

## *Liquid Polybutadiene Resins As Coagents And Modifiers For Elastomers*

### **Introduction**

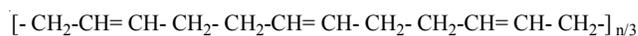
Liquid polybutadiene resins (LPBs) have demonstrated considerable applicability in the rubber and plastics industry now that many are commercially available, and especially now that various technicians have developed data and procedures for their use in modification of polymers. These liquid resins can be used as thermosetting plastic materials, and are cured and handled by methods analogous to polyester resins.<sup>23</sup> Liquid polybutadiene resins are available containing the majority of the unsaturation in the backbone chain of the molecule, and in this form may be thought of as liquid rubbers. They undergo very similar reactions as the unsaturated elastomers, with differences largely attributable to lower molecular weight. Other types of liquid polybutadiene resins have high unsaturation, mainly present in the form of pendant vinyl groups. These materials have a very high capacity for crosslinking other polymer systems. Copolymers with styrene and acrylonitrile are also available commercially. The commercial styrene copolymers may contain unsaturation in either the chain or as pendant vinyl. The liquid acrylonitrile copolymers are currently available only in the unsaturated chain form. The liquid polybutadiene resins can be chemically modified easily. Types are commercially available with carboxy, hydroxy, and amino terminal functionality.<sup>23</sup> The resins may be chlorinated, brominated, hydrogenated, epoxidized, maleated, etc. The epoxidized and maleated forms are also commercial products. All these materials are available to the rubber chemist and compounder, but the variety of materials can create

confusion and uncertainty in their use. It is the purpose of this paper to partially clarify this situation.

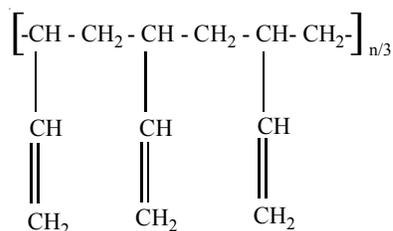
### **Liquid Polybutadiene Resins**

Liquid polybutadiene (LPBs) resins may be manufactured with either high or low vinyl functionality, as can be seen from the following structures:

#### Elastomer



#### Ricon® Liquid Resins



### **Low Vinyl Liquid Polybutadienes**

1,4-LPBs are mixtures of cis, trans, and vinyl unsaturation. Compared to the 1,2-LPBs, they are much less viscous. The lower molecular weight 1,4-LPBs have similar viscosities as extender oils, with which they are normally completely miscible. Chemically, they behave like unsaturated rubbers, such as cis 1,4-PBD and polyisoprene, but of course, they are much lower in molecular weight. Because of this, they require more curing agent. Not much is known about the use of these materials as rubber additives, and the effect they have on various elastomer systems. It is known that these 1,4-LPBs are effective non extractible plasticizers, which do not degrade physical properties of cured elastomers. A liquid low vinyl SBR (Ricon® 184)

is also commercially available. This material has polarity more akin to high aromatic oils, and may

be more compatible with elastomers which require aromatic extender oils. Available low vinyl materials are listed in Table 1.

**Table 1**

LOW VINYL RICON® RESINS			
Property	RICON® 131	RICON® 142	RICON® 184
Chemical Composition	Polybutadiene	Polybutadiene	Liquid SBR
Microstructure cis	35	10	35
(approx.) trans	45	35	45
vinyl	20	55	20
Styrene	None	None	30%
Molecular Weight appx.	5000	3900	9200
Viscosity (Brookfield) poise	35	97	720
Specific Gravity @25°C	0.89	0.89	0.90
Flash Point (Tag Closed cup) °F	>300°F	>300°F	>300°F
Non Volatile Matter Weight %	98.5%	98.5%	98.5%
MW Distribution	Narrow	Moderate	Moderate

### High Vinyl Polybutadiene Resins

Liquid high vinyl 1,2-polybutadiene resins have different cured properties than the familiar 1,4-polybutadienes. They cure to hard, glass-like polymers, but since they are unsaturated hydrocarbons like the majority of elastomers, the 1,2-polybutadienes are compatible with these elastomers. These resins have a pendant vinyl group for every other chain carbon and are thus capable of crosslinking to a very high degree. It is this structure which gives high vinyl content polybutadienes special usefulness as additives and coagents. 1,2-LPB resins have been explored much more thoroughly than have the 1,4-LPBs as coagents and modifiers for elastomeric materials and therefore most of the remainder of the discussion will be devoted to 1,2-LPBs.

Liquid 1,2-polybutadienes have been used as coagents in a number of elastomer systems.<sup>1,2,3</sup> They have found the widest commercial application in EPDM and EPM elastomers due to a combination of high crosslinking ability, and resistance to chemicals, solvents, and heat.<sup>1,4,5,10,11</sup> These

properties are due to their saturated backbone and the large number of unsaturated and reactive vinylic side chains. The saturated backbone confers unusual thermal and chemical resistance to the vulcanized elastomer, and as a consequence, these structures undergo reversion only under extremely severe conditions. Until now, no generally compatible additive for peroxide curable silicone rubber has been available which can modify elastomer properties in a variety of useful ways and still maintain these properties for which silicone rubber has become so uniquely suited. Liquid 1,2-polybutadienes are such additives.<sup>14,15</sup>

The high vinyl resins shown in Table 2 are also available. Ricon® 151 is the least expensive of the resins shown above, and in general, is used in EPDM and EPM, if a cheaper coagent is needed. Ricon® 152 and Ricon® 153 are general purpose coagents. Most of the information provided in this paper for EPDM and EPM is based on work with Ricon® 153. Ricon® 154 is used in heat resistant down well elastomers, where greatest possible crosslinking is needed.<sup>6,7</sup>

