increased heat build-up. These handicaps are at a minimum in the 15 phr silica compound where bond fatigue life has improved by a factor of 10.

Phenolic resin bonding systems involve a more complex technology. Just as the zinc reaction with resorcinol is a basis for RFL bonding, so magnesium activation of phenolic oligomers is a requirement for subsequent resin bonding. Experimental evidence for this relationship is forcibly presented in Table 6.21 in a simple two level design for phenolic resin, zinc oxide and magnesium oxide.

Table 6.21 Dynamic Adhesion of PE Cord to SM Neoprene

Durez phenolic resin 12687	5	5	10	10
Magnesium oxide	1.5	6	6	1.5
Zinc oxide	2	8	2	8
MDR cure rate 155°C, T_{50} min	5.0	5.1	4.6	3.6
MDR crosslinks, MH-ML, dN-m	26	29	30	28
Mooney scorch 121°C, T_5 min	20	14	10	10
T_{35} min	30+	30+	29	23
Mooney viscosity, ML_4 100	54	56	56	58
Tension Fatigue Adhesion: 90°C; 3.5 Hz; 30N; 12mm;				
Untreated polyester fused cord,				
kc to 63% failure	2.4	12	200	6.5
Durometer hardness, 12 min cure/155°C				
23°C	60	61	64	64
100°C	57	58	60	61
Stress /Strain, Original				
M20, MPa	1.1	1.1	1.2	1.3
M300, modulus, MPa	5.8	5.5	6.3	6.7
Tensile, MPa	14	12	12	13
Elongation, %	750	690	640	665
Stress /Strain, 170 hrs, 110°C				
Durometer hardness	82	85	85	83
M20, MPa	3.5	3.7	3.8	3.6
Tensile, MPa	12	11	12	12
Elongation, %	190	185	160	175
Compression set, 70 hrs, 100°C, %	92	89	90	86
Pendulum Rebound (Zwick), %: 23°C	48	46	45	49
100°C	58	59	59	59
Other ingredients: CR GRT-100; BR 1220-3; 65 m^2/g N_2SA Silica-40; 150 m^2/g N_2SA Silica-20; Naph. Oil-12; CaO-2; Amide wax-1; Stearic acid-3				

Tension fatigue testing of the adhesion of these compounds to untreated polyester cord reveals a remarkable maximum in bond fatigue life at the higher levels of phenolic resin and magnesium oxide.

Little or no variation in crosslink density, hardness, modulus, or resilience among these four compounds helps to resolve the long standing conflict between mechanical and chemical explanations of bonding behavior. In this case we have convincing proof that wide variation in bond strength and fatigue life are not dependent on changes in hardness or static or dynamic mechanical properties. Here the phenomenon is the result of chemical bonding, not mechanical behavior.

6.20 SM NEOPRENE: BRASS ADHESION

As noted in the NSM neoprene section, the beneficial role of silica in brass adhesion must be combined with that of sulfur content and bonding resins to form a total picture of brass adhesion behavior. Table 6.14 provides a partial summary which also involves the role of TMTM as a scorch retarder. In respect to scorch safety, the presence of TMTM adds from 4 to 20 minutes. However, its influence on brass bonding depends entirely on the source of sulfur in the formula. With sulfur donor TMTD, the brass bond suffers greatly when TMTM is present. In startling contrast, the combined presence of 0.5 phr elemental sulfur and TMTM produces extremely high static bond strength which persists at the longer cure time. This value, 35 kN/m or 200 pounds per inch, is the highest recorded in these studies. The bonding resin content is constant in all compounds.

When the 40/10 silica/black ratio of the compounds of Table 6.14 is compared to a 40/80 ratio in a typical hose cover formula, brass adhesion is only slightly reduced. Removal of the resorcinol bonding system from these formulas results in a drastic fall in static adhesion values.

REFERENCES

1. PPG Technical Service Bulletins 150-G-51, -58, -61
2. Hewitt, N.L., “Silica Compounding with Neoprene”, paper presented to Northeast Ohio Rubber Group, February 11, 1997
3. Hewitt, N.L., “Adhesive Systems for Belts and Hoses”, paper presented to ACS Rubber Division meeting, Chicago, IL, April, 1999

Neoprene Formulary

The silica surface areas indicated in the following compounds are N_2SA (BET) surface areas. A listing of commercially available precipitated silica products by surface area is provided in Appendix A. The common abbreviations used in these compounds are provided in Appendix E.

CR 1

Elastomer: CR Durometer: 48
Application: Motor mount

Neoprene WRT	100	DAPD 100AZ	1
Silica or FEF	28	Zinc Oxide	3
Silane A189	0.9	HMT	2.2
Dioctyl Sebacate	10	TMETD	1.2
Rapeseed Oil	5	PEG 3350	3
Magnesium Oxide	2	Specific gravity	1.26

	65 m^2/g Silica	N550 Black[1]
MDR Cure Rate, 155°C, T_{90} minutes	8.0	4.7
Mooney Scorch, 121°C, T_5 minutes	18	15
Mooney Viscosity, ML_4 100	30	29
Compression Set, 70 hrs, 100°C		
Constant Force (Method A), 0.8 MPa		
Set, %	30.5	45.3
Creep	27.0	37.0
Durometer	46	48
Constant Deflection (Method B)		
Set, %	42.2	47.0

Stress/Strain	Original	Aged[2]	Original	Aged[2]
Durometer	49	64	50	74
M300, MPa 5.8	8.0			
Tensile, MPa	13	10	18	10
Elongation, %	595	265	545	130
% Retained	45		24	

[2] 170 hrs, 125°C

Pendulum Rebound (Z), %, 23°C	59	55
100°C	69	65
Goodrich Flexometer Heat Build-up, °C	9	20
DMA Dynamic Modulus: 1 Hz; 15% strain		
E', MPA 0°C	4.1	4.9
80°C	2.6	2.8
E" 80°C	0.4	0.9
Tangent Delta 80°C	0.139	0.210

[1] FEF compound contains no silane and HMT reduced to 1.6 to prevent scorching.

CR 2

Elastomer: CR/BR Durometer: 52
Application: Heat resistance; MRG

Neoprene W	100	Naphthenic Oil	15
BR 1203	5	PEG 4000	3
150 m^2/g Silica	30	Stearic Acid	2
65 m^2/g Silica	30	Zinc Oxide	4
Magnesium Oxide	2	ETU	0.5
ODPA	2		
Castor Oil Ester	3	Specific Gravity	1.38

ODR Cure Rate, 154°C, T_{90} minutes	22
Mooney Scorch, 121°C, T_5 minutes	17
T_{35} minutes	27
Viscosity, ML_4100	49

30 minute cure, 154°C	Original	72 hrs, 121°C
Durometer	52	70
M300, MPa	1.5	
Tensile, MPa	10	9.1
Elongation, %	820	550

Compression Set, 70 hrs, 100°C	50
DeMattia Flex, 20°C, kc to 0.6” Growth	25

Water Immersion, 70°C	Hardness	% Volume
1 day	45	9
7 days	52	15
14 days	52	14

CR 3

Elastomer: CR/BR Durometer: 53
Application: Tear strength; Ply adhesion

Banbury 1		Banbury 2	
Neoprene WRT	100	Zinc Oxide	5
BR 1203	5	Sulfur	0.5
150 m^2/g Silica	50	TMTM	1
DOS	10	DOTG	1
Magnesium Oxide	2		
Stearic Acid	2		
SDPA29	1		
DPPD	2		
DEG	2	Specific Gravity	1.38

ODR Cure Rate, 154^{o}C, T_{50} minutes	14
Mooney Scorch, 121^{o}C, T_5 minutes	25
Viscosity, $ML_4$100	56

25 minute cure, 154^{o}C	Original	500 hrs, 90^{o}C
Durometer	53	75
M300, MPa	2.8	-
Tensile, MPa	15	16
Elongation, %	830	580

MG Trouser Tear, kN/m	19.2
Glass Transition (DMA), ^{o}C	
E' Onset	-33
E' Finish	-22
E" Peak	-27
Tan Delta Peak	-22

CR 4

Elastomer: CR Durometer: 53
Application: Low viscosity; Footwear

Neoprene GRT	100	Stearic Acid	2
Magnesium Oxide	1.5	ODPA	1
150 m^2/g Silica	20	Zinc Oxide	5
65 m^2/g Silica	20	TMTU	0.4
Aromatic Oil	25	Specific Gravity	1.33

	160°C	180°C
ODR Cure Rate, T_{90} minutes	13	7
ODR Scorch, T_2 minutes	7	4

Mooney Scorch, 121°C, T_5 minutes	27
T_{35} minutes	>30
Viscosity, ML_4100	30

30 minute cure, 160°C:	Original	72 hrs, 121°C	72 hrs, 135°C
Hardness	53	67	75
M300, MPa	1.9		
Tensile, MPa	14	12	13
Elongation, %	830	550	220

Die C Tear, kN/m	35
Trouser Tear, Grooved, kN/m	
20°C	13
100°C	4.4
NBS Abrasion Index	68

CR 5

Elastomer: CR/BR Durometer: 54
Application: General MRG; MT replacement; Black

Neoprene W	95	Naphthenic Oil	25
BR 1203	5	TMTM	1
65 m^2/g Silica	40	Sulfur	1
SRF N770	20	ETU	0.3
Magnesia	4	TMTU	0.9
Stearic Acid	1	Zinc Oxide	4
ODPA	0.5		

ODR Cure Rate, 154°C, T_{90} minutes	23
ODR Scorch, T_2 minutes	3.5
Mooney Scorch, 121°C, T_5 minutes	15
Viscosity, ML_4100	36
ODR Minimum	1.5

15 minute cure, 154°C	Original	70 hrs, 121°C
Hardness	54	84
M300, MPa	3.9	-
Tensile, MPa	12.7	11.4
Elongation, %	540	240

Garvey Extrusion	
Rate	7.3 ft/min.
Swell, %	25
Surface	Smooth and Glossy

Cut Groove Trouser Tear, kN/m	6.5
Compression Set, %, 70 hrs, 100°C	48

CR 6

Elastomer: CR/BR Durometer: 56
Application: Fabric Adhesion

Neoprene GRT	100	Zinc Oxide	2
BR 1203	3	Phenolic 12687	3
65 m^2/g Silica	60	TMTM	1
Naphthenic Oil	15		
ODPA	1		
Amide Wax	1		
Stearic Acid	2		
Magnesia	2	Specific Gravity	1.45

ODR Cure Rate, 154°C, T_{50} minutes	6.3
T_{75} minutes	15
Mooney Scorch, 121°C, T_5 minutes	16
Viscosity, ML_4100	42

20 minute cure, 154°C	Original	72 hrs, 121°C	700 hrs, 100°C
Durometer	56	78	88
M300, MPa	3.1		
Tensile, MPa	13	10	11
Elongation, %	840	505	305

Strip Adhesion	Untreated Nylon	Zytel 350
kN/m	20	0

Compression Set, %, 72 hrs, 100°C	74
Pendulum Rebound (Z), %, 23°C	47
100°C	59

CR 7

Elastomer: CR/BR Durometer: 67 (Black vs Silica)
Application: Dynamic ply adhesion

Neoprene GN	100	MgO	2
BR 1203	5	Stearic Acid	2
150 m^2/g Silica	40	SRF Black	10/40
65 m^2/g Silica	15	Banbury 2	
DOS	10	Zinc Oxide	5
DPPD 100	2		
SDPA29	1	Specific Gravity	1.40

SRF Black N774	10	40
Plasticizer SC	-	10
MDR Cure Rate, 154°C, T_{50} minutes	6.7	6.9
T_{90} minutes	26	24
MDR Crosslinks, dN-m	28	30
Mooney Scorch, 121°C, T_5 minutes	17	17
Mooney Viscosity, ML_4100	71	57
Tension fatigue ply adhesion (treated tire cord)		
50°C; 6 Hz; tension weight 9N; 0.9 mm stock thickness		
Cycles/mm separation:		
63% Weibull Life	4300	3500
10% Weibull Life	2600	650
35 minute cure, 154°C:		
Durometer	67	73
M300, MPa	4.4	6.4
Tensile, MPa	12	9.3
Elongation, %	720	455
MG Trouser Tear, kN/m	16	9.9
Compression Set, %, 70 hours at 100°C	67.9	76.7
Glass Transition, DMA: 1 Hz; E' storage modulus		
T_g C, Onset	39	45
Finish	26	31

CR 8

Elastomer: CR/BR Durometer: 58 Black
Application: Ply adhesion

Banbury 1		Banbury 2		
Neoprene WRT	100	Zinc Oxide	3	
BR 1203	5	Sulfur	0.5	
150 m^2/g Silica	40	TMTM	1	
FEF N550	25	DOTG	1	
DOS	10			
Magnesium Oxide	2			
Stearic Acid	2			
ODPA	2			
Amide Wax	0.7	Specific Gravity		1.46

Mercaptosilane A189:	0	1
Cure Rate, 154°C, T_{50} minutes	14	15
Mooney Scorch, 121°C, T_5 minutes	30+	30+
Viscosity, ML_4100	63	100
Mill Tack	Good	Fair
35 minute cure, 154°C:		
Durometer	58	60
M300, MPa	5.0	10.8
Tensile, MPa	17	21
Elongation, %	680	535
Stress/Strain Properties, 170 Hours, 121°C:		
Durometer	78	78
Tensile, MPa	17	16
Elongation, %	200	165
MG Trouser Tear, kN/m	23.3	12.8
Ply Adhesion: 0.5 mm. Skim Between 2 RFL Cord Plies		
Static Strip N/13 mm	96	79
Rubber Cover	100%	30%
Tension Fatigue Life:		
Kilocycles/mm Separation	1.9	0.7
Rubber Cover	100%	80%

CR 9

Elastomer: CR/BR Durometer: 57
Application: Heat resistance; Tear strength

Neoprene W	100	Castor Oil Ester	4
BR 1203	3	Naphthenic Oil	8
150 m^2/g Silica	48	TEA	1
Magnesia	4	Zinc Oxide	5
OPDA	1	ETU	0.3
Stearic Acid	1	Specific Gravity	1.41

Mooney Scorch, 121°C, T_5 minutes	14
Mooney Scorch, 138°C, T_5 minutes	7
Viscosity, ML_4100	64
Garvey Extrusion	
Rate, in/min	96
Edge & Surface	10A
Compression Set, %, 3 days, 100°C	72

30 minute cure, 150°C:	Original	72 hrs, 135°C
Hardness	57	68
M300, MPa	2.8	
Tensile, MPa	15.5	16
Elongation, %	880	740
Die C Tear kN/m	57.5	8.5
Trouser Tear, Cut Groove, kN/m		
23°C	35	18.3
70°C	27	10.5

Water Immersion at 100°C	% Volume Change	Hardness
6 Hours	4.7	62
1 day	13.4	68
7 days	13.9	75

CR 10

Elastomer: CR Durometer: 58
Application: Flex life; Heat resistance; Tear strength

Neoprene W	100	Naphthenic Oil	8
150 m^2/g Silica	30	Stearic Acid	2
35 m^2/g Silica	30	Castor Oil Ester	2
Magnesium Oxide	2	Zinc Oxide	4
Octamine	1.5	ETU	0.4
		Specific Gravity	1.41

Cure Rate, 154°C, T_{50} minutes	25
Mooney Scorch, 121°C, T_5 minutes	17
T_{35} minutes	30+
Viscosity, ML_4100	68

30 minute cure, 154°C:	Original	72 hrs, 121°C
Hardness	58	77
M300, MPa	2.3	
Tensile, MPa	14	12
Elongation, %	870	580

Trouser Tear, Grooved, kN/m	20
Compression Set, %, 70 hrs, 100°C	49
PICO Abrasion Index	55
DeMattia Flex, 23°C, kc to 0.6” growth	50

Water Immersion at 100°C, % Volume Increase	
1 day	8
3 days	13
7 days	12

Goodrich Flexometer, 100°C, 22.5%; 1 MPa, 20 minutes	
Static Compression, %	23
Dynamic Compression, %	13
Set, %	16
Heat Build-up, °C	39

CR 11

Elastomer: CR Durometer: 59
Application: Heat resistance; Low HBU

Banbury 1		Banbury 2	
Neoprene WRT	100	Zinc Oxide	4
35 m^2/g Silica	45	PEG 3350	2
Silane A189	1	ETU 75%	0.8
Magnesia	2		
DOS	10		
ODPA	3	Specific Gravity	1.37

Cure Rate, 154°C, T_{50} minutes	8.3
Mooney Scorch, 121°C, T_5 minutes	11.0
Viscosity, ML_4100	47

	23°C	100°C
Durometer	59	58
Pendulum Rebound (Z), %	58.4	68.8

30 minute cure, 155°C:	Original	700 hrs, 100°C	170 hrs, 125°C
M300, MPa	12	-	-
Tensile, MPa	19	18	19
Elongation, %	405	340	305
Durometer	59	66	71

Compression Set, 72 hours, 100°C	28.5%
PICO Abrasion Index	50

Dynamic Properties, 35 minute cure, 155°C:
Goodrich Flexometer 100C; 22.5%; 1 MPa

Permanent Set, %	1.9
Heat Build-Up, °C	10

DMA; 1 Hz, 20% Strain	Original	340 hrs, 100°C
E’ - 20°C	18	32
E’ + 10°C	5.1	6.1
E’ + 6°0C	3.9	4.8
Tan Delta - 20°C	1.02	1.00
Tan Delta + 30°C	0.173	0.151

CR 12

Elastomer: CR/BR Durometer: 61
Application: Fabric adhesion

CR GNA	60	Stearic Acid	2
CR GRT	40	Amide Wax	1
BR 1203	5	PEG 3350	2
150 m^2/g Silica	45	HMMM 963	3
Magnesium Oxide	4	<u>Banbury 2</u>	
Castor Oil Ester	5	Zinc Oxide	5
Aromatic Oil	10	Resorcinol Resin B19	1
		Specific Gravity	1.35

ODR Cure Rate, 154°C, T_{90} minutes	16
Mooney Scorch, 121°C, T_5 minutes	17
135°C, T_5 minutes	10
Mooney Viscosity, ML_4100	57
Strip Peel Adhesion to Untreated Fabrics, kN/m, 30 minute cure, 154°C	
Nylon Press Cure	11
Air Cure	10
Water Immersed 4 days/60°C	9.2
Rayon Air Cure	7.5
Cotton Air Cure	7.5
Polyester (activated) Press Cure	12.5
RFL Nylon Press Cure	16

30 minute cure, 154°C:	<u>Original</u>	<u>170 hrs, 100°C</u>
Durometer	61	71
M300, MPa	4.0	
Tensile, MPa	19	17
Elongation, %	850	550

CG Trouser Tear, kN/m	14
DeMattia Cut Growth, kc to 500%	13
Pendulum Rebound (G-H), %, 23°C	58
100°C	66
-20°C	14
Low Temperature Stiffness (ASTM 1053)	
T5, °C	-40
T10, °C	-43
T100, °C	-45

CR 13

Elastomer: CR/BR Durometer: 62 Black
Application: Aged tear strength

Neoprene GN	100	ODPA	2
BR 1203	5	Stearic Acid	1
150 m^2/g Silica	22	Zinc Oxide	5
HAF N330 Black	23	Magnesia	4
Naphthenic Oil	10		

Mooney Scorch, 121°C, T_5 minutes	30
Viscosity, ML_4 100	63

20 minute cure, 150°C:	Original	72 hrs, 100°C
Hardness	62	76
M300, MPa	5.2	
T_B	17.8	19.2
E_B	720	480
Die C Tear kN/m	50	59
Trouser Tear (Cut Groove)	17.5	9.6

Compression Set, %, 24 hrs, 100°C	73
Yerzley Resilience, %	65

Varsol Immersion, 72 hrs, 12°C	
% Volume Change	40
Hardness	43

CR 14

Elastomer: CR/BR Durometer: 63
Application: CR types G vs. W; Tear strength

Neoprene 100	100	Zinc Oxide	5
BR 1220	5	MgO	2
65 m^2/g Silica	50	Stearic Acid	2
150 m^2/g Silica	20	Amide Wax	1
Naphthenic Oil	15		
ODPA	2	Specific Gravity	1.44

Neoprene Type	GRT	WRT
PEG 3350	-	3
TMETD	-	1
HMT	-	2
MDR Cure Rate, 154°C, T_{50} minutes	8.2	8.1
T_{90} minutes	23	21
Mooney Scorch, 121°C, T_5 minutes	30+	12
Viscosity, ML_4100	32	47
Durometer (10/30 min cure, 154°C), 23°C	63	62
100°C	56	55

Stress/Strain	Original	Aged*	Original	Aged
Durometer	63	80	62	74
M300, MPa	2.7	-	2.4	-
Tensile, MPa	13	11	10	9
Elongation, %	920	585	810	555

*Aged 72 hrs, 100°C

Immersion, 72 hrs	Oil*	Water	Oil*	Water
*ASTM #1	100°C	60°C	100°C	60°C
% Volume Increase	-0.8	7.3	1.0	11.1
Durometer	58	58	55	55
Tensile, MPa	12	12	10	11
Elongation, %	730	815	755	780

MG Trouser Tear, kN/m	29	29
Die C Tear, kN/m	42	29
Compression Set, %, 70 hrs, 100°C	96	82
Pendulum Rebound (Z), %, 23°C	42	42
100°C	51	51
DeMattia Cut Growth, kc to 500%	30	13
Kinetic Friction Coef, Wet Aluminum	1.06	1.23

CR 15

Elastomer: CR/BR Durometer: 64
Application: Abrasion; Rolls; Heat resistance

Neoprene WRT	100	MgO	2
BR 1220	5	Zinc Oxide	5
Ciptane 1	40	Sulfur	0.2
35 m^2/g Silica	20	TMTU	0.3
Naphthenic Oil	10	DTDM	1
Stearic Acid	2	DPG	0.5
ODPA	1	Specific Gravity	1.41

MDR Cure Rate, 155°C, T_{50} minutes	8.0	
T_{90} minutes	25	
Mooney Scorch, 121°C, T_5 minutes	20	
Viscosity, ML_4100	70	
25 minute cure, 155°C:		
Durometer, 23°C	64	
100°C	59	
	Original	700 hrs, 100°C
M300, MPa	7.2	
Tensile, MPa	19	16
Elongation, %	690	310
Tear Strength, kN/m:		
MG Trouser	18	
Die C	50	
ASTM #3 Oil Immersion, 72 hrs:		
Volume Swell, %	102	
Abrasion Indices: PICO	82	
NBS	126	
Compression Set, %, 70 hrs, 100°C	56.3	
Pendulum Rebound (Z), %, 23°C	41	
100°C	58	
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Dynamic Drift %	8.2	
Permanent Set %	14	
Heat Build-up °C	38	

CR 16

Elastomer: CR Durometer: 65 (Steam), 55 (Press)
Application: MRG; Steam vs press curing

Banbury 1		Banbury 2	
Neoprene WRT	100	Zinc Oxide	10
Magnesia	1.5	Curatives	Below
150 m^2/g Silica	25		
Hard Clay	100		
LP Oil	25		
Chlor. Paraffin 40	8		
ODPA	2		
MC Wax	2		
Stearic Acid	2	Specific Gravity	1.50

Curatives:	A	B
Sulfur	0.5	-
DPG	1.5	-
MBTS	1.3	-
ETU 75%	-	1.0
ODR Cure Rate, 154°C, T_{50} minutes	16	16
ODR Crosslinks @ 55minutes	28	25
Mooney Scorch, 121°C, T_5 minutes	30+	30+

Cure 154°C:	Steam	Press	Steam	Press
Minutes	60	45	60	45
Durometer	66	56	64	53
M300, MPa	2.8	2.3	2.7	2.5
Tensile, MPa	7.5	8.5	7.9	9.2
Elongation, %	820	925	800	900
Aged 3 Days, 100°C				
Durometer	87	72	86	72
Tensile, MPa	6.8	10.2	6.6	9.4
Elongation, %	350	665	500	725
% E_B Retained	43	72	63	81
Compression Set, %, 3 Days, 100°C	-	83	-	85
Pendulum Rebound (Z), %, 23°C	-	33	-	42
100°C	-	38	-	53

CR 17

Elastomer: CR/BR Durometer: 65 Black
Application: General MRG, Heat Resistance

Neoprene GNA	75	Octamine	2
Neoprene W	25	Castor Oil Ester	5
BR 1203	3	Aromatic Oil	5
Magnesium Oxide	1.5	Amide Wax	1
150 m^2/g Silica	40	Stearic Acid	2
FEF N550 Black	17	Zinc Oxide	10
DAPD	2	Specific Gravity	1.35

	Original	Remilled**
ODR Cure Rate, 154°C, T_{90} minutes *	14	13
Mooney Scorch, 121°C, T_5 minutes	15	15
T_{35} minutes	>30	>30
Viscosity, $ML_4$100	60	50

*Curve inflection no plateau

**Remilled 5minutes at 40°C after 4 days shelf aging

35 minute cure, 154°C:	Original	70 hrs, 121°C
Hardness	65	83
M300, MPa	4.4	11
Tensile, MPa	17	15
Elongation, %	730	500

Trouser Tear, Grooved kN/m	20

DeMattia Flex, 20°C, kc to 0.6” cut growth	
Original	>100
1 day, 100°C	50

CR 18

Elastomer: CR/BR Durometer: 66
Application: Abrasion Resistance

Neoprene W	100	ETU	0.2
BR 1203	5	Sulfur	0.2
220 m^2/g Silica	40	DTDM	1
Silane A189	1	TMTM	0.5
Magnesia	4	DPG	0.5
ODPA	2	Zinc Oxide	5
Stearic Acid	2	Specific Gravity	1.35

Cure Rate, 150°C, T_{90} minutes	38
Mooney Scorch, 121°C, T_5 minutes	20
Viscosity, ML_4100	110

30 minute cure, 150°C:	Original	72 hrs, 100°C
Hardness	66	72
M300, MPa	11.2	
Tensile	26.2	22.5
Elongation %	700	470

Abrasion Indices:	
PICO	119
NBS	175

Compression Set, %, 3 days, 100°C 40

CR 19

Elastomer: CR/BR Durometer: 66 Black
Application: Age resistance; Hose

Banbury 1		Banbury 2	
Neoprene GRT	100	Zinc Oxide	5
BR 1203	3	ETU 75%	0.75
Magnesia	3		
150 m^2/g Silica	30		
FEF N550 Black	30		
ODPA	2		
LP Oil	10		
Stearic Acid	2	Specific Gravity	1.36

Cure Rate, 154°C, T_{90} minutes	20	
Mooney Scorch, 121°C, T_5 minutes	14	
T_{35} minutes	26	
Viscosity, ML_4100	60	
40 minute cure, 154°C:		
Durometer	66	
M20, MPa	1.0	
M300, MPa	9.1	
Tensile, MPa	14.4	
Elongation, %	415	
Aged at 100°C	70 hrs	300 hrs
Durometer	73	78
Tensile, MPa	14.3	14.0
Elongation, %	375	335
Percent E_B Retained	90	81
50 minute cure, 154°C:		
Pendulum Rebound (Z), %, 23°C	38	
100°C	61	
Compression Set, %, 70 hrs, 100°C	48	
DeMattia Cut Growth, 23°C, kc to 500%	30	

CR 20

Elastomer: CR/NR Durometer: 67
Application: Tear strength

Neoprene GRT	90	Amide Wax	1.5
SMR	10	Stearic Acid	2
150 m^2/g Silica	50	Naphthenic Oil	10
Magnesia	4	Zinc Oxide	5
ODPA	1	Specific Gravity	1.39

Cure Rate, 160°C, T_{90} minutes	10
Mooney Scorch, 121°C, T_5 minutes	23
Viscosity, ML_4100	68

20 minute cure, 160°C:	
Hardness	67
M300, MPa	2.8
Tensile, MPa	13.8
Elongation, %	840

PICO Abrasion Index	52

Tear Strength, lbs/in	23°C	100°C
Die C	52	24
Cut Groove Trouser	21	8.6
Molded Groove Trouser	24	9.8

CR 21

Elastomer: CR/BR Durometer: 67
Application: Zinc adhesion

Neoprene GRT	90	Stearic Acid	1
Neoprene FB	10	Naphthenic Oil	10
BR 1203	1	Resorcinol Resin B19	1
Magnesium Oxide	4	HMMM	3
150 m^2/g Silica	40	Zinc Oxide	5
35 m^2/g Silica	20		
ODPA	2	Specific Gravity	1.39

ODR Cure Rate, 154°C, 60 DN-m	11
Mooney Scorch, 121°C, T_5 minutes	16
Viscosity, $ML_4$100	55

20 minute cure, 154°C:	Original	24 hrs, 121°C
Hardness	67	86
M300, MPa	6.8	
T_B	13.7	13.2
E_B	700	240

Adhesion to Galvanized Wire, .062” solid (30 minute cure, 154°C)

Pull-Out, kN/m	
Original	27
Aged 8 hrs, 121°C	28
Rubber Cover, %	75

CR 22

Elastomer: CR	Durometer: 70
Application: Non-ETU cure system	

Neoprene W	100	Stearic Acid	2
150 m^2/g Silica	30	DEG	3
35 m^2/g Silica	30	Zinc Oxide	4
Magnesium Oxide	2	TMETD	1.5
ODPA	1.5	HMT/SBR 50%	1.5
Naphthenic Oil	8		
Castor Oil Ester	2	Specific Gravity	1.39

ODR Cure Rate, 154°C, T_{90} minutes	17
Mooney Scorch , 121°C, T_5 minutes	12
T_{35} minutes	10
Viscosity, ML_4100	52

30 minutes, 154°C:	Original	170 hrs, 121°C
Hardness	68	89
M300, MPa	2.1	
Tensile	11	10
Elongation, %	770	300

Trouser Tear, Grooved, kN/m	25

Compression Set, 70 hrs, 100°C, %	
40 minutes, 154°C	50
60 minutes, 154°C	50

Goodrich Flexometer; 100°C; 22.5%; 1 MPa	
Hardness	72
Set, %	14
Heat Build-up, °C	46

Water Immersion, 100°C, % Volume Increase	
1 day	9.7
3 days	5.8
7 days	4.6

CR 23

Elastomer: CR/BR Durometer: 70 (Black)
Application: Tear Strength

Neoprene W	100	Naphthenic Oil	5		
BR 1203	3	Zinc Oxide	5		
150 m^2/g Silica	26	Sulfur	1		
HAF N326 Black	30	DPG	0.5		
Magnesia	4	TMTM	0.2		
ODPA	1	ETU	0.2		
Stearic Acid	3				
Castor Oil Ester	3	Specific Gravity		1.42	

Mooney Scorch, T_5 minutes, 121°C		14
	138°C	6
Viscosity, ML_4100		77

20 minute cure, 150°C	Original	70 hrs, 135°C
Hardness	70	84
M300, MPa	8.6	
Tensile	17.9	16.5
Elongation, %	500	280
Die C, Tear, kN/m	43.5	45.4
Trouser Tear, Cut Groove, kN/m		
23°C	19.2	7
70°C	8.8	4.5
Compression Set, %, 3 days, 100°C	80	

CR 24

Elastomer: CR/BR
Durometer: 70
Application: Low Set

Banbury 1		Banbury 2	
CR WRT	95	Zinc Oxide	4
BR 1203	5	PEG 3350	4
Magnesia	2	ETU	0.4
Ciptane 1	25		
35 m^2/g Silica	20		
Hard Clay	60		
ODPA	1		
Stearic Acid	2		
Naphthenic Oil	8		
Castor Oil Ester	3		
Polyethylene LMW	3	Specific Gravity	1.58

Cure Rate, 154°C (Slope Max), minutes	21
Mooney Scorch, 121°C, T_5 minutes	22
Mooney Viscosity, ML_4100	67

30 minutes cure 154°C:	Original	72 hrs, 121°C
Durometer	70	79
M300, MPa	6.6	
Tensile, MPa	9.6	8.6
Elongation, %	530	260

Compression Set, %, 72 hrs, 100°C	26
22 hrs, 70°C	10
DeMattia Cut Growth, kc to 500%	
23°C	75
100°C	35

Water Immersion 100°C	% Volume Increase
1 day	11
7 days	21
14 days	16

Garvey Extrusion, Edge-Surface	10A

CR 25

Elastomer: CR/BR Durometer: 77 (Black)
Application: High modulus; V-Belt; Milling effects

Neoprene GNA	75	Aromatic Oil	5
Neoprene W	25	Castor Oil Ester	5
BR 1203	3	Stearic Acid	3
Magnesium Oxide	1.5	Resorcinol Resin B19	1
150 m^2/g Silica	40	Amide Wax	1
FEF N550 Black	17	Zinc Oxide	10
ODPA	2	HMMM	5
ADPA	2	(Cyrez 9630)	
Chopped Rayon	15	Specific Gravity	1.44

ODR Cure Rate, 154°C, T_{90} minutes	13	
Mooney Scorch, 121°C, T_5 minutes	11	
T_{35} minutes	28	
Viscosity, ML_4100	63	
30 minute cure, 154°C:		
Original	With Mill Grain	Across Mill Grain
Hardness	77	77
M20, MPa	1.7	0.6
M100, MPa	7.3	2.3
M300, MPa	-	6.2
Tensile, MPa	8.0	8.2
Elongation, %	220	450
Aged 3 days, 121°C		
Hardness	87	
Tensile, MPa	12	10
Elongation, %	90	180
Trouser Tear, Grooved kN/m	11	12
PICO Abrasion Index	59	78
DeMattia Flex, 20°C		
KC to 0.6” Cut Length	2	4
Goodrich Flexometer; 100°C; 22.5%; 1 MPa		
Hardness	75	
Static Compression	9.9	11.3
Dynamic Compression	2.0	1.6
Drift	11.3	
Set	Blow Out	11.4
Heat Build-Up, °C		32

CR 26

Elastomer: CR Durometer: 80 Black
Application: Hose; Brass adhesion

Neoprene W	100	Zinc Oxide	5
Magnesium Oxide	4	DOTG	1
35 m^2/g Silica	50	TMTM	1
Hard Clay	20	Sulfur	1
GPF N660 Black	40	HMMM	5
Naphthenic Oil	18		
Microcrystalline Wax	2		
Stearic Acid	2		
Resorcinol Resin B19S	2		
Diaryl Phenylenediamine	1.5	Specific Gravity	1.50

ODR Cure Rate, 154°C, T_{90} minutes	15
Mooney Scorch, 121°C, T_5 minutes	26
Viscosity, ML_4100	83
ODR Minimum	7.4
30 minute cure, 154°C:	
Hardness	79
M100, MPa	4.9
Tensile, MPa	11.2
Elongation, %	290
Compression Set, %, 70 hrs, 100°C	76
Brass Strip Adhesion kN/m	
25 minutes, 154°C	5.2

CR 27

Elastomer: CR/BR Durometer: 85 Black
Application: General MRG

Neoprene S-3 (GRT)	72	Stearic Acid	2
BR 1203	8	MgO	4
HYCAR 1052	20	Aromatic Oil	7
Sulfur, Insoluble	4	DOP	5
BET 150 Silica	55	Flexricin 9	5
MT N990 Black	25	Zinc Oxide	12
Calcium Oxide, 80%	10		
Octamine	1	Specific Gravity	1.43

ODR Cure Rate, 154°C, T_{90} minutes	20
Mooney Scorch, 121°C, T_5 minutes	16
Viscosity, $ML_4$100	59

30 minute cure, 154°C:	Original	24 hrs, 121°C
Hardness	85	90
M100, MPa	4.8	
Tensile	11	9
Elongation, %	250	100

Abrasion: PICO	85
NBS	65

DeMattia Flex, 100°C, unpunched 4 KC

Goodrich Flexometer 100°C, 20%, 1 MPa, 20 minutes

Static Compression, %	6.8
Set, %	2.2
Heat Build-Up, °C	18

Compression – Deflection, 10 cycles, lbs.*

Deflection: 5%	150
10%	300
20%	450

*On compression set button

CHAPTER 7

COMPOUNDING PRECIPITATED SILICA IN NITRILE

7.1 INTRODUCTION

The highly polar nature of the acrylonitrile-butadiene polymer chains makes this elastomer particularly suitable for reinforcement by precipitated silica. Silica found an early and substantial market in non-black nitrile compounds designed for hose, conveyor belt, oil resistant soling, and mechanical goods applications. Driving factors were the usual silica contributions of heat resistance, tear strength, adhesion, and color. In some cases, accelerated aging tests indicated that silica compounds were capable of performing at service temperatures significantly above those suitable for carbon black compounds.

7.2 SILICA AND CARBON BLACK

Comparisons of precipitated silicas and carbon blacks in nitrile compounds reveal the same differences found in other elastomers. Silica reinforcement, particularly by the higher surface area types, provides improved aging resistance, tear strength and adhesion to metals and fabrics. Semi-reinforcing silicas and blacks, frequently used in nitrile compounds, show the same relationship minus the tear strength feature, which is almost exclusively the province of high surface area fillers. Table 7.1 describes the processing and vulcanizate properties of silica and black compounds based on semi-reinforcing fillers, a 65 m^2/g N_2SA silica and an SRF/FEF carbon black blend. In the third compound silica has been modified with 0.5 phr of mercaptosilane. Among the few significant deviations from black to silica are higher silica viscosity, lower silica M300 modulus and tensile, higher silica aged tensile, and a major silica advantage in adhesion to metal and RFL nylon. Introduction of silane coupling eliminates the stress/strain differences without any change in durometer and only a slight degrading effect on adhesion. Probably the most interesting point here is the possibility of obtaining moderately good adhesion to cemented steel without the use of a second adhesive coat over the primer. The superiority of the silica influenced bond also appears in the 100°C peel strength values found in bonding to RFL treated nylon.

Table 7.1 Silica and SRF Black in NBR: An Equal Hardness Comparison

SRF N770 Black	40	-	-
FEF N550 Black	20	-	-
65 m^2/g N_2SA Silica	-	65	65
Mercaptosilane, MPTS	-	-	0.5
ODR cure rate, 160°C, T_{90} minutes	9.0	11.3	10.3
Mooney scorch, 130°C, T_5 minutes	14.4	10.0	7.4
Mooney viscosity, ML_4100	50	74	74
ODR minimum, dN-m	10	10.4	9.3
Stress/Strain, original (15 min cure/160°C)			
Durometer hardness	70	70	70
M100 modulus, MPa	5.2	2.4	4.9
M300 modulus, MPa	18	6.5	16
Tensile, MPa	19	11	18
Elongation, %	320	430	320
Stress/Strain, 70 hrs, 150°C			
Durometer hardness	72	64	64
Tensile, MPa	4.9	8.4	9.2
Elongation, %	80	100	100
Compression set, 70 hours at 100°C, %	13	16	12
Strip Adhesion at 100°C to Cemented Steel, interior bond, kN/m:			
Prime coat only (Chemlok 205)	0.4	2.5	1.9
Second coat (Chemlock 220)	>4.9	>4.8	>4.8
Strip Adhesion at 100°C to RFL nylon, kN/m	0.9	>2.2	1.5
Adhesion to brass	No	No	No
Other ingredients: NBR BJLT-100; filler-60/65; DOP-10; TMQ-2: Stearic acid-2; ZnO-5; Sulfur-0.4; DTDM-1; TBBS-1			

When we turn from a complete to a partial black replacement, the silica advantages are somewhat curtailed. A case in point is described in Table 7.2 where 25 phr of the total SRF black are replaced by 220 m^2/g N_2SA silica, and in Figures 7.1, 7.2, and 7.3. (These compounds are part of a detailed contour curve study of silica and black contents). The third compound in Table 7.2 contains a five fold increase in DPTH content, which turns out to be far in excess of that required to match the crosslink density of the black control, but necessary to reach a comparable level of abrasion resistance. Further comment on DPTH appears in the acceleration section. The major property changes effected by silica are noted in the contour graphs for tear strength, extrusion swell, and aged elongation. In respect to aging (70 hours at 150°C, Figure 7.3), an optimum silica content is evident at 15-20 phr, but the major influence is total filler content. Low filler contents favor elongation retention during accelerated aging.