**Table 2**

COMPOSITION AND TYPICAL PROPERTIES OF RICON® RESINS				
	RICON® 151 (1)	RICON® 152 (1)	RICON® 153 (1)	RICON® 154 (1)
Chemical Composition	Polybutadiene	Polybutadiene	Polybutadiene	Polybutadiene
Microstructure	70% 1,2 Vinyl	80% 1,2 Vinyl	80% 1,2 Vinyl	90% 1,2 Vinyl
Molecular Weight (appx)	2000	1800	2800	2800
Physical State	Clear viscous liq	Clear viscous liq	Clear viscous liq	Very viscous
Viscosity (Brookfield) Poise	400 (25 °C)	200 (45 °C)	600 (45 °C)	2500 (45 °C)
Specific gravity at 25 °C	0.89	0.89	0.89	0.89
Pounds per gallon	7.4	7.4	7.4	7.4
Flash Point (Tag Closed Cup) °F	>300	>300	>300	>300
Nonvolatile Matter Wt.%	98.5 minimum	98.5 minimum	98.5 minimum	98.5 minimum
MW Distribution	Broad	Moderate	Moderate	Moderate
(1) Contains 100 ppm (2,6 di-tertiary-butyl-p-cresol)				

**EPDM and EPM**

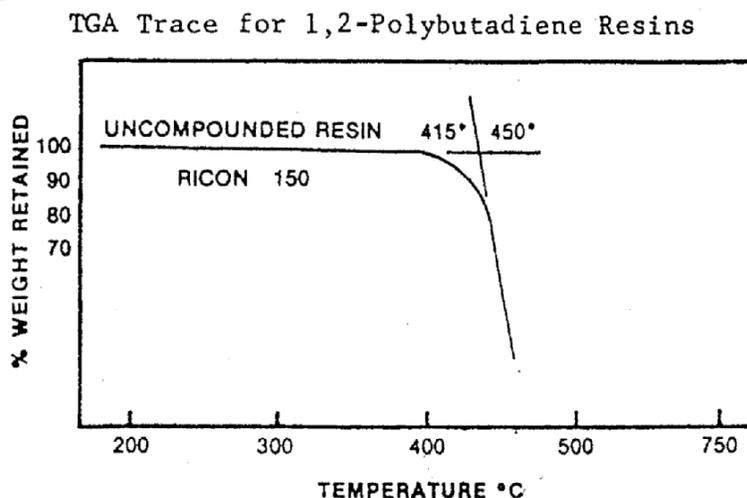
A study was undertaken to determine the effects of 1,2-polybutadiene resins on the physical properties of peroxide and sulfur vulcanized EPDM and EPM. Nordell 1440 was selected as the principal EPDM elastomer for study. Similar data was available for several other EPDM and EPM materials, i.e. Vistalon 404<sup>3</sup>, Nordel 1040<sup>4,8</sup>, Nordel 1660<sup>9</sup>, Royalene 521, Epcar 5465 and Nordel 1070.

EPDM and EPM have hydrocarbon backbone structures with no unsaturation to serve as a point of chemical attack. These resins are known to have excellent resistance to ozone, oxygen, heat and light. They are, however, severely swollen by certain hydrocarbons. This is undoubtedly due to the fact that EPDM and EPM have relatively few crosslink sites and therefore, have relatively open

structures. Solvents are thus able to solvate the material readily.

1,2-polybutadienes having high 1,2 assay also have very few unsaturated sites in the polymer backbone, but unlike EPDM, have extremely high crosslinking potential. When liquid 1,2-polybutadienes are cured with peroxide catalysts, the resulting product is a hard, glassy, brittle solid. Such materials are very heat, corrosion and hydrocarbon resistant. Figure 1 is a thermogravimetric trace of a peroxide cured 1,2-polybutadiene showing that there is little loss in weight when heated in a nitrogen atmosphere until a temperature of 425 °C (800 °F) is attained, where a sharp break appears in the curve corresponding to thermal “cracking” of the polymer into carbon and gaseous hydrocarbon products.

**Figure 1**



All compounds used in this study were prepared on a two-roll laboratory mill from a series of master batches. The compounds were mixed taking care that there were minimum variations in milling and temperature parameters. Tests were conducted with careful adherence to conditions specified by the various ASTM methods and these are listed for data wherever such data appears in the text. Nordel 1440 was selected as the principal EPDM to be studied. The initial study was designed to test physical properties obtained with various concentrations of 1,2-polybutadiene, and to compare the properties so obtained with EPDM containing no polybutadiene and EPDM containing trimethylolpropane trimethacrylate. SR-350 was chosen as the TMPTM and Ricon<sup>®</sup> 153 was chosen as the 1,2-polybutadiene. These materials were from

production batches and were used without further purification. The 1,2-polybutadiene used had an assay for vinyl content of 92 percent and molecular weight by Gel Permeation Chromatography ( $M_n=3140$ ). A Master Batch for Recipes A and C was made with the following composition by weight: Nordel 1440, 100.00 phr; SRF N-762 carbon black, 50.00 phr; ZnO, 5.00 phr; Agerite Resin D, 1.00 phr, and blended on a two-roll mill with catalyst, coagents, and other additives as required. These compounds are shown in Table 3. The samples were cured 25 minutes at 160 °C for peroxide slabs and 20 minutes at 160 °C for sulfur slabs. The samples were processed and aged for 72 hours at 100 °C. Aged Physicals were determined with results shown in Table 4. Mooney Viscosity and Scorch by ASTM method D-1646 is presented in Table 5.

**Table 3**  
**Compound Recipes Used**

Formulation	A	B	C
Nordel 1440	100.0	-	100.0
Vistalon 404	-	100.0	-
SRF N-762 Black	50.0	-	50.0
SRF N-761 Black	-	50.0	-
Zinc Oxide	5.0	-	5.0
Agerite Resin O	1.0	-	1.0
Dicup 40C	7.0	6.75	-
Stearic Acid	-	-	1.0
MBT	-	-	.05
TMTD	-	-	1.5
Sulfur	-	-	1.5
Ricon <sup>®</sup> 153	0, 2 ½, 5, 10	-	0, 2 ½, 5, 10
Ricon <sup>®</sup> 152	-	0.10	-

### Effect of 1,2-LPB on Peroxide Cured EPDM Elastomers

Ricon<sup>®</sup> Resins show significant property enhancement with peroxide cured EPDM rubber. There is evidence that catalyst efficiency is increased many fold<sup>4</sup>, and it is clear that there is a higher degree of crosslinking when using the polybutadiene resin.<sup>3</sup> From Table 4, it can be seen that tensile strength, hardness and modulus are increased and elongation and compression set are reduced.

The information given in Tables 4, 5 and 6 show that peroxide cures with 1,2-polybutadienes

consistently improve physical properties of EPDM and EPM elastomers. This is because Ricon<sup>®</sup> Resins have many crosslink sites for each molecule and are thus able to increase the crosslink density of the overall elastomer system. For peroxide systems this effect causes improved compression set, harder cures, increased modulus, increased resistance to swelling by solvents and increased resistance to oxidative attack on aging. Some of these results may be achieved by increasing the catalyst concentration, but it is usually cheaper to use Ricon<sup>®</sup> Resins than to increase catalyst. Scorch time is reduced as well as degradation due to  $\beta$  scission

and other types of polymer degradation, which is not the case with higher catalyst usage. With peroxide catalysts, the Ricon® Resins cure rapidly at temperatures above 160 °C (320 °F), while at temperatures below 160 °C the occurring reaction is relatively slow.

EPM compounds can, of course, be cured only with peroxide catalysts. Ricon® LPB resins can bring

about really significant improvements in many of the properties of these materials. In some instances, an EPM compound can show properties equal to EPDM compounds. Due to improved efficiency of peroxide catalysts brought about by Ricon® Resins, significant curing can be achieved with relatively low peroxide levels. This is shown for Formulation B in Table 6.

**Table 4**  
**Effect of Ricon® 153 in an EPEM Compound (Peroxide Cure)**

Aged Physicals Aged 72 hrs. @100°C	1,2-LPB	0	Concentration		
			2 ½	5	10
Tensile MPA	D-573	14.3	13.9	14.1	12.5
Elongation %	D-573	440	370	310	250
100% Modulus, MPa	D-573	1.4	1.7	1.9	2.6
200% Modulus, MPa	D-573	3.4	5.0	6.4	8.8
300% Modulus, MPa	D-573	7.6	10.3	13.7	-
400% Modulus, MPa	D-573	12.4	-	-	-
Hardness, Shore A	D-2240	60	63	63	65
Compression Set	D-395, Method B	22.0	14.5	18.6	12.8

**Table 5**  
**Mooney Viscosity and Scorch by ASTM method D-1646 (Mooney Viscosity: ML 1+4 at 121 °C)**

LPB	0	2 ½	5	10
Initial Reading	74.3	73.9	73.8	64.5
4 Minute Reading	54.5	52.0	49.0	43.0
Mooney Scorch: MS at 121°C Time to 5 Point Rise Minutes	69.0	71.0	59.0	60.0

**Table 6**  
**Effect of Ricon® 152 in an EPM Compound**

(Peroxide Cure) Properties Aged 72 hrs. @ 300°F.	Formulation B Concentration	
	0%	10%
Modulus, MPa	1.2	5.9
Tensile Strength, MPa	8.3	12.6
Elongation at Break, %	450	150
Shore A Hardness	55	57
Compression Set, %	35	9

### Effect of 1,2-LPB on EPDM Elastomers (Sulfur Cure)

Formulation C was prepared and studied in the same way as was done for the peroxide vulcanized Formulation A, except that sulfur cured slabs were heated for only 20 minutes at 160 °C. The results obtained are shown in Table 7. Data on Mooney Viscosity and Mooney Scorch is shown in Table 8.

The plasticizing effect of the 1,2-LPB is quite obvious, but there is little effect on scorch time. This study contains data showing that there is an appreciable and unexpected increase in the tensile strength of sulfur cured EPDM containing polybutadiene. The effect was startling and we spent considerable time and effort repeating the experiments to verify this phenomenon. This can be seen from the data in Table 7.

**Table 7**  
**Effect of Ricon® 153 1,2-LPB in an EPDM Compound**

Aged Physicals Aged 72 hrs. @100°C	1,2-LPB	0	Concentration		
			2 ½	5	10
Tensile MPA	D-573	8.2	11.1	12.5	13.3
Elongation %	D-573	210	310	400	560
100% Modulus, MPa	D-573	3.3	2.9	2.5	2.2
200% Modulus, MPa	D-573	7.7	6.6	5.2	4.2
300% Modulus, MPa	D-573	-	10.5	8.9	6.9
400% Modulus, MPa	D-573	-	-	12.4	9.7
500% Modulus, MPa	D-573	-	-	-	12.1
Hardness, Shore A	D-2240	69	68	66	69
Compression Set	D-395, Method B	52.4	41.5	51.1	48.9

**Table 8**  
**Effect of 1,2-LPB Concentration on Mooney Viscosity and Mooney Scorch (Mooney Viscosity: ML 1+4 at 121°C)**