Table 7.2 Partial Replacement of SRF Black by Silica at Equal Hardness

SRF N774 Black	95	75	75
220 m^2/g N_2SA Silica	-	20	20
Dioctyl phthalate	10	15	15
DPTH	0.2	0.2	1.0
TBBS	2	2	1
MDR cure rate, T_{90} minutes	17	22	7.4
MDR crosslink, MH-ML, dN-m	30	27	49
Mooney scorch, 121°C, T_5 minutes	23	>30	10
Mooney Viscosity, ML_4100	76	87	71
150°C cure, minutes	25	25	15
Durometer hardness: 23°C	78	78	79
100°C	62	60	70
Stress/Strain, original			
M300 modulus, MPa	12	8.4	14
Tensile, MPa	15	14	16
Elongation, %	560	655	450
Stress/Strain, 700 hrs, 115°C			
Durometer hardness	97	95	98
Tensile, MPa	18	12	10
Elongation, %	55	20	5
Stress/Strain, 70 hrs, 150°C			
Durometer hardness	96	97	97
Tensile, MPa	9.5	10	7.8
Elongation, %	15	20	10
MG Trouser tear, kN/m	18	26	14
DIN Abrasion loss, mg	155	247	186
Pendulum rebound, %: 23°C	12	14	13
100°C	46	31	50
Goodrich flexometer heat build-up, °C	blow	blow	39
DMA Dynamic modulus at 60°C			
E”, MPa	1.04	1.45	1.25
E’, MPa	4.1	5.0	6.4
Tangent delta	0.255	0.290	0.195
Other ingredients: NBR386B-100; 25C resin-8; ZMTI-2; ODPA-2; Stearic acid.-1; ZnO-3; PEG3360-1; Sulfur-0.5; DTDM-1; TBBS-2/1; DPTH-0.1/0.2/1			

Extrusion swell reduction with silica (Figure 7.1) is a reminder that all silica, particularly lower surface area grades, produces smoother extruded and calendered surfaces than those of comparable hardness black compounds. In this study, the traditional tear strength advantage of silica is somewhat muted, and tends to disappear at increased DPTH concentrations (Figure 7.2).

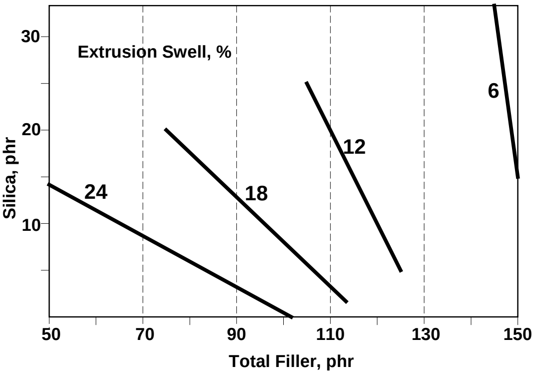

Figure 7.1 Effect of Silica Filler Fraction on Extrusion Swell

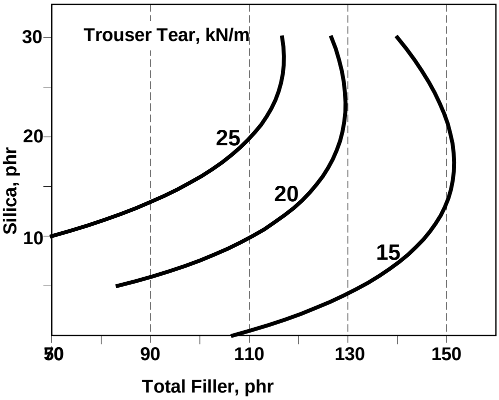

Figure 7.2 Effect of Silica Filler Fraction on Trouser Tear

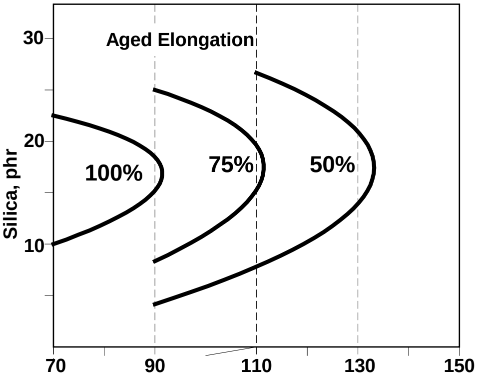

Figure 7.3 Effect of Silica Filler Fraction on Aged Elongation

7.3 SILICA SURFACE AREA

A comparison of silica surface area effects in a medium ACN NBR with sulfur acceleration is made in Table 7.3. The surface area values of 35, 65 and 150 m^2/g correspond to average primary particle sizes of 75, 45 and 19 nanometers. In contrast to reinforcement effects in other elastomers, the 65 m^2/g silica is not very far removed from the 150 m^2/g grade in respect to modulus and abrasion resistance. At the same time, it provides definite advantages in lower viscosity and compression set with somewhat higher resilience. Definitive descriptions of compounds based on this 65 m^2/g silica appear in several of the Formulary compounds, in particular NBR 12.

Table 7.3 Silica Surface Area Effects in NBR

Silica N_2SA, m^2/g	150	65	35
ODR cure rate, 150°C, MS 135	16	13	7.0
Mooney viscosity, MS 135	55	27	27
Durometer hardness	78	70	64
M300modulus, MPa	8.3	8.3	4.8
Tensile, MPa	24	17	9.6
Elongation, %	600	560	500
Cut Groove Trouser tear,kN/m	16	7.0	5.0
PICO Abrasion index	90	88	35
NBS Abrasion index	110	100	50
Compression set, 70 hrs, 100°C, %	70	35	44
DeMattia cut growth, kc to 500%	4	1	0.5
Other ingredients: NBR 1042-100; silica-60; DOP-10; Stearic acid-1; ZnO-5; Sulfur-1.5;TMTD-0.5; MBTS-1.5			

The surface area comparison in Table 7.3 includes only one fully reinforcing silica grade at 150 m^2/g N_2SA,. For silicas in the 150 to 250 m^2/g range, little change in properties is seen. However, when the evaluation is made in zinc-free system compounds, the hidden reinforcement potential of the higher surface area grades appears, particularly in respect to rising abrasion index, M300 modulus, and slightly increased dynamic modulus at 200°C, as illustrated in Table 7.3a. Dynamic storage modulus change with temperature is plotted in Figure 7.4 where higher surface area leads to increased stiffness at 200°C.

Fumed silica has successfully replaced the 150 m^2/g precipitated grade in some NBR compounds for oil field operations. Improved tear strength is the main advantage. When a precipitated grade with surface area comparable to that of the fumed silica is involved, the balance of tear strength and other property comparisons changes.

Table 7.3a Silica Surface Area Effects in Zinc-Free NBR

Silica N_2SA, m^2/g	150	215	250
MDR cure rate 150°C, T_{90} minutes	9.4	+	+
MDR crosslinks, MH-ML dN-m: 10 min	39	32	30
40 min	43	46	47
Compression set, 70 hrs, 100°C, %	82	82	85
Mooney scorch 121°C, T_5 minutes	14	22	18
Mooney viscosity, ML_4100	74	84	117
Stress/Strain, original			
M300 modulus,MPa	8.7	10.6	11.3
Tensile, MPa	27	28	31
Elongation, %	585	540	560
Stress/Strain, 700 hrs, 105°C			
Durometer hardness	90	92	92
Tensile, MPa	19	21	20
Elongation, %	140	135	125
MG Trouser tear, kN/m: 23°C	18	15	16
125°C	2.3	1.8	2.1
PICO abrasion index	85	97	119
Pendulum rebound (Z), %: 23°C	32	32	33
100°C	58	60	60
DMA dynamic modulus: 1 Hz; 20%			
E', MPa 30°C	27	28	32
100°C	19	21	23
200°C	13	15	16
E" MPa 30°C	3.1	2.9	3.7
100°C	1.5	1.4	1.6
200°C	0.5	0.9	1.0
Goodrich flexometer: 100°C; 22.5%; 1 MPa			
Static compression, %	9.6	7.5	5.8
Dynamic Compression, %	1.7	-0.3	-2.6
Heat build-up, °C	blow-out	-	-

Ingredients: NBR 685B-100, silica-50; DOS-10; CI P25-8; TMQ-1; ZnO-1; HMT-2; TBBS-2; DPTH-1.5

An equal hardness and equal viscosity comparison of fumed and precipitated silica appears in Table 7.4. In order to obtain hardness and viscosity equality the fumed silica content has been reduced to 35 phr. However, such a reduction (8 phr, dry silica basis) does affect the dynamic properties involved in both flexometer and DMA tests. An uncontested advantage for fumed silica in this study is seen in its superior elongation retained after aging at 115°C.

Table 7.4 Fumed, Precipitated and Silanized Silica in Zinc-free NBR

Cabosil M7 (2.9% water)	35		-		-	
Minusil 10 (0.1% water)	10		-		-	
Hi-Sil 190 (7.9% water)	-		45		-	
Ciptane I (8.0% water)	-		-		47	
MDR cure rate 150°C, T$_{50}$ min.	10		5.7		2.5	
T$_{90}$ min.	44		39		3.2	
MDR Xlinks, dN-m, MH-ML	39		35		30	
Compr. set, %, 70 hrs, 100°C	96		96		88	
Mooney scorch 121°C, T$_5$ min.	30		26		11	
Mooney viscosity, ML$_4$100	78		80		53	
Durometer hardness: 23°C	74		75		75	
100°C	69		70		70	
PICO abrasion index	56		67		84	
MG Trouser tear, kN/m	23		34		12	
Die C tear, kNm	45		44		45	
Stress/Strain, 150°C cure, min.	20		15		10	
Original :						
M20 modulus, MPa	1.2		1.2		1.2	
M300 modulus, MPa	4.8		4.2		10	
Tensile, MPa	25		27		27	
Elongation, %	665		775		565	
700 hrs, 115°C (oven):						
Durometer	90		90		90	
Tensile,MPa	17		14		15	
Elongation, %	185		80		105	
70 hrs, 140°C (reflux):						
Durometer	88		88		86	
Tensile, MPa	6.0		5.8		7.5	
Elongation, %	55		60		80	
Pendulum rebound (Z), %, 23°C	33		34		30	
100°C	56		56		57	
Goodrich Flexometer: 100°C; 22.5%; 1 MPa						
Static compression, %	15		17		14	
Dynamic compression, %	7.6		9.0		4.3	
Heat build-up, ^{o}	47		40		34	
DMA dyn mod; 1 Hz, 20%, °C	23°	200°	23°	200°	23°	200°
E', MPa	17	6.3	20	9.7	23	8.7
E" MPa	2.3	0.8	2.9	0.7	3.0	0.9
Tangent delta	0.132	0.101	0.146	0.073	0.129	0.108

Other ingredients: NBR 685B-100; DOS-10; C.I.P25-8; TMQ-1; ZnO-1; Sulfur-1.5; TBBS 2; DPTH-1; HMT-2

Unfortunately this does not occur after the 70 hour period at 140°C. The silane treated silica compound here shows a slight positive margin in aging at 140°C and abrasion, with the usual sacrifice in trouser tear strength. The relatively high 200°C dynamic modulus of the high surface area silica compound suggests a recommendation for use in down hole operations.

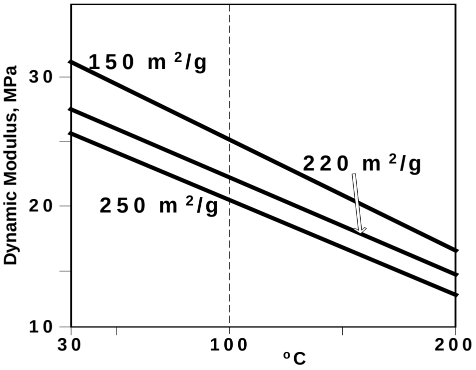

Figure 7.4 Silica Surface Area vs Dynamic Modulus and Temperature

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7.4 NBR/PVC BLENDS

Polymer blends of NBR and PVC involve most of the compounding techniques described below. The principal advantage of these blends is a resistance to ozone cracking not available from NBR alone. This improvement considerably broadens the uses of silica in NBR to include colored hose cover applications for outdoor exposure and long storage periods. Formulary examples are compounds NBR 5, 12, 13, 28, 32, and 35.

7.5 ACCELERATION - SULFUR CONTENT

The difference between normal sulfur (1.5-2.5 phr) and low sulfur (0.2-0.5 phr) nitrile compounds resides mainly in heat resistance characteristics. Although compression set can be expected to fall at low sulfur, this effect is often obscured by the set reducing action of ultra accelerators in normal sulfur compounds. Sulfur content effects in a formula based on a highly plasticized NBR reinforced with a 150 m^2/g silica and accelerated with ZMBT and MBTS are shown in Table 7.5. Although the aging period here is very mild, the improved stability of the 0.2 sulfur compound is apparent. A further look at a narrow range of low sulfur contents shows the influence on set values as seen in Table 7.5a. The interesting point here is that an indefinite lowering of sulfur content will not produce the lowest set values;

the optimum appears to fall in the 0.3 to 0.45 range.

Table 7.5 Sulfur Content Effect

Sulfur	2.5	1.5	0.2
TMTM	1.2	1.2	-
TMTD	-	-	3
ODR cure rate 150°C, T_{90} minutes	10	12	11
ODR crosslinks, dN-m	71	48	44
Elongation, %:			
Original	480	680	760
Aged 100 hrs, 100°C	300	550	680
Compression set, 70 hrs, 100°C, %	55	66	60

Table 7.5a Sulfur Content Effect on Compression Set

Sulfur content, phr	0.15	0.3	0.45
Compression set, %:			
70 hrs, 100°C	31	21	21
70 hrs, 121°C	32	27	23

When a mercaptosilane coupling agent is present, the sulfur optimum remains in the same range. However, percent retained elongation after aging is relatively unchanged over the low sulfur range. Beginning with Formulary compounds NBR 3, 6 and 8, there are a number of low sulfur recommendations. Compound NBR 27, based on a high ACN polymer, offers the ultimate in heat resistance.

7.6 ACCELERATORS

Accelerator combinations for silica reinforced NBR compounds contain representatives from three classes: 1) Delayed action, such as MBTS and the sulfenamides; 2) Ultra fast, such as thiurams and dithiocarbamates; 3) Sulfur donors with no accelerating action such as DTDM and MDB. The delayed action types appear in both normal and low sulfur systems. The ultra fast group includes sulfur donors, but their major function, in addition to speed, is the production of mono and disulfide crosslinks, which are required for low heat build-up and low compression set properties. Among the thiurams, tetrabutylthiuramdisulfide (TBTD versus TMTD) produces an increase in cure rate and state as well as lower set, with no change in scorch safety. The sulfur donor accelerators offer no accelerating action but their addition may, in some cases, improve scorch safety. Their main function is to supply single sulfurs for crosslinking in low sulfur systems. Higher amounts of both delayed action and sulfur donors improve scorch safety.

The two level trend line graphs of Figures 7.5a through 7.5e illustrate the relative effectiveness of DTDM and two thiurams (also donors). Scorch safety considerations indicate that blends of these materials will be necessary to attain compounds suitable for production. Formulary examples of such blends include compounds NBR 6, 9, 14, 20, 34 (zinc-free), 36 and 38. Although low sulfur content is a primary source of heat resistance, this property has been found to improve in direct proportion to the total concentration of accelerators.

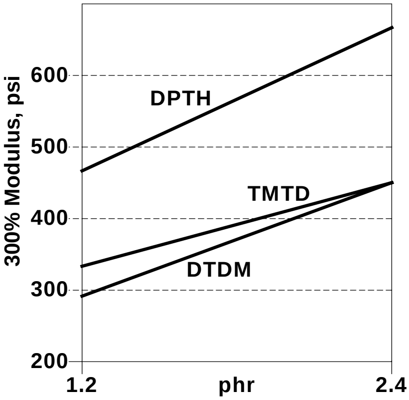


Figure 7.5a Effect of Accelerators on Modulus

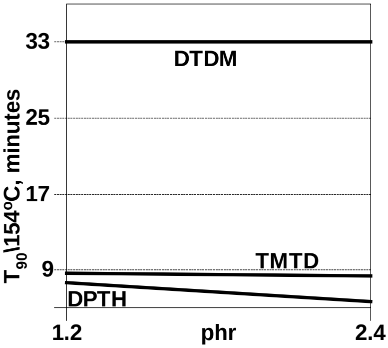


Figure 7.5b Effect of Accelerators on ODR Cure

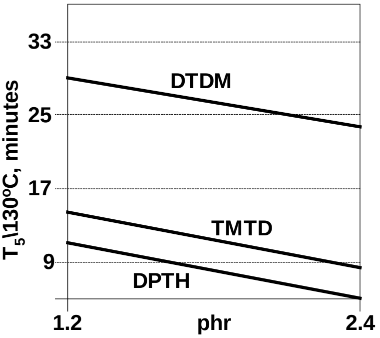


Figure 7.5c Effect of Accelerators on Mooney Scorch

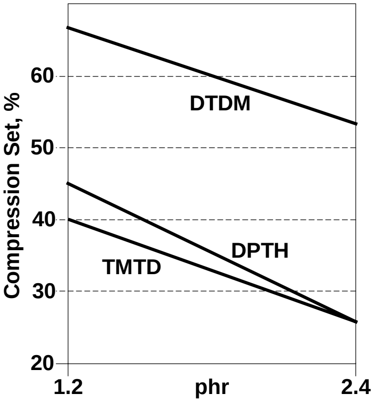


Figure 7.5d Effect of Accelerators on Compression Set

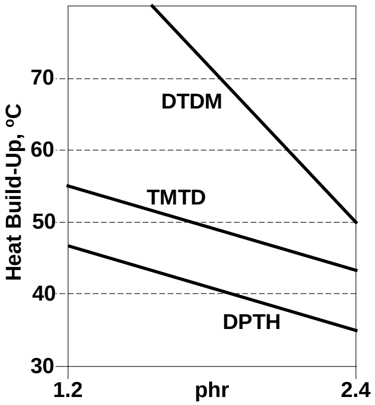


Figure 7.5e Effect of Accelerators on Flexometer Heat Build-up

7.7 ACTIVATORS

The term activator is used here to apply to additives, silanes excepted, which have been shown to alter processing, curing and vulcanizate properties. In silica reinforced NBR these include zinc oxide, magnesium oxide, stearic acid, glycols, resorcinol and melamine bonding agents. At one time, cadmium oxide was included in this list, but toxicity problems have all but eliminated its use. The facts that many of these materials interact, and their efficiency varies with sulfur content, silica type and ACN content, result in considerable variability in their influence on compound properties.

A two level study among triethanolamine (TEA), polyethylene glycol (PEG) and magnesia produced the trend line graphs in Figures 7.6a through 7.6f. Mixed responses are seen for 300% modulus and aged elongation, where PEG influence is strongest in producing higher M300 and elongation values. TEA has the opposite effect on modulus (reduction), and magnesia on aging. The zero point in these graphs refers to a control compound which contains no activator except zinc oxide. Reference to this point makes it clear that all activators have a positive effect in reducing set and original elongation and improving age resistance. PICO abrasion index suffers in all cases. This loss can be explained in terms of interference with silica-polymer bonding, particularly by TEA. Complete data for these compounds are found in Table 7.6. A comparison of magnesia to PEG at equal hardness is given in Formulary compound, NBR 23. Here and in Figure 7.6f the pre-eminent magnesia effect is viscosity reduction, due, evidently, to the devastating influence of magnesia on the silica hydrogen bonded network. Loss in 300% modulus and abrasion index are also characteristic of magnesia addition, both related to interference with silica-polymer bonding.

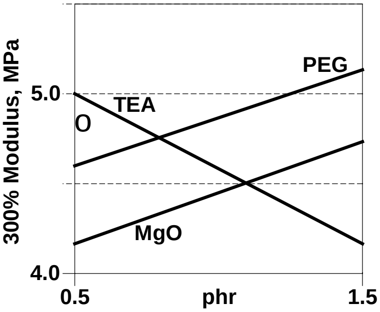


Figure 7.6a Effect of Activators on Modulus

Table 7.6 NBR Activators: TEA, PEG, MgO

TEA	0.5	1.5	-	-	-	-	-
PEG 3350	-	-	0.5	1.5	-	-	-
Magnesia	-	-	-	-	1.5	4.5	-
ORD cure rate, 154°C, T_{90} min							
Original	8.5	6.5	8.0	8.5	7.0	6.5	8.5
Re-milled@ 60°C	8.5	7.0	9.5	9.0	8.5	6.5	10
Mooney scorch, 130°C T_5 min							
Original	17	14	18	19	13	9	18
Re-milled	20	17	23	23	21	22	23
Mooney viscosity, ML_4100							
Original	96	86	100	106	63	67	102
Re-milled	77	60	74	87	44	46	78
Durometer hardness, avg	75	76	75	75	72	72	77
DeMattia cut growth, kc to 500%	40	4	38	9	18	14	100
Monsanto flex fatigue, kc	115	45	130	95	125	105	250
Trouser tear, cut groove, kN/m	14	7.8	15	11	12	14	16
Goodrich flexometer: 100°C; 17.5%; 1 MPa							
Permanent set, %	12	6.5	13	7.1	11	8.0	18
Heat build-up, °C	47	37	49	37	44	41	50
Water immersion, 100°C, % volume change							
24 hours	17	17	22	21	14	12	20
168 hours	12	12	14	16	11	10	13
Durometer, 168 hours	71	72	73	70	80	85	69

Other ingredients: Banbury 1:NBR N612-100; 150 m^2/g N_2SA silica-35;
65 m^2/g N_2SA silica-35; DOP-10; ODPA-2; Stearic acid-2
Banbury 2: Sulfur-1.5; MBS-1.5; TETD-0.4; ZnO-5

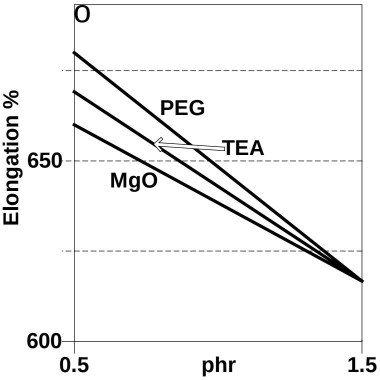


Figure 7.6b Effect of Activators on Elongation

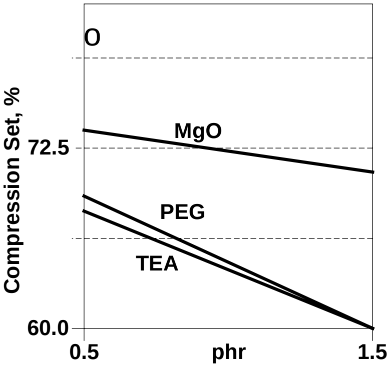


Figure 7.6c Effect of Activators on Compression Set

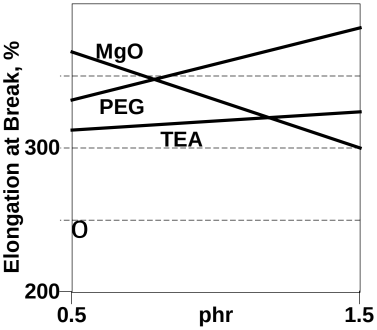


Figure 7.6d Effect of Activators on Aged Elongation

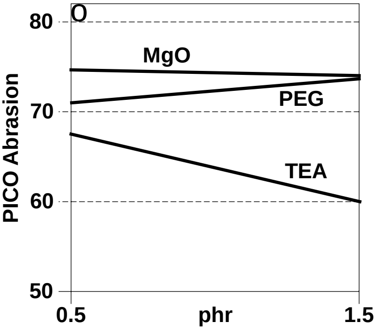


Figure 7.6e Effect of Activators on Abrasion

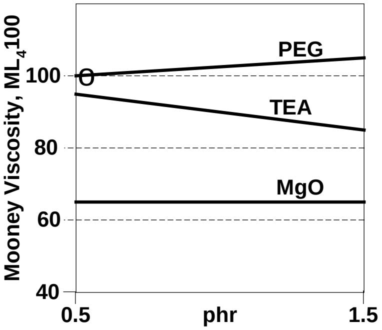


Figure 7.6f Effect of Activators on Mooney Viscosity

As noted in Figure 7.6c, triethanolamine is most effective in reducing compression set. In this respect it surpasses mercaptosilane MPTS (Table 7.7, NBR with sulfur donor cure and 50 phr 150 m^2/g N_2SA silica).

Table 7.7 Compression Set: TEA vs MPTS

	TEA	MPTS
Activator Content, phr	2	1
ODR cure rate, 165°C, T_{90} minutes	6.0	4.5
Mooney viscosity, ML_4100	64	53
Compression set, %: 70 hrs, 100°C	30	37
70 hrs, 150°C	43	52

The role of magnesia in viscosity reduction reflects its ability to dissipate the hydrogen bonded silica network. However, in a cured compound, magnesia interaction with silica shows a different face. The water immersion data in Table 7.6 indicate that the magnesia compounds are unique in producing a marked hardness increase. Since volume swell values are no higher than for the other activators, it can be inferred that magnesia is an integral part of the hydrogen bonded silica network here. Evidence of this same phenomenon in neoprene can be seen in the hardness data in Table 6.12 where the durometer increase at high silica water contents is a significant 10 points. In the early days of neoprene use in filter press gaskets, compounds reinforced with calcium silicate showed the same increased durometer behavior,

Other property trends in this study are evidence of improved crosslink density and more mono-sulfide crosslinks, rather than changes in filler-polymer or silica structure modifications. For example, at the higher activator levels, cut growth, trouser tear and flex fatigue resistance are all lost, but flexometer set and heat build-up improve.

Stearic acid is generally present in its role as zinc oxide activator (solubilizer). Higher than normal amounts of stearic acid are found to improve the water resistance of SBR compounds. This is not the case in NBR, but other effects at 6 and 10 phr, in Table 7.8, are worth noting. Although crosslinking data are not available , it can safely be assumed that these changes are the result of increased crosslink density with higher mono-sufide content.

Table 7.8 Effects of Stearic Acid Content in NBR

Stearic acid, phr	2	6	10
Mooney viscosity, ML_4100	64	40	50
ODR cure rate, 154°C T_{90} minutes	16	10	9
Durometer Hardness	55	59	62
Compression set, 70 hrs, 100°C,%	40	35	36

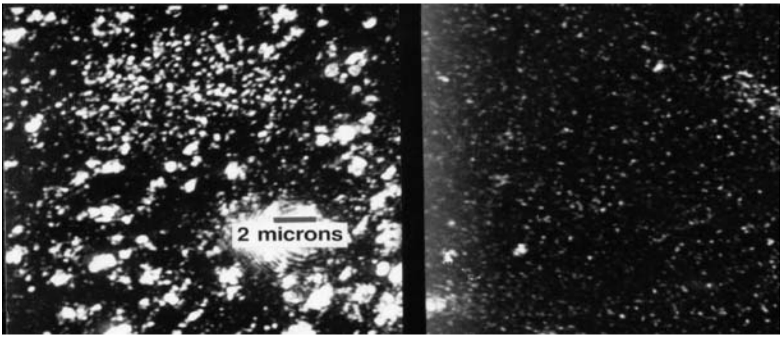
Bonding resin systems (HRH) which comprise the reaction products of resorcinol resins and hexamethoxymethylmelamine generally provide increased M300 modulus and reduced viscosity, in addition their bonding role.

7.8 SILANE COUPLING

Mercaptosilane coupling of silicas in NBR generally produces the same dramatic changes as seen in other elastomers. An interesting insight of the extent of silica surface modification by mercaptosilane is seen in the Figure 7.7 5000X laser scan micrograph of two silica reinforced compounds, with and without silane coupling. In these two views the prominent white particles are unreacted zinc oxide. Without silane, the silica silanols are free to remove soluble zinc, which has almost disappeared from the view on the right. With silane modification, the silanols have disappeared and the unreacted zinc oxide remains in full view. The processing and physical property effects of this manipulation of zinc are described in Formulary compound NBR 9.

Table 7.1 shows the effects of a relatively small silane addition (0.5%). The major benefits here are large improvements in modulus and tensile, a reduction in compression set and no change in hardness. These property modifications, together with the usual improvements in abrasion resistance and heat build-up, can vary considerably with various silicas, NBR elastomers and silane concentrations.

Compound viscosity is generally reduced significantly by mercaptosilane. Modification of the silica silanol surface by the silane alkoxy groups partially eliminates the hydrogen bonded silica-water network and its production of high compound viscosities. Elimination of the normal 6% free water from a silica has much the same effect on viscosity, and by the same mechanism of network reduction. In Formulary compound NBR 9 the silane effect is based on a concentration of 1 phr for 60 phr silica, with a sulfur donor cure system. Other Formulary examples include NBR 3, 6, 8, 10, 12, 14, 20, 24 and 31. Ciptane, the silane pre-treated form of silica, appears in NBR 7, 16, 27, 29, 37, 38, and 40. On an equal silane basis, Ciptane in NBR is less effective than separate silane addition in improving abrasion resistance.



With mercaptosilane Without mercaptosilane

Figure 7.7 Effect of Mercaptosilane on Silica-ZnO Reaction
5000X Laser Scan of NBR Compounds

When several silica grades, with and without silane treatment, are ranked in a "viscoelastic series" in order of increasing elongation (decreasing elasticity or rebound), relationships among surface area, coupling and individual properties become apparent. In Table 7.9 several silicas, including a fumed variety, are listed according to increasing elongation. Trouser tear strength ranking exactly follows elongation, but low heat build-up and compression set show an almost complete reversal from tear and elongation, as does pendulum rebound at both room temperature and 100°C. These property reversals illustrate the compounding futility of attempting to combine tear strength or high elongation with good dynamic and set properties. Surface area, as well as silane, determines property rank, but silane coupling places these silicas in the elastic part of the viscoelastic spectrum.

The viscoelastic rankings in this series also afford a qualitative evaluation of silane coupling effects with a 150 m^2/g silica. In this case the significant reductions in elongation and trouser tear strength with silane coupling are offset by equally significant reductions in heat build-up and compression set and increased resilience. Since a viscoelastic analysis reflects crosslinking rather than filler-polymer effects, abrasion and hardness do not fit well in the Table 7.9 picture. However, silane coupling always produces enhanced abrasion resistance [5].

Table 7.9 Surface Area and Silane Coupling Effects in a Viscoelastic Series

	Viscoelastic Rank				
	Trouser	**Low**	**Low**	**High Rebound**	
Silica*	**Tear**	**HBU**	**Set**	100°C	23°C
65 m^2/g silica + silane	6	1	1	1	1
150 m^2/g silica + silane	5	2	2	2	3
185 m^2/g silica + silane	3	4	3	4	4
190 m^2/g fumed silica + silane	3	3	4	3	2
150 m^2/g silica	2	5	5	5	6
190 m^2/g fumed silica	1	6	6	6	4

* Listed in order of increasing elongation

Ingredients: NBR 612B-100; silica50 (fumed 47); silane A189-1 or 0; DOP-10; TMQ-2; Stearic acid-2; ZnO-5; Sulfur-0.4; MBS-1.5; DTDM-2; TMETD-1

7.9 PEROXIDE CURING

The advantages of peroxide curing systems in silica reinforced nitrile compounds include low compression set, heat resistance, high modulus and hardness, and reduced swelling in oils and water. Original elongation and trouser tear strength decline. Comparisons of peroxide and sulfur systems appear in Formulary compounds NBR 10 and 11, and peroxide alone in NBR 31 and 39. Zinc oxide is retained in peroxide systems to maintain maximum heat resistance. Sulfur, even at 0.4 phr, lowers the cure state with considerable loss in modulus and hardness.

The effects of silane coupling and co-agent addition are described in Table 7.10. The response to the addition of triallylcyanurate (TAC) includes the expected increase in rheometer crosslinking accompanied by slight improvements in abrasion index and set, and a loss in trouser tear and elongation. Silane coupling with methacrylsilane (A174) has a profound influence on all processing and cured compound properties, with or without co-agent. Scorch safety requirements indicate that silane be used without co-agent. Studies by J.Byers [1] have shown that the methacrylsilane is uniquely effective in raising the abrasion index of a silica reinforced peroxide cured compound well above that of a comparable black control.

When the properties of a peroxide compound are compared to those of a zinc-free compound, the relationships noted above (with a *normal* soluble zinc cure system) are somewhat altered.

Table 7.10 Peroxide Cure System in NBR

Triallylcyanurate	--	--	3	3
Methacrylsilane (A174)	--	1.5	--	1.5
MDR cure rate, 150°C, T_{50} minutes	9.3	8.7	9.3	8.5
MDR crosslinks, MH-ML, dN-m	46	60	63	60
Mooney scorch 121°C, T_5 minutes	15	>30	10	9
Mooney viscosity, $ML_4$100	97	78	90	73
Durometer, 15 min cure, 150°C: 23°C	78	83	80	84
100°C	75	79	77	83
Pendulum rebound (Zwick), %: 23°C	34	37	36	37
100°C	59	65	63	66
Compression set, %, 70 hrs, 100°C	37	18	33	20
Stress/Strain, original				
M20 modulus, MPa	1.3	1.9	1.5	1.9
M300 modulus, MPa	8.6	--	10.4	--
Tensile, MPa	21	13	17	13
Elongation, %	455	175	385	190
Aged 700 hrs, 115°C				
Durometer hardness	91	90	92	91
Tensile, MPa	11	12	10	11
Elongation, %	45*	40*	40	45
Aged 70 hrs, 140°C				
Durometer	87	88	86	87
Tensile, MPa	8.8	8.5	9.4	12
Elongation, %	75	60	70	85
MG Trouser tear, kN/m	14	5.7	9.2	4.6
Die C tear, kN/m	37	28	36	31
PICO abrasion index	60	103	69	108
	*brittle			

Other ingredients: NBR 685B-100; 220 m^2/g N_2SA silica -45; DOS-10; P25 DLC-10; TMQ-1; Zinc oxide-2; Dicumyl peroxide 40-7

Abrasion and tear resistance and cure rate of a peroxide compound cannot match those obtained with a zinc-free system. Dynamic properties however, are still superior with peroxide. In particular, DMA testing at 200°C reveals a remarkable reduction in tan delta to 0.038, based on a relatively high elastic modulus value E' of 13 MPa and a loss modulus E" of 0.5 MPa. Complete details appear in Table 7.11.

Table 7.11 Peroxide and Zinc-Free Curing Systems for NBR

		Zinc free	**Peroxide**
Sulfur		1.5	0
TBBS		2	0
DPTH		2	0
DCP		0	2.8
MDR cure rate, 150°C, T_{50} minutes		3.5	9.3
MDR crosslinks, MH-ML, dN-m		37	32
Mooney viscosity, ML_4100		84	97
Durometer hardness:	23°C	77	78
	100°C	71	75
DMA: 1 Hz; 20%;			
E’, MPa	30°C	22	17
	100°C	15	12
	200°C	10	13
E”, MPa	30°C	2.6	2.1
	100°C	1.3	0.9
	200°C	0.8	0.5
Tangent delta	30°C	0.115	0.123
	100°C	0.081	0.073
	200°C	0.081	0.038
Pendulum rebound (Zwick), %:	23°C	33	34
	100°C	55	59
Compression set, 70 hrs, 100°C, %		98	37
Tensile, MPa:	Original	32	21
	700 hrs, 115°C	11	9
Elongation, %:	Original	700	455
	Aged	20	45
PICO Abrasion index		83	60
MG trouser tear, kN/m		24	14
Ingredients: see Table 7.10			

7.10 PROCESSING

The usual silica mixing procedure recommendations hold true for NBR compounds: early addition of the silica with or without plasticizer or oil. A compound mixed by the upside down procedure has the same processing and vulcanizate properties as compounds mixed in the normal manner with polymer first. A normal mix in which the DOP plasticizer was added after, rather than with, the silica showed no change other than a slightly higher compression set value. Low surface area silicas are very effective in producing smooth, even glossy, extruded and calendered surfaces. As noted in Chapter 1, the mechanism appears to be one of improved flow combined with the nerve reducing filler structure. Formulary compound NBR 18 provides an excellent example.

Relatively high Banbury mixing temperatures have some benefit in respect to stress/strain properties. In a direct bonding NBR/PVC formula (NBR 13), adhesion to activated polyester increased by 22% in a compound mixed at 170°C. Mix temperature effects are also noted in Table 7.12.

Table 7.12 NBR/PVC: Mixing and Magnesium Oxide Effects on Adhesion

Magnesium oxide	0	0	1	1	1	1
Banbury stage addition	--	--	1st	1st	2nd	2nd
Compound temperature, °C	120	145	120	150	120	150
ODR cure rate 154°C, T_{90} min	17	23	12	11	11	11
Mooney scorch 121°C T_5 min	30	30^+	24	24	24	24
Mooney Viscosity, ML_4100	37	36	37	37	30	36
Durometer Hardness:						
20 min cure, 154°C	72	70	67	67	68	70
45 min cure,154°C	72	70	67	67	70	69
Pull-out Adhesion to Brass Wire (6+3), N/25mm embedment:						
30 min cure, 154°C	400	620	520	645	530	620
60 min cure, 154°C	420	690	490	620	530	570
Rubber cover, %	100	100	100	100	100	100
Strip Adhesion to activated polyester hose fabric, kN/m:						
30 min cure, 154°C	6.5	6.6	11	11	9.3	7.5
60 min cure, 154°C	4.4	5.6	6.2	8.8	6.2	5.6
Press cure, 154°C:						
M300 modulus, MPa, 20 min	7.1	5.4	4.0	3.8	4.2	4.2
45 min	7.3	5.4	4.0	4.5	4.9	5.1
Tensile Strength, MPa, 20 min	11	9.0	8.0	8.0	8.0	8.0
45 min	11	9.0	7.8	8.5	8.5	9.0
Elongation, %: 20 min	480	550	600	600	600	590
45 min	500	560	580	580	570	540
Compression set, %, 70 hrs, 100°C	76	82	85	83	87	84
PICO Abrasion index	54	55	42	40	45	46

Other ingredients: NBR/PVC(ozo)-100; 65 m^2/g N_2SA silica -60; DOP-30; ODPA-1; Stearic acid-2; ZnO-5; R-F resin R6-3; sulfur-1.5; MBS-1.5; HMMM 963- 3

7.11 ZINC-FREE CURE SYSTEMS

With NBR polymers produced without fatty acid emulsification it is possible to examine the processing and vulcanizate effects of a soluble zinc-free cure system in NBR. Unfortunately, there is little evidence of improved silica reinforcement. In Table 7.13, PICO abrasion index improves only by a disappointing 10%. A possibly significant and unexpected change is seen in aging resistance, 700 hours at 115°C, where the brittleness of the control becomes a flexible 65% elongation in the zinc-free compound with DPG. The addition of 2 phr DPG in the latter may be the primary influence on aging behavior. Since the usual reduction in zinc oxide content in zinc-free systems degrades aging resistance, the restorative action of DPG is significant. Unfortunately, few of the formulary zinc-free recommendations contain DPG.

Table 7.13 Zinc-free Cure Systems in NBR

	Normal	**Zinc-Free**	**Zinc-Free**
Stearic acid	2	0	0
Zinc oxide	3	1	1
HMT	0	1	1
DPTH	1	1	2
DPG	0	2	0
MDR cure rate, 150°C, T_{50} minutes	4.0	4.5	3.5
MDR crosslinks, MH-ML, dN-m	34	34	37
Mooney scorch 121°C, T_5 minutes	21	15	18
Mooney viscosity, ML_4 100	84	78	84
Durometer, 10 min cure, 150°C: 23°C	72	78	77
100°C	67	71	71
PICO Abrasion index	74	83	83
MG Trouser ear, kN/m	22	35	24
Die C tear, kN/m	45	48	46
Stress/Strain, original			
M20 modulus, MPa	1.0	1.1	1.2
M300 modulus, MPa	4.5	4.0	5.1
Tensile, MPa	29	29	32
Elongation, %	710	770	700
Aged 700 hrs, 115°C			
Durometer hardness	94	90	90
Tensile, MPa	10	14	7.6
Elongation, %	35Br	65	45
Pendulum rebound (Z), %: 23°C	32	32	33
100°C	55	53	55
Compression set, 70 hrs, 100°C, %	85	100	98
DMA: 1 Hz; 20%; E’, MPa , 30°C	14	-	22
100°C	10	-	15
200°C	6.4	-	10

Other ingredients: NBR 685B-100; 220 m^2/g N_2SA silica -45; DOS-10; C.I.P25-8; TMQ-1; Sulfur-1.5; TBBS-2

Possibly the most important aspects of the zinc-free system in NBR are the significant increases in durometer, static stiffness (M20), and dynamic modulus, achieved without loss in resilience or stress/strain properties or increase in viscosity. The enhanced dynamic behavior is retained at 100°C and 200°C. Since increased hardness is generally a function of filler content, the use of a zinc-free system to augment durometer provides a new compounding technique which effectively eliminates the usual degradation in dynamic properties which accompanies increased hardness. The mechanism here can be related to the characteristic silica-silanol-water network structure, unimpeded by soluble zinc, and its strong cohesion at low strains; sulfur crosslink density is not a factor.