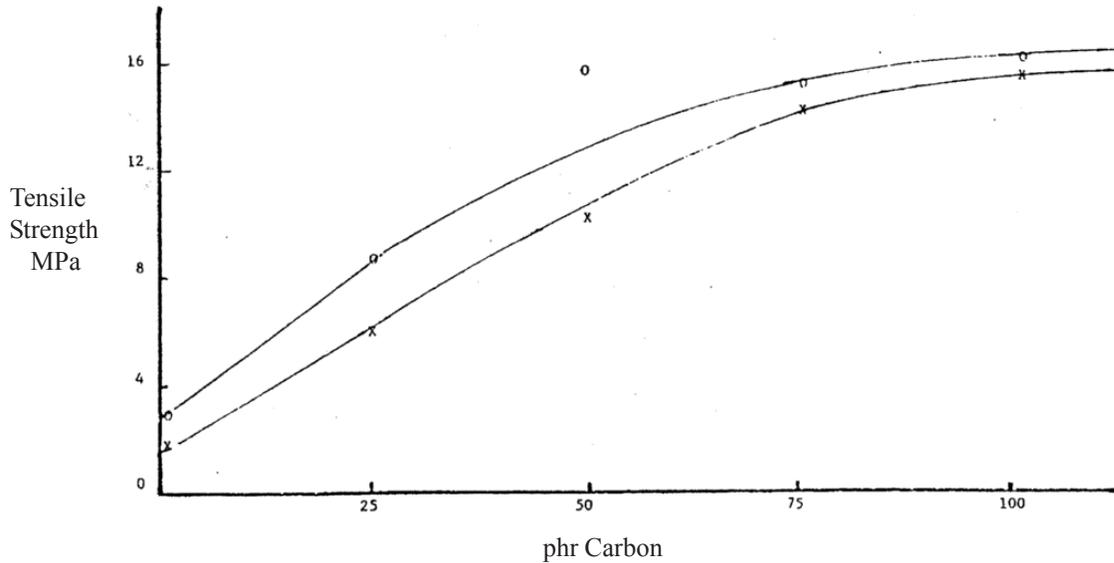
1,2-LPB	0	2 ½	5	10
Initial Reading	78.0	76.0	67.5	65.0
4 Minute Reading	53.5	51.0	48.0	44.8
Mooney Scorch: MS at 121°C Time to 5 Point Rise Minutes	22.5	22.5	21.0	30.0

A series of master batches were made where the carbon black content was increased from 0 to 100 phr. Referring to Figure 2, the data is plotted to show the increased tensile strength found at different carbon black loadings for specimens containing 2.5 phr 1,2-polybutadiene compared to specimens with none. Not only did the 1,2-polybutadiene additive increase tensile strength at all levels of carbon black tested, but the tensile strength enhancement was greater with higher additive level as can be seen in Figure 2. We observed that, although the samples at 100 phr carbon loading were hard (82 Shore A), they were also quite resilient. This study includes oil extended EPDM. The effect disappear or diminish as the oil content increases, since a highly carbon loaded, oil extended material containing Epcar 5465

formulated as a stair tread compound was reported not to show tensile strength improvement. We found that there is a significant tensile strength enhancement effect, and that tensile strength decreases as expected as oil content is increased as shown in Figure 3. We have not yet looked at any of the white fillers, nor studied the effects of different sulfur cure systems and all different types of EPDM. In case the effect was limited to Nordel 1440, we repeated some portions of the study with Epcar 545. Tensile strength increases were also demonstrated for this EPDM as shown in Table 9. One of the advantages of increased tensile strength in EPDM, through addition of 1,2-polybutadiene coagents may be the substitution of cheaper grades of reinforcing carbon in existing compounds without reducing tensile strength.

**Figure 2**

Effect of 2.5 phr 1,2 polybutadiene resin on sulfur cured carbon black reinforced EPDM unaged tensile ASTM D-412



o - 2,5 phr 1,2 polybutadiene

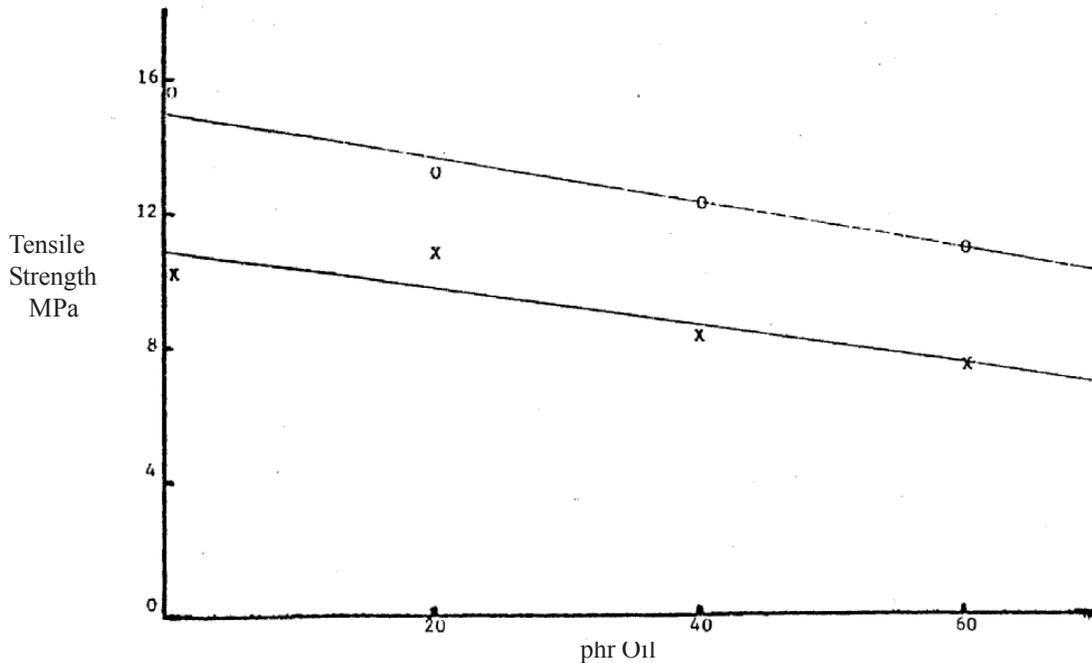
x - without coagent

Master Batches made with Nodel 1440 100phr; SRF N 762 0, 25, 50, 75 and 100 phr; ZnO, 5 phr and Agerite Resin D, 1 phr.