Table 7.14 Sulfur Concentration Effect in Zinc-free Systems

Sulfur		0.5	1.0	2.0
DPTH		2	2	1.5
MDR cure rate, 150°C, T_{50} minutes		3.3	3.1	3.2
MDR crosslinks,MH-ML, dN-m		31	37	39
Compression set, %, 70 hrs, 100		82	83	92
Durometer hardness		76	78	79
M300 modulus, MPa		6.3	6.6	8.2
Tensile, MPa		29	27	30
Elongation, %		660	605	580
PICO Abrasion index		68	68	88
MG Trouser Tear, kN/m		18	16	16
DMA: 1 Hz; 20%;				
E’, MPa	30°C	23	24	27
	100°C	15	16	19
	200°C	9	10	13
E”, MPa	30°C	3.0	3.1	3.1
	100°C	1.6	1.6	1.5
	200°C	0.9	0.9	0.9
Tangent delta	30°C	0.129	0.129	0.114
	100°C	0.103	0.098	0.079
	200°C	0.108	0.091	0.069
Other ingredients: NBR 685B-100; 150 m^2/g N_2SA silica -50; DOS-10; C.I.P25-8; ODPA-1; ZnO-1; TBBS-2; HMMT-2				

The importance of maintaining adequate accelerator content in zinc-free systems has been described previously, and is illustrated in Table 7.13. To attain the full advantages of a zinc-free system in NBR, a combined accelerator content of 4 or 5 phr is recommended, 4 with 2 phr DPTH and 5 with DPG. If TBBS is omitted from this system, rheometer crosslinking is inadequate and zinc-free advantages are lost. The DPTH zinc-free compound shows a very interesting dynamic modulus property at 200°C, where the stiffness retention at 200°C is considerably higher than that of the normal zinc control. Plasticizer compatibility may be a problem in zinc-free NBR compounds. After several months of shelf aging, exudation (presumably DOS) appeared on the surface of this compound.

The importance of sulfur level in zinc-free systems cannot be overstated. It appears, in Table 7.14, that a minimum of 1.5 to 2.0 phr is necessary to realize the abrasion and dynamic property potentials of zinc-free acceleration. The retention of dynamic stiffness at 200°C is of particular interest.

Table 7.15 Silane Coupling Effects in Zinc-free NBR

150 m^2/g N_2SA silica	50	50*	50
Mercaptosilane, MPTS	-	1.5*	-
Mercaptosilane, TESPT	-	-	3
MDR cure rate, 150°C, T_{90} minutes	7.5	5.4	7.0
MDR crosslinks, MH-ML, dN-m	37	37	37
Mooney scorch 130°C, T_5 minutes	9	7	10
Mooney viscosity ML_4100	79	61	67
Durometer, 20 min cure, 150°C: 23°C/100°C	78/72	75/73	79/74
Stress/Strain, Original: M20 modulus, MPa	1.3	1.3	1.3
M300 modulus, MPa	6.6	13.6	11.2
Tensile, MPa	27	26	24
Elongation, %	505	465	515
Aged 700 hrs, 115°C: Durometer hardness	90	92	92
Tensile, MPa	14	16	14
Elongation, %	100	120	80
MG Trouser tear, kN/m	16	10	11
PICO Abrasion index	68	104	90
Compression set, 70 hrs, 100°C, %	83	74	87
Pendulum rebound (Zwick), %: 23°C/100°C	31/58	29/58	31/58
DMA: 1 Hz; 20%; E', MPa 30°C	24	19	17
100°C	16	13	12
200°C	9.7	6.8	7.6
E", MPa 30°C	3.1	2.6	2.3
100°C	1.6	1.3	1.1
200°C	0.9	0.7	0.6
Tangent delta 100°C	0.098	0.98	0.88
200°C	0.091	0.102	0.076
Goodrich flexometer heat build-up. °C	41	36	37
Other ingredients: NBR 685B-100; Silica-50; DOS-10; C.I.P25 8; TMQ-1; ZnO-1; HMT-1; Sulfur-1; TBBS-2; DPTH-2 *pre-blended as Ciptane			

As detailed in Table 7.15, silane coupling of zinc-free compounds produces a favorable combination of tear and abrasion resistance with the usual modulus increase and reductions in viscosity and elongation. The modulus increase, attained without change in crosslink density, is an indication of the improvement in silica-NBR bonding afforded by silane coupling.. Although there is little to choose between MPTS and TESPT, the latter develops a possibly significant reduction in tangent delta at 200°C, due to a greater retention of stiffness (E') at this temperature. This advantage is not apparent at 30°C or 100°C; the addition of silane causes a reduction of dynamic stiffness from that of the original zinc-free compound. Examples of zinc-free compounds appear in Formulary compounds NBR 26, 30 and 40.

7.12 PHENOLIC RESINS

The high degree of compatibility between nitrile elastomers and certain phenolic resins has led to many commercial applications of this combination, frequently with silica reinforcement.

Table 7.16 Phenolic Resin Effects with Silane Coupling

Cashew nut oil phenolic resin (Durez 12686)	-	20
HMT	-	1
ODR cure rate, 154°C, T_{90} minutes	16	11
Mooney scorch 130°C, T_5 minutes	17	12
Viscosity ML_4100	64	52
ODR minimum, dN-m	6.2	4.0
Stress/Strain, Original		
Durometer hardness	67	75
M300 modulus, MPa	10.6	5.8
Tensile, MPa	24	21
Elongation, %	500	760
Aged 700 hrs, 150°C		
Durometer A (C)	92 (68)	95 (82)
Tensile, MPa	6.5	6.5
Elongation, %	60	60
Trouser tear, cut groove, kN/m	5.3	22
PICO Abrasion index	104	113

Oher ingredients: NBR 1052-100; 150 m^2/g N_2SA silica -50; MPTS -1; DOP-10; ODPA-1; ZnO-5; Stearic acid-2; sulfur-0.3; DTDM-2; MBS-2; TMTD-0.5

The unusual feature of phenolic plasticization is the occurrence of reduced viscosity in the uncured compound together with increased hardness of the vulcanizate. Table 7.16 illustrates a somewhat special case where a silane coupled silica reinforced NBR with sulfur donor cure is modified by a cashew nut oil phenolic resin. M300 modulus suffers a drastic loss which is reflected in the 4 fold increase in tear strength, all in a compound 8 points harder than the control!

7.13 NBR ADHESION TO BRASS

Adhesion of NBR covers and tubes to the brass coated wires used in high pressure hose construction is an important compounding topic. Among the major formula ingredients critical in respect to achieving good brass adhesion are silica, sulfur, magnesia and resin bonding agents. Although there can be some interaction, the sulfur and accelerator contents are fairly independent of the others. A limited study in a formula which contains relatively high silica and resin contents as well as magnesia compares sulfur at 0.5 and 1.5 phr and thiazole-sulfenamide versus thiuram accelerators in Table 7.17.

Table 7.17 Sulfur and Accelerator Effects on NBR Brass Adhesion

Sulfur	0.5	1.5	1.5
DTDM	2	1	--
TMETD	1	1	--
MBTS	--	--	1
TBBS	--	--	2
MDR cure rate, 150°C, T_{50} minutes	5.6	4.4	8.0
MDR crosslinks,MH-ML, dN-m	33	38	30
Mooney scorch 121°C, T_5 minutes	19	13	>30
Mooney viscosity $ML_4$100	56	56	47
Durometer hardness: 23°C/100°C	74/66	76/71	76/68
Pull-out adhesion to brass cord (6+3), N/25mm			
30 min press cure /150°C			
Low pressure (0.7 MPa)	60	700	180
High pressure (13 MPa)	60	530	170
Rubber cover, %	0	40	5
Stress/Strain			
M300 modulus, MPa	12	15	14
Tensile, MPa	19	20	22
Elongation, %	490	440	470

Other ingredients: NBR 386b-100; 150 m^2/g N_2SA silica -30; 65 m^2/g N_2SA silica-35; DOP-18; TMQ-1.5; ODPA-1.5; MgO-2; ZnO-3; Stearic acid-2; R-F resin-4; HMMM-2

Here an increase in sulfur from 0.5 to 1.5 produces a ten fold increase in brass pull-out adhesion. When MBTS-TBBS is substituted for TMETD, adhesion falls precipitously. A related contour curve study of TMETD and sulfur, Figure 7.8 indicates that the thiuram has a only a minor role and that the optimum sulfur content lies between 1.6 and 1.9 phr.

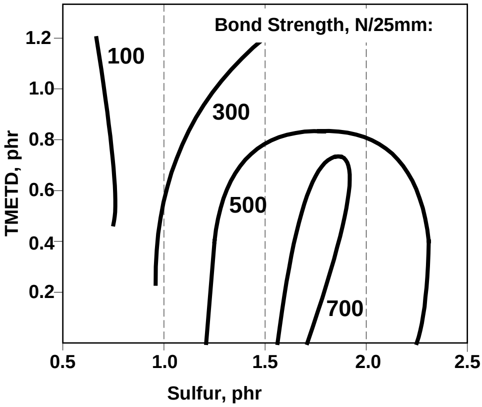


Figure 7.8 Effect of Sulfur and Thiuram on Brass Adhesion

Sample preparation in laboratory studies is of critical importance. For example, adhesion values in Table 7.17 are recorded for two different press cure pressures, 0.7 and 13 MPa. The lower pressure is typical of that used in many hose curing operations. In this instance (but not in the contour studies), the highest bond strengths are obtained at the low pressure cure.

Silica content has a major influence on brass adhesion. A contour study of silica content (balance of filler is FEF black) and resorcinol resin shows, in Figure 7.9, that the resin has a significant positive effect only at silica contents above 40 phr. Generally lower adhesion values here reflect the use of a low sulfur cure system. The data used in this figure is from low pressure samples aged 170 hours at 100°C before testing. Aged values are generally 20 to 80% higher than those recorded before aging.

These same compounds cured at high pressure produced higher wire adhesion. More importantly, resin addition at 40 phr silica reduced the brass bond. This bond degradation by the resorcinol/HMMM resin additives also occurred at a lower silica content of 30 phr. At present, the mechanism of these reversals remains unresolved.

Brass wire adhesion data for compounds with and without magnesia were noted in Table 7.12. Compounds mixed at 120°C benefit from the addition of 1 phr magnesia (both cures); at a mixing temperature of 150°C there is no change whatsoever. Unfortunately, all separations occurred in the compound, which indicates that the "adhesion" values are probably related more to tear strength than to bond strength. A fair correlation between adhesion and elongation values lends credibility to this view. Formulary examples of NBR brass adhesion recommendations include compounds NBR 4, 15 and 19.

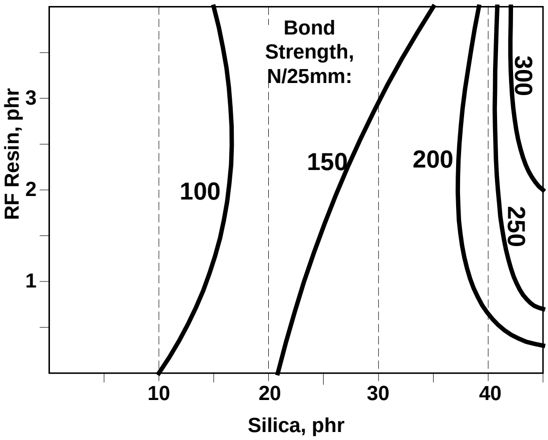


Figure 7.9 Effect of Silica and RF Resin on Brass Adhesion

7.14 NBR ADHESION TO FABRIC

Bonding NBR compounds to fabric, treated or untreated, requires a combination of silica, zinc oxide, resorcinol (or RF resin) and HMT (or HMMM). In addition to these bonding system components, the order in which they are mixed is a critical factor. The mixing relationship is illustrated in Table 7.18, in a two level screening study in which the three variables are added in either a first or second Banbury stage.

The fabric here is untreated nylon, the use of which reveals adhesion distinctions which an RFL treatment would obscure. Bonding mechanism insights are also possible with untreated fabric. The most interesting result of this mixing study is the complete loss of adhesion that occurs when all three variables are mixed together in the first Banbury. Evidently a premature zinc-resin-HMT reaction has prevented compound attachment to untreated fabric, notwithstanding the wetting function of the silica.

Only one other mixing factor is evident: zinc oxide addition in the second stage leads to a significant loss in static adhesion, particularly in the 30 minute cure specimens. The indication here is that the complete zinc-resorcinol reaction requires more than 30 minutes in this particular system. This loss, however, disappears when the cure time is increased from 30 minutes to 60 minutes, or after oven aging. Lowest M300 modulus in the zero adhesion compound appears to be due to a loss in filler-polymer bonding rather than in crosslink density, as the rheometer maximum torque value shows no reduction.

Table 7.18 Adhesion to Untreated Nylon Fabrics : Mixing Order

Mixing Order: (Banbury 1 or 2)						
ZnO	HMT	Resin	Adhesion, N/25mm	Durometer	M300 MPa	Elongation %
1	1	1	nil	67	5.3	620
1	1	2	400+	67	5.8	520
1	2	2	400+	69	6.4	540
1	2	1	400+	70	6.7	550
2	1	2	350	69	7.3	550
2	1	1	310	72	6.3	540
2	2	1	320	71	6.7	540
2	2	2	350	72	7.0	520
Other ingredients: NBR 1052-100; 150 m^2/g N_2SA silica-30; SRF N770-50; DOP-25; PBNA-1; Resorcinol-3; HMT-2; Sufur-1.5; MBS-1.7; ZnO-5						

The influence of magnesium oxide on adhesion to untreated polyester hose fabric was described in Table 7.12. A 1 phr addition produces higher peel values, particularly when added in the first Banbury stage with RF resin. Mixing temperature has little effect. The effect of magnesia in a resorcinol/HMT or an RF resin/HMMM system appears to be similar to that of zinc oxide in activating the basic resin reaction.

REFERENCES

1. Byers, J. et al., “Compounding Silica in NBR”, Rubber and Plastics News, p 38, June 13, 1988

2. Hewitt, N.L. "Adhesion Systems for Belts and Hose" ACS Rub. Div. Meeting, Chicago, Il., April 13, 1999

3. Hewitt, N.L. "Compounding Silica in NBR", paper presented at Energy Rubber Group, January 16, 1997

4.Horvath, J., “Silica effect on aging of bound anti-oxidant NBR”, paper at Southern Rubber Group meeting, San Antonio, Feb. 28, 1975.

5. Hewitt, N.L. "Using Viscoelastic Series for Compound Design", Rubber World, November,1984

Nitrile Formulary

The silica surface areas indicated in the following compounds are N_2SA (BET) surface areas. A listing of commercially available precipitated silica products by surface area is provided in Appendix A. The common abbreviations used in these compounds are provided in Appendix E.

NBR 1

Elastomer: NBR Durometer: 49 Black
Application: Textile adhesion; Fast cure; Low viscosity

Chemigum N6B	100	DOP	15
35 m^2/g Silica	50	TP90B	15
FEF N550	20	<u>2nd Stage</u>	
Zinc Oxide	5	Sulfur	1.5
Resorcinol Resin B19	2	MBS	1.7
TMQ	1	TMTM	0.4
Stearic Acid	2	Cyrez 963	2
Aromatic Resin 25°	15	Specific Gravity	1.20

ODR Cure Rate, 153°C, T_{90} minutes	6.5
Mooney Scorch, 121°C, T_5 minutes	18
Viscosity, ML_4100	17

10 minute cure, 153°C:	
Hardness	49
M300, MPa	3.6
Tensile, MPa	11
Elongation, %	620

Adhesion to Untreated Nylon Fabric, kN/m

	Original	Isooctane/Toluol*
10 minutes, 153°C	>5.2	7.0
20 minutes, 153°C	>7.9	>6.2

*immersed 4 days, 57°C

Adhesion to Untreated Cotton Fabric, kN/m

30 minutes, 150°C	4.4

NBR 2

Elastomer: NBR Durometer: 51
Application: Textile adhesion; 127°C Cure

Hycar 1052	100	Zinc Oxide	5
35 m^2/g Silica	60	Sulfur	1.5
DOP	20	MBS	1.2
Aromatic Resin 25°	15	Cyrez 963	3
Stearic Acid	2		
Resorcinol Resin	3	Specific Gravity	1.25

ODR Cure Rate, 153°C, T_{90} minutes	60
Viscosity, ML_4100	25

60 minute cure, 150°C:	
Hardness	51
M300, MPa	2.1
Tensile, MPa	8.4
Elongation, %	930

Adhesion to Untreated Fabric, kN/m

	Nylon	Cotton
127°C Air Cure		
2 hours	7.9	8.7
4 hours	9.7	7.0
6 hours	10	7.0

NBR 3

Elastomer: NBR Durometer: 58
Application: Low set; Seals; Low HBU

NBR 685B	100	Zinc Oxide	5
65 m^2/g Silica	50	Sulfur	0.5
Silane A189	0.5	MBTS	1.5
TiO_2	3	TMTD	0.7
DOP	9	TETD	0.7
DOS	9	PEG 3350	1.5
Stearic Acid	2		
DAPPD	1	Specific Gravity	1.20

Cure Rate 165°C, T_{90} minutes	2.5
Mooney Scorch 121°C, T_5 minutes	13
Viscosity, ML_4100	34

4 minute cure, 165°C:	Original	70 hrs, 150°C	700 hrs, 110°C
M20, MPa	0.7	0.9	2.0
M300, MPa	7.7		
Tensile, MPa	21	6.8	9.4
Elongation, %	655	200	200

14 minute cure, 165°C	
Durometer, 23°C	60
100°C	56
Pendulum Rebound (Z), %, 23°C	45.4
100°C	64.6
Compression Set, %, 70 hrs, 100°C	29.3
DeMattia Cut Growth, kc to 500%	18
PICO Abrasion Index	84

Goodrich Flexometer: 100°C; 22.5%; 1 MPa	
Static Compression, %	22
Dynamic Compression	10
Dynamic Drift	0
Permanent Set	2.4
Heat Build-Up, °C	22

NBR 4

Elastomer: NBR/CR/BR Durometer: 55
Application: Brass adhesion; Textile adhesion

Chemigum N600	50	Cyrez 963	3
Neoprene W	50	2nd Stage	
BR	3	Sulfur	1.5
65 m^2/g Silica	60	Zinc Oxide	5
Magnesium Oxide	3	Resorcinol Resin	1
DOP	15	MBS	1
Flexricin 9	5	DPG	0.6
Stearic Acid	2	Specific Gravity	1.33

ODR Cure Rate, 153°C, T_{90} minutes	38
Mooney Scorch, 121°C, T_5 minutes	21
Viscosity, MS 121	17

30 minute cure, 150°C:	Original	72 hrs,121°C
Hardness	55	89
M300, MPa	3.9	
Tensile, MPa	12	6.3
Elongation, %	660	40

Adhesion to Brass and Untreated Fabric lbs./in. kN/m

Cure:	30 min, 150°C	60 min, 150°C
Brass Strip	17	13
Nylon	7.9	8.7
Activated Polyester	8.7	8.7

NBR 5

Elastomer: NBR/PVC Durometer: 60
Application: Fabric adhesion; Tear strength; Hose

NBR/PVC, 70/30	100	Sulfur	1.5
150 m^2/g Silica	38	MBS (MOR)	1.5
DOP	30	TMTM	0.4
ODPA	1	HMMM964	2.0
Zinc Oxide	3	Resorcinol Resin*	0.5
Zinc Octoate	2		
Stearic Acid	2	Specific Gravity	1.25