Catalyst for all batches was MBT, 0.5 phr; TMTD, 1,5 phr and Sulfur, 1.5 phr

**Figure 3**

Effect of oil on tensile strength of sulfur cured EPDM compound containing 50 phr reinforcing carbon. Unaged, ASTM D-412



o - 2,5 phr 1,2 polybutadiene (Ricon® 153)

x - without coagent

Master Batches were made with Nodel 1440 100phr; SRF N 762, 50 phr; Circosol 4240, oil 0, 20, 40 and 60 phr; ZnO 5 phr and

Agerite Resin D, 1 phr. Catalyst for all batches was MBT, 0.5 phr; TMTD, 1,5 phr and Sulfur, 1.5 phr

**Table 9**

COMPARISON OF SULFUR VULCANIZATES OF NORDEL 1440 AND EPCAR 545 CONTAINING 1,2 POLYBUTADIENES				
Master Batch				
Nordel 1440	100.0		--	
Epcar 545	--		100.0	
SRF N 762	50.0		50.0	
Zinc Oxide	5.0		5.0	
Agerite Resin D	1.0		1.0	
Compounds were cured with 0.5 phr MBT, 1.5 phr TMTD and 1.5 phr sulfur cured for 20 minutes at 160°C.				
Unaged Physicals, ASTM D-412 and D-2240				
	Nordel 1440		Epcar 545	
1,2 Polybutadiene	--	2.5 phr	--	2.5 phr
Elongation %	270	440	320	440
Modulus, MPa 100%	3.1	2.9	3.7	3.0
Modulus, MPa 200%	7.3	6.3	7.9	6.1
Modulus, MPa 300%	--	10.5	11.2	9.5
Modulus, MPa 400%	--	14.2	--	12.8
Tensile, MPA	10.1	15.7	12.3	14.3
Hardness, Shore A	72	75	77	77

**Comparison of 1,2-LPB With TMPTM**

In EPDM and EPM elastomer formulations, Ricon® Resins are one of several coagents which may be used for peroxide vulcanization. The most successful competitors are di and tri functional methacrylates such as trimethylolpropane trimethacrylate. Ricon® Resins have several advantages over the methacrylate such as low toxicity, low odor, less scorchy cures, lower brittle point, no surface bloom on storage and somewhat softer cures.

Physical property enhancement of 1,2-polybutadiene with trimethylolpropane trimethacrylate (TMPTM) is compared. It can be seen from data in Tables 10 and 11 that amounts of 1,2-polybutadiene as low as 2.5

phr have significant effects on compression set and hardness. The effects compare quite favorably with TMPTM; the compression set values are quite close and tensile strength values favor the poly-butadienes. Mooney scorch values are much better with 1,2-LPBs than with TMPTM.

The data in Table 11 is also interesting when we look at the comparative effects produced by sulfur cures with polybutadienes and TMPTM coagents. Indeed, the TMPTM does not serve to increase any cured property appreciably. The polybutadiene on the other hand serves to increase tensile strength and improve compression set while acting as a non-extractable plasticizer.

**Table 10**  
**Formulation for Co-Agent Comparisons**

	Peroxide			Sulfur		
Master Batch*	156.0	156.0	156.0	156.0	156.0	156.0
Stearic Acid	-	-	-	1.0	1.0	1.0
Ricon® 153	-	2.5	-	-	2.5	-
Sartomer 350	-	-	2.5	-	-	2.5
Dicup 40C	7.0	7.0	7.0	-	-	-
MBT	-	-	-	0.5	0.5	0.5
TMTP	-	-	-	1.5	1.5	1.5
Sulfur	-	-	-	1.5	1.5	1.5
*Master Batch contains 100 phr Nordel 1440, 50 phr SRF n-762 Carbon Black, 5.0 phr ZnO and 1.0 phr Agerite.						

**Table 11**  
**Comparative Co-Agent Compound Properties**

Aged Physicals Aged 72 Hrs. @ 100°C		Peroxide			Sulfur			
		LPB	0	2 1/2	-	0	2 ½	-
		TMPTM	-	-	2 ½	-	-	2 ½
Tensile MPa	D-573		14.3	13.9	13.4	8.2	11.1	8.2
Elongation %	D-573		440	370	410	210	310	240
100% Modulus, MPa	D-573		1.4	1.7	1.8	3.3	2.9	3.1
200% Modulus, MPa	D-573		3.4	5.0	4.8	7.7	6.6	7.0
300% Modulus, MPa	D-573		7.6	10.3	9.1	-	10.5	-
400% Modulus, MPa	D-573		12.4	-	13.0	-	-	-
Hardness, Shore A	D-2240		60	63	63	69	68	69
Compression Set	D-395, Method B		22.0	14.5	14.4	52.4	41.5	52.1
Mooney Viscosity @ 121°C – Initial Reading			74.3	73.9	75.7	78.0	76.0	72.3
Four Minute Reading			54.5	52.0	61.8	53.5	51.0	50.5
Mooney Scorch @ 121°C-Time to 5 Point Rise			69.0	71.0	26.5	22.5	22.5	28.0

### Heat, Hydrocarbon and Chemical Resistant EPDM Formulations

A number of newly developing applications as well as some old ones require high heat, hydrocarbon and chemical resistant elastomers. For example, geothermal steam, deep oil wells, solar ponds, roofing sheet, and solar collector bladders and seals all have rapidly developing requirements for rubbers that can withstand conditions not previously thought possible. Today's oil wells are operating in more difficult environments than

ever before.<sup>12,16</sup> Wells are being drilled deeper, dramatically increasing temperature and pressure conditions which the downhole elastomer must withstand. In addition, harsh chemicals and steam are being injected into the well for various purposes. Elastomers currently in use are no longer doing an adequate job in these more difficult environments.<sup>18</sup> These older elastomers react to brine and oil at 260 °C as shown in Table 12.<sup>16,17</sup>

**Table 12**

1. Butyl (IIR)-softens, undergoes reversion
2. Nitril (NBR)-hardens and becomes nonelastic. Embrittles on aging in presence of H<sub>2</sub>S.
3. Epichlorohydrin (CO)-softens, hydrolyzes, extrudes.
4. EPDM-softens, swells, resists chemical attack.
5. Fluoroelastics (FKM)-embrittles on aging, loses HF.
6. Polyacrylics (ACM)-not resistant to hot water and steam at 260 °C.<sup>9</sup>
7. Chloroprene (CR)-hydrolyzed.
8. Silicone (VMQ)-has good physicals, but swells in hydrocarbons and is destroyed in 260 °C brine.<sup>9</sup>
9. Fluorosilicones (FVMQ)-destroyed by 260 °C brine, has excellent physicals at 260 °C and is resistant to hydrocarbons. Possibly has selected downwell uses.<sup>9</sup>

Those rubber materials which have a significant future in deep oil wells are presently limited to EPDM and the fluoroelastomers.<sup>12,29</sup> All the other materials listed in Table 12 have a short life span at 260 °C in contact with hydrocarbons and brine. It should be noted that in deep oil wells there is a strong chemically reducing environment, whereas from about 30 feet to the surface an oxidizing environment is present. Thus, elastomers designed for deep oil well or geothermal use may not have the same requirements as ones designed for a surface application. Nevertheless, it can be shown that

LPB crosslinked EPDM has very high heat resistance and quite respectable chemical resistance in oxidizing environments also.

Electric cables for down-well pumps have been manufactured for some time using LPB crosslinked EPDM.<sup>19,20,21</sup> These cables have a significantly improved life span, and have made it possible to operate pumps deeper and hotter than ever before. The pumps have also been improved by using LPBs for electric wire varnishes.<sup>22</sup> Significant improvements in elastomers used in oil wells and in geothermal wells have been made since 1976. A program was carried out under the auspices of the U.S. Department of Energy known as the Geothermal Elastomeric Materials (GEM) program. The work was done at L'Garde, Inc., and the report is now published.<sup>9</sup> This work concentrated on development of elastomers for packer assemblies and o-ring seals. Since 1979, work has continued to perfect and transfer this technology to industry. This work has resulted in several recent reports.<sup>24,25,26,27,28</sup>

The chemical resistance of EPDM is well known.<sup>9,11,25</sup> Due to the saturated backbone of the EPDM chain, there is little opportunity for chemical attack. Thus the elastomer is resistant to oxygen, ozone, steam, and most acids, bases, and aqueous solutions. It is swelled by aliphatic and chlorinated hydrocarbons, as well as relatively non-polar aromatic solvents such as toluene. It is fairly resistant to swell by polar hydrocarbons.

**Table 13**

Chemical resistance of 1,2-polybutadiene mineral filled molded specimens at elevated temperatures: 20% resin: 80% filler				
Tested one week at refluxing temperature.				
Solvent	Relux Temp °C	% Weight Change	% Flex Strength Change	Hardness Change
Tap Water	100°	+0.25	-10	-2
Toluene	115°	+2.5	-70	-1.5
Kerosene	145°	+4	-35	-2
DMSO	189°	+1.5	+15	+12
Glacial Acetic Acid	118°	+2.0	-30	+5
96% H <sub>2</sub> SO <sub>4</sub>	200°	+5	-50	-9
20% H <sub>2</sub> SO <sub>4</sub>	100°	+2	+5	+1
10% NaOH <sub>(1)</sub>	100°	+2	-2	+1

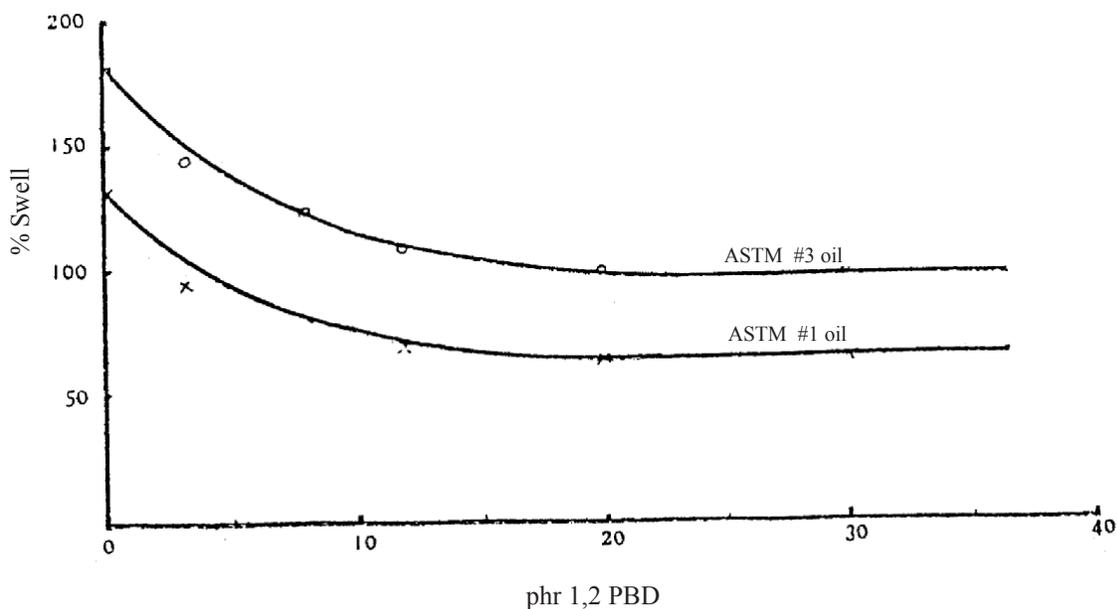
(1) Coke filled specimen; silica filled sample was attacked severely when tested.