*B19S or R-6

MDR Cure Rate 150°C, T_{50} minutes	11
Mooney Scorch 121°C, T_5 minutes	30+
Mooney Viscosity $ML_4$100	27
45 minute cure, 150°C:	
Durometer, 23°C	60
100°C	42
Strip Adhesion to Untreated Nylon N/25 mm	435
MG Trouser Tear, kN/m	30
30 minute cure, 150°C:	
M300, MPa	3.6
Tensile, MPa	15
Elongation, %	725
Pendulum Rebound (Z), %, 23°C	23
100°C	45

NBR 6

Elastomer: NBR Durometer: 60
Application: Gaskets; Seals, ATF service

Paracril J4940	100	Zinc Oxide	5.0
Silane A189	1	PEG 3350	1.5
65 m^2/g Silica	55	MBS	1.5
TMQ	2	DTDM	2.0
Stearic Acid	2	TMTD	1.0
DOP	18	Sulfur	0.4
		Specific Gravity	1.21

ODR Cure Rate, 154^{o}C, T_{90} minutes	20
Mooney Scorch, 130°C, T_5 minutes	22
Viscosity, $ML_4$100	72

30 minute cure, 154°C:	Original	72 hrs, 150°C
Hardness	60	65
M300, MPa	16	
Tensile, MPa	17	13
Elongation, %	310	190
Die C Tear, kN/m	44	

Compression Set (45 minute cure, 154°C), %	
70 hrs, 100°C	18
70 hrs, 121°C	25
70 hrs, 150°C	42

Oil Immersion: 70 hrs, 150°C	ASTM #1	ASTM #3	ATF*
Hardness	65	55	58
Tensile, MPa	18	17	14
Elongation, %	290	300	300
% Volume Change	-13.7	+0.8	-7.8

*WSX7999D

NBS Abrasion Index 235

NBR 7

Elastomer: NBR/BR Durometer: 64
Application: Soling; Abrasion; Zinc-free

NBR 40E65	60	Sulfur	2
BR 1220	40	TBBS	2
Silica	35	DPTH	2
DOP	5	HMT	1
DOA	10		
MC Wax	1		
HPPD	2		
Stearic Acid	1	Specific Gravity	1.11

	150 m^2/g Silica		Ciptane I	
Cure Rate, 150ºC, T_{50} minutes	8.2		8.3	
Mooney Scorch 121ºC, T_5 minutes	28		26	
Viscosity, ML_4100	44		41	
20 minute cure, 150ºC:	Original	Aged*	Original	Aged*
Durometer	64	86	62	85
M300, MPa	4.1	-	6.3	-
Tensile, MPa	12	5.3	13	5.6
Elongation, %	595	40	470	40
*72 hrs, 125ºC				
Abrasion Index: PICO	72		88	
NBS	230		440	
Compression Set, %, 72 hrs, 100ºC	86		84	
Fuel B 48 hrs, 23ºC, % Swell	31.0		30.4	
Pendulum Rebound (Z), %, 23ºC	34		34	
100ºC	67		68	
Cut Growth, kc to 500%: Ross	70		100+	
DeMattia	100+		18	
Goodrich Flexometer: 100ºC, 22.5%, 1 MPa				
Set, %	16		13	
Heat Build-Up, ºC	30		23	
Dynamic Mechanical Analysis: 0ºC; 1 Hz, 15% Deflection				
E’, MPa	15		13	

NBR 8

Elastomer: NBR Durometer: 64
Application: Low heat build-up; Low water swell

1st Stage		2nd Stage	
NBR 1052	100	Zinc Oxide	5.0
Silane A189	0.5	Magnesia	1.5
65 m^2/g Silica	55	Sulfur	0.5
TMQ	2	MBS	1.5
Dioctyl Phthalate	15	DTDM	2.0
Stearic Acid	2	TMTD	1.0
TEA	1.5	Specific Gravity	1.21

Cure Rate, 154ºC, T_{90} minutes	16
Mooney Scorch, 121ºC, T_5 minutes	9
T_{35} minutes	18
Viscosity, $ML_4 100$	38

20 minute cure, 154ºC	Original	72 hrs, 150ºC
Hardness	64	72
M300, MPa	800	
T_B	1260	1140
E_B	430	280

Compression Set, %, 72 hrs, 100ºC	18
Goodrich Flexometer: 100ºC, 22.5%; 1 MPa	
Static Compression, %	10.6
Permanent Set, %	0.7
Heat Build-Up,ºC	17

Water Immersion, 82ºC, % Volume Change	
16 hours	8.6
24 hours	10.3
7 days	6.6
14 days	5.7

NBR 9

Elastomer: NBR Durometer: 65
Application: Heat resistance; High modulus (mercaptosilane)

Paracril BJLTHX	100	Zinc Oxide	5.0
150 m^2/g Silica	25	PEG 4000	1.5
65 m^2/g Silica	35	Sulfur	0.3
TMQ	2	MBS	1.5
Stearic Acid	1.5	DTDM	2.0
DOP	20	TETD	1.0
		Specific Gravity	1.19

Mercaptosilane MPTS (A189)	0	1
ODR cure Rate, 154ºC, T_{90} minutes	17	16
Mooney Scorch, 130ºC, T_5 minutes	17	15
Viscosity, ML_4100	85	63
30 minute cure, 154ºC:		
Hardness	66	69
M300, MPa	5.0	16
Tensile, MPa	14	18
Elongation, %	545	330
Die C Tear kN/m	40	60
Aged 5 days, 150ºC (Oven):		
Hardness	90	88
Tensile, MPa	11	12
Elongation, %	100	90
Compression Set, %, 70 hrs, 121ºC	43	36
DeMattia Flex, 20ºC, kc to 500%	1	1.8

NBR 10

Elastomer: NBR/SBR Durometer: 60-70
Application: Heat resistance; O-rings

Paracril CLT	80	Stearic Acid	2.0
SBR 1503	20	PEG 4000	1.5
Silane A189	0.7	Sulfur	0.3*
65 m^2/g Silica	35	MBS	1.0*
TMQ	2	*omit with peroxide	
Paraplex G25	5	Specific Gravity	1.16

Acceleration	CdO	S-Donor	Peroxide
Cadmium Oxide	5	-	-
Magnesium Oxide	5	-	-
Zinc Oxide	-	5	5
Ethyl Cadmate	2.5	-	-
TETD	-	1	-
DTDM	-	2	-
Vul-Cup 40KE	-	-	8
ODR cure Rate, 165ºC, T$_{90}$ minutes	13	13	23
Mooney Scorch, 135ºC, T$_5$ minutes	8	21	9
Viscosity ML$_4$100	61	60	66
Cure, 165ºC, minutes	15	15	30
Original			
Hardness	61	60	72
M300, MPa	4.0	8.0	-
Tensile, MPa	14	13	12
Elongation, %	620	400	200
Oven Aged 3 Days, 150ºC			
Hardness	69	75	82
Tensile, MPa	16	10	11
Elongation, %	640	200	200
Compression Set, %, 70 hrs, 150ºC	65	66	42
ASTM #3 Oil Immersion, 70 hrs, 150ºC			
%Volume Increase	39	30	14
DeMattia Flex, kc to 0.6" Cut Growth:			
Cure, 165ºC, minutes	25	25	40
Hardness	72	74	75
kc, 20ºC	>200	100	0.5
kc, 100ºC	30	14	<0.5

NBR 11

Elastomer: NBR Durometer: 65-72
Application: Food Grade (Black)

Cure System:		Sulfur	Peroxide
Hycar 1032-45	100		
150 m^2/g Silica	15		
ISAF N220	18		
Platy talc	30		
Zinc Oxide	5		
Stearic Acid	2		
PEG 4000	1		
DOP	7		
TP 95	8		
Sulfur		1.5	-
TMTM		0.5	-
Vul-Cup 40KE		-	4

	Sulfur	Peroxide
ODR cure Rate, 165ºC, T_{90} minutes	10	21
Mooney Scorch, 121ºC, T_5 minutes	>30	>30
Viscosity $\mathrm{ML}_4$100	48	48
Cure, 165ºC, minutes	15	25
Hardness	65	72
M100, MPa	1.2	2.6
M300, MPa	3.9	10
Tensile, MPa	19	17
Elongation, %	700	400
Die C Tear, kN/m	48	48
Oven Aged 3 days, 121ºC		
Hardness	88	88
Tensile, MPa	9.5	12
Elongation, %	90	150
Compression Set, %, 3 days, 100ºC	40	15
ASTM #3 Oil Immersion, 3 Days, 100ºC		
%Volume Change	9.2	7.3
Hardness	57	66
Water Immersion, 100ºC		
% Volume Change, 1 day	5.9	3.3
3 days	6.5	4.1
7 days	10.3	5.8

NBR 12

Elastomer: NBR/PVC Durometer: 66-71

Application: Fire resistance; Heat resistance; Silica comparison

NBR/PVC (OZO)	100	Zinc Oxide	5
Silica	45	TMTD	1.8
Silane A189	1.8	TETD	1.2
Santicizer D148	20		
Antimony Oxide	8		
TMQ	2		
Naugard 445	2	Specific Gravity	1.21

Silica CTAB Surface Area	42	133
MDR Cure Rate 150ºC, T_{50} minutes	13	4.2
Mooney Scorch 121ºC, T_5 minutes	22	12
Mooney Viscosity, ML $_4$100	36	43
Durometer (30 min cure, 150ºC), 23ºC	66	71
100ºC	45	54
Original		
M300, MPa	8.0	9.4
Tensile, MPa	10	15
Elongation, %	515	565
Aged 700 hrs, 110ºC		
Durometer	82	87
Tensile, MPa	19	21
Elongation, %	295	315
Aged 72 hrs, 135ºC		
Durometer	87	89
Tensile, MPa	18	19
Elongation, %	245	310
PICO Abrasion Index	67	90
NBS Abrasion Index	107	110
DIN Abrasion Loss, ml	132	130
MG Trouser Tear, kN/m	8.1	19.0
Die C Tear	47	50
Low Temperature Flexibility, -40ºC: DMA		
Dynamic Modulus E', MPa	1690	2180
Compression Set, %, 70 hrs, 100ºC	69	59
Pendulum Rebound (Z), %, 23ºC	23	21
100ºC	42	46
DeMattia Cut Growth, kc to 500%	60	55

NBR 13

Elastomer: NBR/PVC Durometer: 67
Application: Textile Adhesion; Hose; Mix temperature

NBR/PVC 70/30	100	Zinc Oxide	3
150 m^2/g Silica	40	Zinc Octoate	3
65 m^2/g Silica	20	Sulfur	1.5
DOP	30	MBS	1.5
ODPA	1	ZMDC	0.4
R-6 Bond Agent	3	Cyrez 963P	4
Magnesia	1		
Stearic Acid	2	Specific Gravity	1.26

Banbury Stage 1 Stock Temperature	145ºC	170ºC
Cure Rate, 154ºC, T_{90} minutes	11	13
Mooney Scorch, 121ºC, T_5 minutes	23	28
Viscosity, $ML_4$100	39	38
20 minute cure, 154ºC:		
Hardness	67	67
M300, MPa	4.0	4.4
T_B	7.7	11
E_B	590	630
PICO Abrasion Index	52	56
Adhesion to Activated Polyester Fabric		
Interior Bond, kN/m		
Press Cure		
40 minutes, 145ºC	7.4	8.7
60 minutes, 145ºC	8.4	10.6
Heater Cure		
60 minutes, 145ºC	7.5	7.5

NBR 14

Elastomer: NBR	Durometer: 67	
Application: Low set; Hose		

NBR 1052	100	Zinc Oxide	5
65 m^2/g Silica	55	Magnesia	1.5
Silane A189	0.5	Sulfur	0.5
DOP 70% DLC	20	TBBS	1.5
TMQ	2	TMTD	1.0
Stearic Acid	2	DTDM	2.0
PEG 3350	1.5	Specific Gravity	1.22

Cure Rate, 154ºC, T_{90} minutes	20
Mooney Scorch 130ºC, T_5 minutes	30+
Viscosity, ML_4100	36

25 minute cure, 154ºC:	Original	72 hrs, 150ºC
Durometer	67	74
M100, MPa	3.3	6.6
M300, MPa	13.7	
Tensile, MPa	15.5	7.8
Elongation, %	345	115

MG Trouser Tear, kN/m	5.3

Goodrich Flexometer; 100ºC; 22.5%; 1 MPa:	
Permanent Set, %	1.4
Heat Build-Up, ºC	25

Compression Set, %, 72 hrs, 100ºC	31.6

Water Immersion 100ºC; % Volume Increase:	
24 hours	7.7
72 hours	9.0
170 hours	8.2

ASTM #3 Oil; 72 hrs, 100ºC, % Swell	4.9

NBR 15

Elastomer: NBR Durometer: 68
Application: Brass adhesion

NBR 683B	100	Magnesia	1
65 m^2/g Silica	60	Zinc Oxide	5
DOP	12	Sulfur	2
25C CI Resin	5	DPTH	0.5
TMQ	1	MOR	1.5
ODPA	1	HMMM 964	3
Stearic Acid	2		
R-F Resin	3	Specific Gravity	1.22

MDR Cure Rate, 150ºC, T_{50} minutes	8.6
T_{90} minutes	22
Mooney Scorch 121ºC, T_5 minutes	30+
Mooney Viscosity, $ML_4$100	28

Stress/Strain	Original	700 hrs, 110ºC
Durometer, 23ºC	68	94
100ºC	62	
M300, MPa	11	
Tensile, MPa	20	9.4
Elongation, %	505	15

Adhesion, Brass Wire (6+3), N/25 mm	320
Compression Set, %, 70 hrs, 100ºC	82

Goodrich Flexometer, 100ºC; 22.5%; 1 MPa	
Dynamic Compression, %	5.3
Dynamic Drift, %	19
Permanent Set, %	23
Heat Build-Up, ºC	42

Pendulum Rebound (Z), %, 23ºC	29
100ºC	55

NBR 16

Elastomer: NBR/BR Durometer: 68
Application: Abrasion; Soling; NBR/XNBR/BR

NBR 40% ACN	50	Zinc Oxide	3
XNBR NX 775	25	Stearic Acid	2
BR 1220	25	Sulfur	2
150 m^2/g Silica	15	TBBS	2
Ciptane I	20	DPTH	1
DOP	5	HMT	1
DOS	10		
HPPD	2		
MC Wax	1	Specific gravity	1.13

MDR, 150ºC, T_2 scorch, minutes	2.8
T_{90} minutes	6.4
Viscosity, ML_4100	46
15 minute cure, 150ºC:	
Durometer, 23ºC	68
100ºC	65
M300, MPa	11.5
Tensile, MPa	12
Elongation, %	300
Abrasion Indices: NBS	510
PICO	196
Fuel B, 48 hrs, 23ºC, % Swell	26
Compression Set, %, 70 hrs, 100ºC	61
Pendulum Rebound (Z), %, 23C	32
100ºC	65

NBR 17

Elastomer: NBR Durometer: 70
Application: Fuel hose; Low extractables

NBR 1092-30	100	Sulfur	1.5
35 m^2/g Silica	35	MBS	1.0
Platy Talc	30	TMTD	0.2
Zinc Oxide	5		
Stearic Acid	2	Specific Gravity	1.28

Cure Rate, 154ºC, T_{90} minutes	11
Mooney Scorch, 130ºC, T_5 minutes	27
Viscosity, $ML_4$100	60
Garvey Extrusion, 121ºC	
Swell. %	40
Edge and Surface	10A

15 minute cure, 154ºC:	Original	72 hrs, 121ºC	72 hrs, 150ºC, #3 Oil
Hardness	70	80	47
M300, MPa	4.5		
Tensile	16	9.9	9.8
Elongation	760	200	730
Volume Change, %			23

Compression Set, %, 3 days, 121ºC	74
Fuel B Extraction, 4 days, 40ºC	
Soluble in fuel, %	4.1

NBR 18

Elastomer: NBR Durometer: 72
Application: Extrusions; Heat resistance

NBR 1042	100	Zinc Oxide	3
35 m^2/g Silica	140	Sulfur	0.2
DOP	35	MBS	1
25C Aromatic Resin	5	TMETD	3
Stearic Acid	1	Specific Gravity	1.30

Cure Rate, 150ºC, T_{90} minutes	8
Mooney Scorch, 121ºC, T_5 minutes	30
Viscosity, $ML_4$100	68
Garvey Extrusion	
Rate, m/min	6
Die Swell, %	12
Surface	Glossy

20 minute cure, 150ºC:	Original	72 hrs, 121ºC
Hardness	72	85
M300, MPa	5.1	9.3
Tensile, MPa	5.9	9.3
Elongation, %	620	300
Die C Tear, kN/m	37	37

Compression Set, %	
1 day, 70ºC	18
3 days, 100ºC	46

Fluid Immersions	#3 Oil, 3 days, 100ºC	Fuel B, 7 days, 70ºC
% Volume Change	-2.8	7.3
Hardness	81	55
Tensile, MPa	6.6	5.9
Elongation, %	450	280
Die C Tear kN/m	37	17.5

NBR 19

Elastomer: NBR Durometer: 68
Application: Textile adhesion; Brass adhesion

NBR 1092-30	100	Zinc Oxide	5
65 m^2/g Silica	65	Sulfur	0.5
Magnesium Oxide	1.5	MBS	1
TMQ	2	DTDM	2
ODPA	2	TETD	0.3
Resorcinol Resin	3	Cyrez 963P	5
Stearic Acid	2		
DOP	15	Specific Gravity	1.27

ODR Cure Rate, 154ºC, T_{90} minutes	30
Mooney Scorch, 121ºC, T_5 minutes	>30
Viscosity, ML_4100	43

30 minute cure, 154ºC:	Original	72 hrs, 150ºC
Hardness	68	58 (Durometer C)
M100, MPa	1.0	
M300, MPa	4.8	
Tensile, MPa	12	7.5
Elongation, %	670	60

Compression Set, %, 3 days, 100ºC	69

Adhesion to Fabric and Brass, kN/m

Cure: 45 minutes, 154ºC

Brass Strip	>8.8
Untreated Nylon	>25
Treated Polyester	13

Polyester Cord Stability (45 minute cure, 154ºC)

Tensile, N, Original	147
4 hours, 175ºC	142

NBR 20

Elastomer: NBR Durometer: 69
Application: Heat Resistance; Hose; Soling

1st Stage		2nd Stage	
Paracril BJLT HX	100	Zinc Oxide	5
Mercaptosilane A189	1	PEG 4000	1.5
65 m^2/g Silica	35	Sulfur	0.3
150 m^2/g Silica	25	MBS	1.5
DOP	20	DTDM	1.0
Stearic Acid	1.5	TETD	1.0
		Specific Gravity	1.20

ODR Cure Rate, 154ºC, T_{90} minutes	16
Mooney Scorch, 132ºC, T_5 minutes	15
Viscosity, ML_4100	63

30 minute cure, 154ºC:	Original	5 days, 150ºC
Hardness	69	88
M300, MPa	17.1	
Tensile, MPa	17.5	11.4
Elongation, %	330	100
Die C Tear, kN/m	6.1	

Compression Set, %, 70 hrs, 121ºC	36
NBS Abrasion Index	190

Fluid Immersions, 70 hrs, 150ºC	ASTM #3	WSX7997:D
Hardness	67	70
Tensile, MPa	17.8	16.4
Elongation, %	340	330
%Volume Change	2	-7

NBR 21

Elastomer: NBR Durometer: 70
Application: Heat resistance; Tear strength

Banbury 1		Banbury 2	
NBR 1091-50	100	Zinc Oxide	5
150 m^2/g Silica	50	Magnesia	1
DOP	15	DEG	2
ODPA	2	Sulfur	0.4
TMQ	1	MBS	2
Stearic Acid	2	TMETD	2
		Specific Gravity	1.20

Cure Rate, 150°C, T$_{90}$ minutes	17
Mooney Scorch, 130°C, T$_5$ minutes	16
Viscosity, ML$_4$100	65

20 minute cure, 150°C	Original	72 hrs, 150°C
Hardness	71	89
M300, MPa	2.7	
Tensile, MPa	21	18.5
Elongation, %	680	450