Table 13 shows chemical resistance data from treatment of a carbon and/or silica filled molding formulation containing 1,2-polybutadiene for 7 days under conditions shown. There is good resistance to chemical attack for a wide range of corrosive chemicals including

a representative spectrum of hydrocarbons. Therefore, it is not surprising that 1,2-polybutadienes significantly improve resistance of EPDM and EPM materials to solvent (Figure 4) and chemical attack.

#### Figure 4

Oil Swell - Data points from reference 4  
 Samples swelled in oil 72 hours at 149°C (300 °F)



Masterbatches made with Nordel 1040 EPDM, 100 phr, N550 black, Sunpar 2280 oil, 20 ZnO, 5.0; Dicap R, 2.5, 3000 Mw 1,2-PBD (Hystyl B-3000) 0, 3, 8, 12, 20, 30 phr

The work done at L'Garde, Inc. by A.R. Hirasuna and co-workers for the DOE report has shown that EPDM containing 20 phr LPB can be used to make very resistant packers and o-rings for geothermal brine wells. This compound passed rather strenuous tests at 260 °C submerged in a synthetic geothermal brine containing enough H<sub>2</sub>S to destroy unsaturated rubbers. This data is summarized in Table 14 where it can be seen that the physical properties of the composition were little changed by 22 hours of aging at 260 °C immersed in synthetic geothermal brine. This has proven to be an exceptionally severe environment for elastomers. When this work was started, no commercial or experimental elastomers known could withstand these conditions. Hirasuna and co-workers

developed several elastomers which could withstand these conditions. These materials are fully described in their published papers,<sup>9,12</sup> and the performance is outlined in Table 15. The 1,2-polybutadiene crosslinked EPDM (Compound #267) appeared to be the best material. It was chemically aged in geothermal brine at 315 °C for 22 hours as a further test of its high temperature properties. This data is given in Table 16. At this very high temperature, there was some softening and loss of tensile strength, but considering these severe conditions, the material will undoubtedly perform useful work functions where no other elastomers can survive. Under these conditions, the fluoroelastomers embrittled and became useless.

**Table 14**

L'Garde compound #267 physical properties before and after 22 hours aging in synthetic brine at 260 °C (500 °F). Brine composition: H<sub>2</sub>S-300 ppm; NaCl – 25,000 ppm; CO<sub>2</sub> -1000 ppm; H<sub>2</sub>O remainder

	Before	After CA	% Retention
Extrusion, PSIA	17.9	17.7	99
Hardness, Shore A	92	92	100
Elongation %	141	138	98
Tensile, PSI	1610	1554	97
Swell %	-	.46	-
Wt.gain%	-	-	2.29

FORMULATION L'GARDE COMPOUND #267 FROM 4,2,1 PAGE 60

COMPONENT

Nordel 1660 (Dupont)	100 phr
Hypalon 20 (Dupont)	5
Statex 160 (N110, SAF) (Cities Service)	75
Cyanox 2246 (American Cyanamid)	0.5
Di-Cup R (Harwick Chemical Corp.)	3.5
Thermoguard S (M&T Chemicals, Inc.)	5
Polybutadiene #6081 (Polysciences, Inc.)	20

Press Cure: 350 °F/60 minutes  
 Post Cure: N<sub>2</sub> atmosphere  
 350 °F preheat  
 50 °F/hr. Step-up to 550 °F. Started at insertion.  
 550 °F for 5 hours

Polybutadiene #6081 was Hystyl B-3000 polybutadiene resin.

**Table 15**

Slide 10 Summary of extended time packer seal SIM tests  
 T=260 °C (500 °F); 50 mil Diametral gap

COMPOUND	TRADE NAME	RUN TIME HRS.	DIFF. PRESS. PSI	COMMENTS RELATIVE TO 22 HR. RUN
255-1X-2	Fluoroelastomer (FKM) Viton	94	4030	Extrusion at both ends, some breakage at champfer
267-11-8	EPDM Nordel 1660	94	4240	Slight more extrusion
266-11-3	Nordel/Viton	46	4220	Slightly more extrusion at both ends
275-11-1	Nordel/Viton	46	3310	Very slightly more permanent deterioration
291-11-2	AFLAS	46	3530	Very slightly more extrusion

Table taken from L'Garde paper 3.1.2. Page 25

**Table 16**

Retention of properties after 22 hours. Chemical aging in synthetic geothermal brine at 315 °C (600 °F).

	Before Aging	After Aging	% Retention
Extrusion PSIA	17.9	10.2	57
Hardness, Shore A	91	77	85
Elongation %	116	210	181
Tensile, PSI	1257	817	65
Swell %	-	.6 (width) 1.2 (thick)	-
% Wt. Gain	-	3.2	-

Data is taken from L'Garde paper 3.1.3 Page 28.

One of the consequences of adding very high levels of 1,2-polybutadiene to an EPDM formulation is that a hard material results. The compound discussed above had a Shore A hardness of 92. In this case, a hard, non-extrudable compound is desirable since a major failure mode of packer assemblies is extrusion between the casing and back-up plate under the driving force of the very high heat and pressure encountered in oil wells. These new materials may find applications in deep oil wells, geothermal and process steam, under-the-hood and underfloor automotive products, solar collectors, and other stressful applications.