MG Trouser Tear kN/m, 23°C	25
100°C	7.9
Compression Set, %	
3 days, 100°C	66
3 days, 121°C	85
DeMattia Flex, 23°C, kc to 0.6” Cut	13
Water Immersion, 82°C, % Volume Change	
1 day	8.0
7 days	10.0
14 days	8.0

Goodrich Flexometer (30 minute cure, 150°C), 100°C; 17.5%			
MPa	1.0	1.3	1.6
Static Compression	16	21	28
% Set	7.1	11	14
Heat Build-Up °C	28	33	40

NBR 22

Elastomer: NBR Durometer: 70 Black
Application: Textile adhesion

NBR 1052	100	Stearic Acid	2
150 m^2/g Silica	30	Zinc Oxide	5
SRF N770	50	<u>2nd Stage</u>	
DOP	25	Hexa(50% MB)	3
Octamine	1	Sulfur	1.5
Resorcinol	2.5	MBS	1.7
		Specific Gravity	1.22

ODR Cure Rate, 154ºC, T_{90} minutes	25
Mooney Scorch, 132ºC, T_5 minutes	27
Viscosity, ML_4100	45

30 minute cure, 154ºC	Original	70 hrs, 121ºC
Hardness	70	85
M300, MPa	6.5	
Tensile, MPa	14	13
Elongation, %	550	230

Compression Set, %, 70 hrs, 100ºC	70

Adhesion to Untreated fabric, kN/m		
Original:	Nylon	Rayon
30 minutes, 154ºC	16	5.3
60 minutes, 154ºC	16	6.1
5 days, 60ºC		
30 minutes, 154ºC	7.9	

(no adhesion to brass)

NBR 23

Elastomer: NBR Durometer: 70
Application: Tear strength; Flex life; Heat resistance

Krynac 805	100	DOP	10
150 m^2/g Silica	50	Zinc Oxide	5
Octamine	2	Sulfur	0.4
TMQ	1	MBS	2
Stearic Acid	2	TMETD	2
25C Aromatic Resin	10	Specific Gravity	1.20

Activator:	Magnesia-7 phr	PEG 4000-2 phr
ODR Cure Rate, 154ºC, T_{90} minutes	11	11
Mooney Scorch, 121ºC, T_5 minutes	11	25
Viscosity, ML_4100	60	83

20 minute cure, 154ºC:	Original	Aged*	Original	Aged*
Hardness	70	85	71	86
M300, MPa	2.7		1.9	
Tensile, MPa	21	11	21	10
Elongation, %	800	250	770	210

*3 days, 150ºC

Trouser Tear, Grooved, kN/m, 23ºC	22	26
70ºC	18	12
100ºC	7.8	7.8
Compression Set, %		
70 hrs, 100ºC	47	38
70 hrs, 150ºC	81	84
DeMattia Flex, 20ºC, kc to 500%		
Original	100	35
3 days, 121ºC	90	45
Monsanto Flex Fatigue, HC		
Original	59	18
3 days, 121ºC	55	46
Goodrich Flexometer 100ºC, 22.5%; 1 MPa; 20’		
Hardness	68	70
Set, %	22	13
Heat Build-Up, ºC	56	47

NBR 24

Elastomer: NBR Durometer: 68-73
Application: Flex life; Heat resistance; Low heat build-up

NBR (med. ACN)	100	DOP	10
Mercaptosilane	1.2	25C Arom. Resin	10
150 m^2/g Silica	50	Zinc Oxide	5
Octamine	2	Sulfur	0.4
TMQ	1	MBS	2
Stearic Acid	2	TMETD	2
		Specific Gravity	1.20

NBR:	Kyrnac 805	Hycar 1052
ODR Cure Rate, 154°C, T_{90} minutes	19	12
Mooney Scorch, 121°C, T_5 minutes	24	23
Viscosity, ML$_4$100	64	68

20 minute cure, 154°C:	Original	Aged*	Original	Aged*
Hardness	73	85	68	83
M100, MPa	1.0		0.95	
M300, MPa	6.5		5.2	
Tensile, MPa	23	9.7	22	7.9
Elongation, %	640	170	670	200

*3 days, 150°C

ASTM #3 Oil Immersion at 150°C	Duro.	Δ Vol., %	Duro.	Δ Vol., %
1 day	73	0.8	73	0.1
3 days	83	-0.1	76	-0.8
14 days	82	1.5	87	-0.3

	Kyrnac 805	Hycar 1052
Trouser Tear, Grooved, kN/m		
23°C	15	12
70°C	8.0	8.0
100°C	5.1	6.1
Compression Set, %		
70 hrs, 100°C	39	42
70 hrs, 150°C	71	78
DeMattia Flex, 20°C, kc to 500%	100	90
3 days, 121°C	40	100
Goodrich Flexometer 100°C, 22.5%; 1 MPa; 20’		
Hardness	72	68
Set, %	8	8
Heat Build-Up, °C	45	43

NBR 25

Elastomer: NBR Durometer: 69-71
Application: Low heat build-up; NBR comparisons

NBR	100	PEG 3350	1.5
Silane A189	1	Sulfur	0.3
150 m^2/g Silica	25	MOR	1.5
65 m^2/g Silica	35	DTDM	2
DOP	20	TETD	1
Zinc Oxide	1.5		
TMQ	5		
Stearic Acid	1.5	Specific Gravity	1.0

NBR:	BJLT	685	40E65
MDR Cure Rate, 150ºC, T$_{50}$ minutes	11	11	15
Mooney Scorch, 121ºC, T$_5$ minutes	30+	30+	30+
Mooney Viscosity, ML$_4$100	44	28	49
154ºC cure: Durometer, 23ºC/100ºC	71/68	72/70	69/66
Goodrich Flexometer: 100°C; 22.5%; 1 MPa			
Dynamic Drift, %	0	1.5	2.2
Permanent Set, %	3.5	3.4	5.2
Heat Build-Up, °C	19	21	20
Compression Set, %, 70 hrs, 100°C	40	46	53
Die C Tear, kN/m	40	40	46
Original:			
M300, MPa	16	13	11
Tensile, MPa	18	16	17
Elongation, %	340	365	475
Aged 700 hrs, 115ºC:			
Reflux: Hardness	80	79	78
Tensile, MPa	17	14	16
Elongation, %	215	185	230
Oven: Hardness	89	95	89
Tensile, MPa	3.8	5.8	4.8
Elongation, %	15	2	25
DIN Abrasion Loss, ml	150	175	178
NBS Abrasion Index	145	135	118
Pendulum Rebound (Z), %, 23°C	37	39	27
100°C	66	66	62

NBR 26

Elastomer: NBR Durometer: 73
Application: Zinc-free; Tensile strength

Banbury 1		Banbury 2	
NBR 683B	100	Sulfur	1
150 m^2/g Silica	50	TBBS	2
DOP	10	DPTH	1
25C Aromatic Resin	10	MDB	1
ODPA	2		
Stearic Acid	1	Specific Gravity	1.21

Cure Rate, 150ºC, T_{50} minutes	12
T_{90} minutes	30
Mooney Scorch 130ºC, T_5 minutes	18
Viscosity, ML_4100	64
30 minute cure, 150ºC:	
Durometer	73
M300, MPa	5.3
Tensile, MPa	28
Elongation, %	730
Pendulum Rebound (Z), %, 23ºC	30
100ºC	48
PICO Abrasion Index, 23ºC	80
70ºC	115

NBR 27

Elastomer: NBR Durometer: 75
Application: MRG; Hose; Heat resistance

Banbury 1		Banbury 2	
NBR 40-65	100	Sulfur	0.2
150 m^2/g Silica	22	TMTD	1.5
Ciptane I	43	TETD	1.5
Plasticizer SC	10	TBBS	2.0
ZMTI	2		
Antioxidant 445	2		
MC Wax	2		
Stearic Acid	0.5		
PEG 3350	1		
Zinc Oxide	5	Specific Gravity	1.24

	Original	Shelf Aged 1 Week
Cure Rate, 150ºC, T_{90} minutes	7.3	6.6
Mooney Scorch 121ºC, T_5 minutes	19	19
Viscosity, ML_4100	76	78

Garvey Extrusion: 121ºC; 75 rpm	
Die Swell, %	51
Edge-Surface Rating	10A

12 minute cure, 150ºC	Original	3 days, 150ºC	28 days, 125ºC*
Durometer	74	86	87
M20, MPa	1.3	2.5	2.6
M300, MPa	12		
Tensile, MPa	27	24	25
Elongation, %	530	355	370

*90 Durometer and 24% E_8 after 28 days 135ºC

Compression Set, %, 3 days, 100ºC	55.9
Glass Transition: E" Peak	-7.4ºC
Fuel C Immersion, 2 days, 23ºC	
% Volume Increase	32.3
Goodrich Flexometer: 100ºC; 22.5%; 1 MPa	
Static Compression, %	11
Dynamic Compression, %	6.2
Drift, %	2.4
Set, %	6.9
Heat Build-Up, ºC	25

NBR 28

Elastomer: NBR/PVC Durometer: 75
Application: MIL-C-85052

NBR/PVC (OZO)	100	Zinc Oxide	3
220 m^2/g Silica	35	Stearic Acid	2
Antimony Oxide	5	DTDM	2
Titanium Dioxide	3	TMETD	2
TBEP	10		
ODPA	1	Specific Gravity	1.28

MDR Cure Rate, 150ºC, T_{50} minutes	7.6
T_{90} minutes	14
Mooney Scorch 121ºC, T_5 minutes	16
Mooney Viscosity, ML_4100	60
Durometer, 23ºC	75
100ºC	61

20 minute cure, 150ºC:	Original	Aged[1]	Aged[2]	Aged[3]
Durometer	79	87	89	95
M300, MPa	6.0			
Tensile, MPa	22	15	19	18
Elongation, %	580	205	360	85

[1] 70 hrs, 135ºC [2] 300 hrs, 115ºC [3] 700 hrs, 115ºC

Die B Tear, kN/m	60
Compression Set, %, 70 hrs, 100ºC	54
DIN Abrasion Loss, ml	183
Pendulum Rebound (Z), %, 23ºC	19
100ºC	54

NBR 29

Elastomer: NBR Durometer: 76
Application: Abrasion; Zinc-free

NBR 685B	100	Zinc Oxide	1
Ciptane I	50	Sulfur	0.75
DOS	10	TBBS	2
CI 25C Resin DLC	10	DPTH	2
TMQ	1	HMT	1
		Specific Gravity	1.20

Cure Rate 150ºC, T_{90} minutes	4.2
Mooney Scorch, 130ºC, T_5 minutes	7
Viscosity, $ML_4$100	62
Durometer, 23ºC	76
100ºC	72

8 minute cure, 150ºC:	Original	70 hrs,140ºC	700 hrs,115ºC
Durometer	76	86	90
M300, MPa	12.6		
Tensile, MPa	26	12	16
Elongation, %	490	135	145

MG Trouser Tear, kN/m	11
Die C Tear, kN/m	42
PICO Abrasion Index	96
Compression Set, %, 70 hrs, 100ºC	74
Pendulum Rebound (Z), %, 23ºC	30
100ºC	58

NBR 30

Elastomer: NBR Durometer: 77
Application: Tear strength, Zinc-free

NBR 685B	100	Sulfur	1.5
220 m^2/g Silica	45	HMT	2
DOP	10	TBBS	2
25C Resin, DLC	10	DPTH	1
TMQ	1	DPG	1.5
Zinc Oxide	1	Specific Gravity	1.19

MDR Cure Rate, 150ºC, T_{50} minutes	4.5
Mooney Scorch, 121ºC, T_5 minutes	17
Mooney Viscosity, ML $_4$100	79

20 minute cure, 150ºC:	
Durometer, 23ºC	77
100ºC	71

10 minute cure, 150ºC:	Original	700 hrs, 115ºC
Durometer	75	90
M20, MPa	1.1	
M300, MPa	4.0	
Tensile, MPa	29	14
Elongation, %	770	65

MG Trouser Tear, kN/m	40
PICO Abrasion Index	83
Compression Set, %, 70 hrs, 100ºC	100

NBR 31

Elastomer: NBR Durometer: 78
Application: Low set; Low viscosity, Peroxide cure

NBR N612	100	Vul-Cup 40KE	4
Silane A189	1		
65 m^2/g Silica	70		
TMQ	2		
Stearic Acid	2		
DOS	16		
PEG 4000	1.5		
Zinc Oxide	5		

ODR Cure Rate, 165ºC, T_{90} minutes	23
Mooney Scorch, 133ºC, T_5 minutes	12
Viscosity, ML_4100	32
ODR Minimum	2

30 minute cure, 166ºC	Original	72 hrs, 150ºC
Hardness	78	92
M300, MPa	7.3	
Tensile, MPa	10.7	13.5
Elongation, %	170	40
Die C Tear, kN/m	53	40

Compression Set, %, 70 hrs, 100ºC	11

Low Temperature Durometer Hardness	
4 hours, -40ºC	85

NBR 32

Elastomer: NBR/PVC Durometer: 80
Application: Extrusions; Heat resistance

NBR/PVC 70/30	100	Sulfur	1.5
35 m^2/g Silica	75	MBTS	1.5
DOP	20	TMTD	0.3
Zinc Oxide	3		
Stearic Acid	1	Specific Gravity	1.29

Cure Rate, 150ºC, T_{90} minutes	6
Mooney Scorch, 121ºC, T_5 minutes	20
Viscosity, ML_4100	85

6 minutes cure, 150ºC:	Original	72 hrs, 121ºC
Hardness	80	88
M300, MPa	5.9	
Tensile, MPa	9.3	8.5
Elongation, %	500	280
Die C Tear, kN/m	32	35

Compression Set, %	
1 day, 70ºC	39
3 days, 100ºC	67

Fluid Immersions	#3 Oil 3 days, 100ºC	JP4 Fuel 7 days, 70ºC
% Volume Change	8	18
Hardness	75	60
Tensile, MPa	10.3	4.7
Elongation, %	450	290
Die C Tear, kN/m	28	7.0

NBR 33

Elastomer: NBR Durometer: 78
Application: Brass adhesion

NBR 386B	100	Magnesia	2
150 m^2/g Silica	30	Sulfur	1.5
35 m^2/g Silica	35	DTDM	1
DOP	18	TMETD	1
TMQ	1.5	HMMM 67%	3
ODPA	1.5	R-F Resin	3
Zinc Oxide	3		
Stearic Acid	2	Specific Gravity	1.25

MDR Cure Rate, 150ºC, T_{50} minutes	4.5
T_{90} minutes	20
Mooney Scorch, 121ºC, T_5 minutes	13
Mooney Viscosity, ML_4100	56
30 minute cure, 150ºC:	
Durometer, 23ºC	76
100ºC	71
Brass Wire (6 + 3) Pull-out, N/25 mm	
Low mold pressure	700
High mold pressure	530
% Rubber cover	50
Stress/Strain	
Durometer	80
M300, MPa	15
Tensile, MPa	20
Elongation, %	440
MG Trouser Tear, kN/m	9.3
PICO Abrasion Index, 23ºC	85
100ºC	47
Compression Set, %, 70 hrs, 100ºC	67
Pendulum Rebound (Z), %, 23ºC	19
100ºC	56

NBR 34

Elastomer: NBR Durometer: 79
Application: Zinc adhesion; Zinc-free

NBR 386B	100	Zinc Oxide	3
150 m^2/g Silica	30	Magnesia	3
35 m^2/g Silica	35	TMETD	0.4
DOP	20	DPTH	0.4
ODPA	1.5	DTDM	2
TMQ	1.5	Sulfur	1.5
Amide Wax	1		
Sodium Carbonate	20	Specific Gravity	1.0

MDR Cure Rate, 150°C, T_{50} minutes	6.8
T_{90} minutes	10
Mooney Scorch, 121°C, T_5 minutes	21
Mooney Viscosity, $ML_4$100	51
Durometer, 23°C	79
100°C	72

Pull-out adhesion to galvanized cable (2 mm)	N/25 mm	% Cover
20 minute cure, 150°C	500	10
40 minute cure, 150°C	730	40
60 minute cure, 150°C	630	20

Stress/Strain	Original	700 hrs, 110°C
M300, MPa	7.6	
Tensile, MPa	16	20
Elongation, %	510	95

Water Immersion, % swell, 70 hrs, 70°C	3.7
Compression Set, %, 70 hrs, 100°C	85
Pendulum Rebound (Z), %, 23°C	19
100°C	58

NBR 35

Elastomer: NBR/PVC Durometer: 80
Application: Textile adhesion

Paracril OZO	100	Sulfur	1.3
65 m^2/g Silica	60	2nd Stage	
DOP	20	MBS	1.5
Stearic Acid	2	TMTM	0.5
Zinc Oxide	5	Cohedur RL	5
Microcrystalline Wax	1	Specific Gravity	1.30

ODR Cure Rate, 150ºC, T_{90} minutes	18
Scorch, T_2 minutes	12
Viscosity, ML_4100	70

30 minute cure, 150ºC:	
Hardness	80
M300, MPa	8.2
Tensile, MPa	12
Elongation, %	600

Adhesion to Untreated Fabric, kN/m	Nylon	Rayon
Press, 30 minutes, 150ºC	11	7.0
Heater, 60 minutes, 100ºC	8.7	3.5

NBR 36

Elastomer: NBR Durometer: 80
Application: Flex life; Heat resistance; Cadmium oxide

Hycar 1091-50	100	PEG 4000	2
150 m^2/g Silica	35	Zinc Oxide	5
65 m^2/g Silica	35	Magnesia	7
TMQ	1	CdO	5
ODPA	2	Sulfur	0.4
DOP	20	TMETD	1.5
Stearic Acid	2	DTDM	2
		Specific gravity	1.30

ODR Cure Rate, 154ºC, T_{90} minutes	16
Mooney Scorch, 130ºC, T_5 minutes	14
Viscosity, ML_4100	50
Garvey Extrusion, 121ºC	
Swell, %	33
Edge and Surface	10A

30 minute cure, 154ºC:	Original	3 days, 150ºC	7 days, 150ºC
Hardness	80	71	80
M300, MPa	5.1		
Tensile, MPa	12	13	12
Elongation, %	600	200	55
180° Bend			Flexible

Trouser Tear, Grooved; kN/m, 23ºC	26
100ºC	6.1
Compression Set, %, 70 hrs, 100ºC	66
PICO Abrasion Index	63
Ross Flex, aged 10 days, 100ºC,	
kc to 500%	55
Durometer	86

NBR 37

Elastomer: NBR Durometer: 80
Application: Seals

NBR N300	100	PEG 3350	1.5
Silica	50	Sulfur	1.5
Barytes	1	MBTS	1.5
Polyester G25	6.5	MBS	1.0
TBEP	3.5	TMETD	1.5
Stearic Acid	2		
Zinc Oxide	5	Specific Gravity	1.25

Silica:	180 m^2/g Silica	Ciptane 1
MDR Cure Rate, 150°C, T_{90} minutes	3.0	4.0
Mooney Scorch, 121°C, T_5 minutes	18	16
Mooney Viscosity, ML_4100	70	72
Durometer, 23°C/100°C	80/72	81/73
Original:		
M20, MPa	1.8	1.7
M300, MPa	8.5	16
Tensile, MPa	18	17
Elongation, %	430	325
Aged 70 hrs, 121°C:		
M20, MPa	1.9	2.4
Tensile, MPa	16	16
Elongation, %	360	250
Immersed 70 hrs in Reference Fuel C:		
M20, MPa	0.66	0.87
Tensile, MPa	3.6	5.7
Elongation, %	165	135
Volume %	50	57
Immersed 70 hrs, 121°C in IRM 903:		
Volume %	3	3
Tear Strength, Die B, kN/m	46	48
PICO Abrasion Index, 23°C/100°C	60/30	77/39
DIN Abrasion Loss, ml	256	215
Pendulum Rebound (Z), %, 23°C	15	14
100°C	57	59
Goodrich Flexometer: 100°C; 22.5%; 1 MPa		
Permanent Set, %	4	3
Heat Build-Up, °C	32	29

NBR 38

Elastomer: NBR	Durometer: 86
Application: Rice roll	

Banbury 1		Banbury 2	
NBR 34-35	100	ZnO 168	5
150 m^2/g Silica	70	TBBS	1
Silane A189	1	DTDM	1
Aromatic 25C Resin	8		
DOP	5		
Stearic Acid	2		
Sulfur	7	Specific Gravity	1.27

Cure Rate, 150ºC, T_{90} minutes	38
Mooney Scorch, 121ºC, T_5 minutes	30+
Viscosity, $ML_4$100	78

50 minute cure, 150ºC:

Durometer, 23ºC/100ºC	86/82
M20, MPa	2.5
M100, MPa	11.6
Tensile, MPa	21.2
Elongation, %	165

PICO Abrasion, mg Loss, 70ºC	25
100ºC	38
Pendulum Rebound (Z), %, 23ºC	19.0
100ºC	75.0

Goodrich Flexometer: 100ºC; 17.5%; 1 MPa

Static Compression, %	3.8
Dynamic Compression, %	-2.5
Drift, %	18
Set, %	2.0
Heat Build-Up, ºC	11

NBR 39

Elastomer: NBR Durometer: 88
Application: Rolls; Peroxide

NBR 34-35	100	Zinc Oxide	5
65 m^2/g Silica	30	Sulfur	0.1
150 m^2/g Silica	10	Saret 500	15
Treated Clay	25	BPDIB 40%	3.6
Titanium Dioxide	5		
TMQ	2		
Stearic Acid	1	Specific Gravity	1.18

MDR Cure Rate, 160ºC, T_{50} minutes	12
Mooney Scorch, 121ºC, T_5 minutes	30+
Mooney Viscosity, $ML_4$100	38

45 minute cure, 160ºC:	Original	170 hrs, 125ºC
Durometer, 23ºC	88	92
100ºC	85	
M20, MPa	3.9	5.7
M100, MPa	12	
Tensile, MPa	15	17
Elongation %	150	100

MG Trouser Tear, kN/m	7.7
PICO Abrasion Index	104
NBS Abrasion Index	90

Compression Set, %, 70 hrs, 100ºC	21
Goodrich Flexometer, 100ºC; 22.5%; 1 MPa:	
Static Compression, %	5.0
Permanent Set, %	1.1
Heat Build-Up, ºC	28

Pendulum Rebound (Z), %, 23ºC	24
100ºC	58

NBR 40

Elastomer: NBR Durometer: 95
Application: Rolls, Zinc Free

NBR 683	100	Sulfur	5	
HSR S6B	10	Zinc Oxide	1	
Ciptane 255LD	77	TBBS	2	
CI 25C Resin	10	HMT	2	
DOP	5	DPTH	1	
ODPA Antioxidant	1	Specific Gravity		1.28

MDR Cure Rate, 150ºC, T_{50} minutes	6.7
Mooney Scorch, 121ºC, T_5 minutes	10
Mooney Viscosity, ML_4100	120
40 minutes, 150ºC:	
Durometer, 23ºC	96
100ºC	90
Abrasion Tests	
NBS Index	175
PICO, 100ºC, mg loss*	11
*normal cure loss 20-40 mg	
Goodrich Flexometer, 100ºC; 15%; 1 MPa	
Static Compression, %	1.9
Dynamic Drift, %	4.8
Permanent Set, %	7.8
Heat Build-Up, ºC	20
Stress/Strain	
M20, MPa	4.9
M300, MPa	12.7
Tensile, MPa	28
Elongation, %	210
Pendulum Rebound (Z), %, 23ºC	21
100ºC	90

Appendix A

COMPOUNDING BASICS

A.1 THE COMPOUND

Rubber compounding can be defined as the science of mixtures. An elastomer compound is a mixture of an elastomer and a wide variety of chemicals, soluble and insoluble, which have been mixed according to a specific formula in a closed chamber (e.g., Banbury, Shaw, Moriyama mixers) or on a two roll mill. The gigantic thermoplastic lump of mixed compound is subsequently formed into sheets, tubes or other shapes, and vulcanized (crosslinked) in its final form.

A rubber compound is made up of three major classes of chemicals: elastomers, fillers and curatives. Additional classes include antioxidants and processing chemicals such as oils and resins. Fillers include reinforcing materials such as carbon black and precipitated silica, and extender minerals such as clay, talc and whiting. Curatives are those chemicals responsible for vulcanization or crosslinking. They include sulfur, accelerators, and activators such as zinc oxide and stearic acid. Without these modifying ingredients an elastomer alone is generally useless for commercial applications. Table A.1 contains a list of the major material classes and the compound properties each group supplies. Compounding research and development consists of evaluating the properties of compounds in which materials and their concentrations have been systematically varied. The objectives are to determine the mechanisms by which each material functions, and to develop compounds with certain well defined properties.

A.2 THE FORMULA

The formula defines the compound and determines its properties. It is a list of the ingredients and the amount of each, by weight, expressed as parts per hundred (phr) of elastomer. Thus, each formula begins with 100 parts of elastomer. Filler contents range from 30 to 70 phr for reinforcing materials, to 300 phr for extender materials. Softener oils, which control compound hardness and processing properties, can range from 5 to 150 phr. Most sulfur cured formulas contain from 0.3 to 3.0 phr sulfur. Lower concentrations are supplemented with sulfur donating accelerators. Sulfur or other types of crosslinkers are required to transform the thermoplastic compound to its final thermoset, crosslinked or cured state. Free radical curing by peroxides provides advantages in age resistance, low set and color. In silica compounds, peroxide curing eliminates the competing reaction between silica and soluble zinc oxide.

Table A.1 Formula Components and Associated Properties

Formula Component	Associated Properties
Elastomer	Resilience
A. Natural rubber	Environmental Resistance:
B. Synthetic elastomer	Temperature; oil; UV; Ozone; solvents
C. Blend	Reinforcement
	Processing requirements
	Cost
Filler	Reinforcement (Abrasion, Tear)
A. Carbon black	Durometer hardness
B. Silica	Processing (viscosity)
C. Extenders	Color - translucence
	Cost
Crosslinking (Cure) System	Cure state: (Rheometer)
A. Sulfur; peroxide	Hardness;
B. Accelerators	Modulus; Set; Heat build-up
C. Activators	Cure Rate
	Scorch safety
	Heat and Aging resistance
	Cost
Plasticizer (Softener)	Processing:
A. Oils	Viscosity; Mixing; Extrusion;
B. Esters	Calendering
C. Resins	Hardness
	Elastomer Compatibility
	Low temperature Flexibility
	High temperature Stability
	Cost
Antidegradant	Heat resistance
	Ozone resistance
	Staining; Color
Miscellaneous	Adhesion promoter
	Cell formation
	Coupling silica to elastomer

A.3 DESIGN OF FORMULAS

Formula design involves the judicious selection of ingredients and their concentrations, to be mixed together to create an elastomer compound which will satisfy the processing and performance requirements of a specified use. Formula design projects fit into two categories: 1) modification of an existing formula, or 2) development of a new formula to meet specific requirements. It is likely that modification of existing compounds accounts for the majority of commercial compounding projects.

The bifurcation of the design requirements into the two categories of *processing* and *performance* is crucial to an understanding of the design process. This division reflects the physical change which compounds undergo during manufacture: the crosslinking of elastomer molecular chains (vulcanization or curing) which changes the compound’s physical nature from thermoplastic to thermosetting. After curing, remnants of plastic behavior are still present, to an extent determined by crosslink density and filler content. The combined presence of plastic or viscous flow and elastic response to deformation give rise to the term *viscoelasticity* to describe the physical nature of a crosslinked (cured) elastomer. The viscous component leads to high tear strength, high set and heat build-up, and poor dynamic properties. The elastic component provides the reverse of these effects; it can be promoted by the use of highly unsaturated elastomers, low filler content, efficient cure systems or silane coupling. Compound properties associated with flow or elastic responses are noted in Table A.2, where compound properties are classified according to their dependence on predominantly elastic or plastic behavior, although this is not applicable for hardness, low strain modulus or abrasion resistance. In many silica compounding projects a major objective is to attain a viable balance between elastic and plastic behavior.

Table A.2 Compound Properties from Elastic and Plastic Behavior

Elastic	Plastic (Viscous)
Resilience (rebound)	High Trouser Tear Strength
Hysteresis:	
Low Heat Build-up	High Elongation at Break
Low Dynamic Set	
Low Creep	Low Flex Cracking
Low Stress Relaxation	Low Fatigue Life

Laboratory compounding experiments are conducted in groups of formulas; each group usually contains from 8 to 32 separate compounds. Variables include formula ingredients and their concentrations in phr units, and, in some cases, processing variations. Tabular compounding reports contain a column for each formula and its test properties. Experimental designs include a saturated scheme in which each variable material is evaluated at all pertinent concentrations, or a statistical design, which drastically reduces the number of formulas required. Compound design objectives include an evaluation of new or replacement ingredients (e.g., replacement of black by silica) or development of a formula to meet certain test properties, as dictated by the application in question. In much of the work described in this book the objective has been to explore the mechanisms of silica reinforcement and the compounding behavior of reinforcing silica. The modest number of occasions on which a successful resolution of compounding objectives was attained are listed in the Formulary sections of each chapter.

A.4 FORMULA MIXING

The mixed formula is called the compound. Mixing of formula ingredients takes place in a closed container under mechanical pressure. The mixing chamber contains two rotors with surface fins, which rotate in opposite directions. Dispersion of ingredients takes place by a shearing action between rotor and chamber wall surfaces. The most frequently used machine is the Banbury mixer, named after its inventor, Fernley Banbury. Mixing can also be carried out on open mill equipment where two parallel, smooth surface, counter rotating rolls disperse ingredients by shear in the narrow space (nip) between the rolls. The open mill generally provides superior dispersion, but is limited in batch size. Each internal mixer discharges mixed compound onto a two roll mill which transforms compound from lump to sheet form.

In Banbury mixing, the order in which ingredients are added is critical. This is particularly true for silica reinforced compounds where undesirable reactions can occur between silica and zinc oxide. Premature reaction of curatives (sulfur and accelerators) is also a mixing problem. This reaction, called *scorching*, forms partial crosslinking which reduces the plastic nature of the compound and makes it unfit for subsequent milling, extrusion or calendering operations. Similar problems can be encountered when silane coupling agents are present in the mixer.

A.5 DISPERSION

The term dispersion relates to the filler and has two distinct meanings. The most obvious is the appearance of visible particles in the mixed compound. This is a particular problem with silica because white particles are immediately evident. Poor dispersion of carbon black is not visible, but appears in the form of degraded physical properties. Silica particles represent only an insignificant part of the total amount, and have little or no effect on reinforcement or performance. As noted in Chapter 1, visible, 300 micron silica particles relate to gel content, and appear mainly in rotary dried, unmilled, non-dusting grades.

The most important aspect of dispersion is the ultimate size of the filler particle or agglomerate in the cured compound. This size, measured in terms of diameter in nanometers by electron microscopy, accurately predicts the reinforcement properties of silica. As noted in several chapters, the ultimate size of silica primary and agglomerate particles is affected by mixing variables and the presence of silane additives.

A.6 PROCESSING PROPERTIES

Compound characterization is generally divided into two sections: processing and physical test properties. Processing refers to the behavior of the uncured, thermoplastic compound in terms of viscosity, cure rate and crosslinking. The instrument used to determine curing properties is a *rheometer*. In the present work, crosslinking is defined as the difference between rheometer minimum and maximum values, and reflects the extent of polymer chain bonding by sulfur or carbon linkages. This is also referred to as “state of cure.” Cure rate, in contrast, reflects the speed of the crosslinking reaction in terms of the slope of the middle part of the rheometer curve. The initial part of the curve indicates the tendency to crosslink prematurely, a reaction called *scorching*. The final section of the rheometer curve is generally a plateau. The extent to which this plateau drops in value at long cure times is called *reversion*, which relates to losses in hardness and reinforcement properties in the compound after long cure times.

Scorch safety is the time lapse between initial heating and the onset of crosslinking, This is generally determined by the Mooney viscometer operated at processing temperatures, i.e., 121^{o}C or, to accelerate the testing, at 135^{o}C. Scorch rates (time to 5 point rise in viscosity) acceptable for production will vary from 10 to 30 minutes at 121^{o}C. In addition to the compound’s laboratory scorch time, factory scorch times depend on the heat build-up in the machinery involved, the volume of compound being processed, and the skills of the factory personnel.

As the name indicates, the Mooney viscometer was originally designed to measure compound viscosity at a low strain rate at 100^{o}C. This is an important property for silica compounds, which are inclined to be characterized by higher than normal viscosities.

Shrinkage during processing of uncured compounds is sometimes described as “nerve.” It relates to the ability (or lack of it) to retain desired dimensions after deformation during milling, extrusion or calendering. The network structure of silica is effective in reducing shrinkage. When zinc oxide is mixed together with silica, this ability to reduce shrinkage disappears.

A.7 PHYSICAL PROPERTIES

Hardness or *durometer* is a property widely used to classify elastomer compounds. It is expressed by an arbitrary scale of 10 to 95 units (durometer A) which reflect the depth to which a rounded tip indentor deforms the compound surface. Higher numbers denote harder compounds. Silica reinforced compounds tend to give somewhat higher durometer readings than those based on comparable amounts of carbon black. The compounds in the formulary sections of this book are listed in order of ascending hardness.

One of the oldest methods of compound evaluation involves the extension of dumbbell shaped specimens to their breaking point. This determines the *tensile strength* and *ultimate elongation*, expressed as force per area (psi or MPa), and percent. The results are frequently called stress-strain data. Although tensile values of silica and carbon black compounds are comparable, elongations for silica compounds of comparable hardness are frequently double those for black. During extension, the force required to reach a specified percent elongation is also recorded. This is termed *extension modulus* and, in the 50% to 700% range, is characteristically low with silica reinforcement. Both low modulus and high elongation values reflect a low level of silica-to-polymer bonding. When this bond is improved by silane coupling, elongation and modulus values comparable to those with black are obtained. None of these stress-strain properties is particularly useful in designing elastomer compounds for commercial applications. They are, however, of considerable use in noting compound changes during accelerated aging and chemical exposure tests. This function provides a valuable measure of aging and chemical resistance.

Aging resistance is also evaluated by *compression set* testing. Button specimens, after compression for various times and temperatures, are measured to determine the extent of their return to original dimensions. This test is a measure of the efficiency of sulfur crosslinking. Polysulfide crosslinks tend to rearrange during compression deformation and produce a new crosslink configuration, which prevents a return to original dimensions. Monosulfide crosslinks are more stable to rearrangement, and thus produce low set values. Silica compounds usually contain more polysulfide crosslinks and thus produce higher set values. This problem can readily be solved by use of the ultra accelerators and reduced sulfur content cure systems described in several chapters. The easiest remedy for the high set problem is the addition of a silane coupling agent. In all cases, low compression set is achieved at the expense of trouser tear strength.

Extremely high *tear strength* is perhaps the most characteristic property of silica reinforced compounds. In this respect the importance of the tear test procedure cannot be over emphasized. A trouser specimen configuration not only shows the wide advantage of silica over black, but also provides the most reliable prediction of product performance. Die C and other tear test procedures are quite deficient in these respects.

Abrasion resistance is probably the surest indication of elastomer reinforcement. There are a number of different procedures, most of which are based on the use of rotating abrading paper. The PICO test employs rotating parallel knives with vacuum suction to remove abraded material. Its predictive success is somewhat limited by the influence of compound hardness. The DIN test employs a figure 8 abrasion path across the surface of a rotating abrasive paper-covered cylinder. It enjoys international recognition and has, together with PICO, been used for many of the compounding studies reported herein. The NBS procedure is the oldest method of abrasion evaluation and is now generally confined to soling applications. Unfortunately, the lubricating influence of some compounds produces deceptively high values. None of these laboratory procedures can provide a completely accurate prediction of the performance of elastomer based commercial products. For example, the tire industry relies on road testing of tires to evaluate the abrasion resistance of tread compounds. Laboratory evaluations of abrasion, however, have been quite revealing in studies of materials, mechanisms and compound design.

In conventional elastomer formulas, silica has always been inferior to carbon black in providing abrasion resistance. Compounding solutions to this problem involve use of a “zinc-free” cure system or modification of the silica surface by silane coupling. These solutions are described in detail in Chapters 3 and 4.

Dynamic properties are evaluated here in terms of *resilience* by *pendulum rebound*, and *dynamic modulus* by the duPont DMA apparatus (flexural bending). The latter procedure, similar to MTS testing, reports both elastic (storage) and loss components of the modulus. The ratio of loss to storage modulus is expressed as tangent delta. Since relatively low deformations are involved, the data are very revealing of the structure of the fillers present in the compounds. The transient nature of silica structure requires less deformation energy than the permanent structure of carbon black. This relates to lower values of loss modulus and tangent delta. In this respect, silica reinforced compounds are more efficient in dynamic applications of low deformation than those based on carbon black. This superiority becomes more pronounced if the silica is modified by mercaptosilanes. The commercial realization of this superiority became a reality with the advent of the Michelin “green tire tread.”

Heat build-up and *permanent set* in compounds subjected to high frequency flexing has been measured in the Goodrich flexometer. Specimens under compression are subjected to cyclic deformation at 2000 cpm. The heat build-up is recorded at the time of specimen rupture due to internal gas formation. Silica compounds generally produce higher temperatures than do those reinforced by carbon black. An interesting modification of the end point definition, adapted to energy efficient compounds, is described in the Preface and Chapter 5. In this case the heat build-up is not sufficient to produce a blow-out rupture and the end point measures the compression fatigue life in terms of time to specimen disintegration. Silica compounds with fatigue life equal to those of black compounds rely on the silane coupling of low surface area grades.

Chemical resistance of elastomer compounds is generally evaluated by immersion tests, in which the amount of swelling of immersed specimens together with hardness and stress-strain changes are observed at various times and temperatures. In water immersions the silica salt content leads to relatively high initial swelling. However, once the salt has been leached from the compound, imbibed water declines, and the percent swell decreases to a stable value. In contrast, black compounds tend to swell continuously over long immersion periods.

Cut growth resistance, evaluated by DeMattia flexing, has been reported in several of the tables. These data are useful only when compounds of equal hardness are involved.

A.8 SILICA SURFACE AREA

Surface area, expressed as m^2/g, is an indirect measurement of the elastomer reinforcing potential of a fine particle filler. The BET method (Brunauer, Emmett, Teller) involves the deposition of a monomolecular layer of nitrogen on the silica, including pores within agglomerates. In most cases in this book, silica surface area is characterized as N_2SA, i.e., nitrogen (BET) surface area. The large CTAB (cetyl trimethyl ammonium bromide) molecule does not penetrate pore structure and thus provides somewhat lower values. These are a better indicator of the actual contact between silica surface and elastomer chains. However, the ranking among several different silicas is usually the same for both methods. This is demonstrated in Table A.3, which compares the BET and CTAB surface areas of the precipitated silica products commonly used in elastomer compounds.

Table A.3 Commercial Precipitated Silica, by Surface Area

Surface Area, m^2/g^A		
N_2SA (BET)	**CTAB**	
250	230	HI-SIL®[1] 2000
230	-	ZEOSIL®[2] 45
220	170	HI-SIL 190G
190	170	HI-SIL 185GM
190	-	ZEOSIL 175GR+
185	155	ULTRASIL®[3] VN3
180	150	ULTRASIL 7000GR
180	130	HI-SIL 180HM
175	160	ZEOSIL 175
170	155	ZEOSIL1165
160	145	ZETPOL®[4] 8745
160	130	HI-SIL 255G
160	125	HUBERSIL®[4] 1620
155	140	HUBERPOL®[4] 136
150	135	HI-SIL 210, 233, 243
125	125	ZEOSIL 125
125	115	HI-SIL 315
125	115	ULTRASIL VN2
65	35	HI-SIL 532
65	35	DUROSIL®[3]
35	30	SILENE®[1] 732D
35	30	EXTRUSIL®[3]
		Silane Treated:
150^B	-	CIPTANE® 1
150^B	-	CIPTANE TM
190^B	-	CIPTANE 255LD
190^B	-	CIPTANE LP

[A] Average values; lot-to-lot variation may be ± 8 m^2/g

[B] As Measured before silane treatment

[1] PPG Industries [2] Rhodia [3] DeGussa [4] J.M. Huber

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