Additional information is now available on testing of EPDM-LPB blends in deep oil well and geothermal applications. One interesting conclusion was that long term immersion (6 months) in 190 °C oils shows that the EPDM-LPB blend, although swelling more than fluoroelastomers initially, outperforms the fluoroelastomers in the long run. The fluoroelastomers embrittled severely during this long, hot immersion.<sup>28</sup> Similar results have been observed in actual performance tests in severe environments, with the conclusion that these materials are quite serviceable in oil.<sup>26</sup>

### **Silicone Elastomers**

Peroxide vulcanizable silicone elastomers are useful in the industrial and commercial world due to unique properties. There are many applications where silicone elastomers are ideal and no improvement is possible or needed, but there are perhaps as many applications where improvements are needed. Until now, no generally compatible additive for peroxide curable silicone rubber has been available which can modify elastomer properties in a variety of useful ways and still maintain those properties for which silicone rubber has become so uniquely suited. Ricon® 1,2-

polybutadiene is such an additive. LPBs are compatible with silicone gum stocks and base compounds, and following peroxide vulcanization, useful improvements in physical properties result without giving up low and high temperature performance, electrical behavior and long term resistance to environmental degradation. Specifically, LPB resins may be used to increase modulus, decrease compression set, reduce elongation, increase hardness and bring about significant decreased swelling in solvents. Formulated silicone compounds can be made significantly cheaper because useful amounts of low cost reinforcing fillers such as N550 carbon can be used. These modifications can adapt silicone rubbers for applications not previously considered suitable for silicones.

### **Silicone Modification**

The silicone-1,2-LPB blends so far studied have been limited to VMQ type silicones cured with peroxides such as dicumyl peroxide at temperatures suitable for curing polybutadienes (150-190 °C). These peroxides are dibenzoyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-bis (t-butyl peroxy) hexane, and di-t-butyl peroxide. Bis (2,4-dichlorobenzoyl) peroxide was not included in this initial study. Fillers have been limited to N550 carbon, fumed Cabosil, red iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and Minusil. At present, silicone gum stocks have been compounded with RICON® polybutadienes in three different ways. Each formulation type achieves physical values, which are different from each other and the silicone rubber in important ways. Each of these formulations will be developed separately below:

The resins used in this study are similar to rubber grade LPBs, but contain antioxidants designed to improve heat resistance of the polybutadienes. Formulations used in this work are shown in Table 18

**Table 17**

COMPOSITION AND TYPICAL PROPERTIES OF RICON® RESINS		
	RICON® S-201 <sub>(1)</sub>	RICON® S-203 <sub>(1)</sub>
Chemical Composition	Polybutadiene	Polybutadiene
Microstructure	70% 1,2 Vinyl	80% 1,2 Vinyl
Molecular Weight (Approx)	2000	2800
Physical State	Clear Viscous Liquid	Clear Viscous Liquid
Viscosity (Brookfield) Poise	400 (@ 25°C)	600 (@ 45°C)
Specific Gravity @ 25°C	0.89	0.89
Pounds Per Gallon	7.4	7.4
Flash Point (Tag Closed Cup) °F	>300	>300
Nonvolatile Matter, Wt.%	98.5 Minimum	98.5 Minimum
MW Distribution	Broad	Moderate
(1) Contains Proprietary Inhibitors and Antioxidants.		

**Note: Ricon® S-201 and S-203 are no longer offered commercially S-201 (Based on Ricon® 150) and S-203, (Based on Ricon® 153) were specially formulated with proprietary inhibitors and antioxidants. Formulation assistance will be provided upon request.**

**Table 18**

Formulation	D	E	F
Silastic GP-30	100.00	100.00	100.00
Cabosil (Fumed)	15.00	15.00	15.00
Red Iron Oxide, Fe <sub>2</sub> O <sub>3</sub>	2.00	2.00	2.00
Carbon N 550	--	--	0,10,20,40
Dicup 40KE	5.00	5.00	5.00
RICON® S-203	0,2 ½, 5	0,10,20,40	0,10,20,40

### Compounds Using Low Concentrations of LPB Resin

These materials have increased crosslinking compared to the normal peroxide vulcanized silicone rubber. This results in reduced elongation at break, increased modulus, increased hardness, decreased compression set and improved resistance to solvents, oils and fuels. These effects are quite noticeable even at 1.5 phr concentration and increase with increasing concentrations. These changes are likely due to a greater degree of crosslinking brought about by the polybutadiene. The utility of these compounds lies in the fact that the materials have a “snappy” feel that is quite uncharacteristic of silicone rubber, and is undoubtedly due to changes in the dynamic properties of the cured blend. Formulations and their properties are outlined in Table 19.

### Compounds With Higher Concentrations of LPB Resin

The recipes described in Table 20 differ from those in Table 19 only in that higher concentrations of LPB are used. The most important property change is the improved resistance to swell in hydrocarbons along with retention of adequate heat resistance. A necessary trade off is increased hardness and stiffness. Tensile strength and die tear properties are retained to an adequate degree, however at high concentrations, both values decrease. These materials are useful wherever swell resistance to hydrocarbons is needed.

**Table 19**  
**Effect of Ricon® S-203 at low concentration**  
**Formulation D (Peroxide Cure)**

Property:	CONCENTRATION:			
Unaged-Cured 10 minutes @ 166°C (330°F)	0	2 ½ phr	5 phr	10 phr
Tensile, Mpa	5.0	4.7	4.8	4.9
Ultimate Elongation %	220	240	180	160
100% Modulus, Mpa	2.0	1.3	2.5	3.0
Hardness, Shore A	65	68	73	78
Compression Set	26.4	23.7	23.6	23.3
24 Hours @ 150°C (302°F) 25% Deflection				
Rheometer Data:				
Model: MPV Range: 100 Clock: 30 min speed: 900 rpm Die: Micro Arc: 1° Temperature: 166°				
Minimum Viscosity, dNm	21.2	20.2	17.6	12.7
Scorch Time, Minimum	.80	.70	1.10	1.40
Maximum Torque, dNm	59.1	63.8	74.5	79.3
Optimum Cure Torque, dNm	55.3	59.5	68.8	72.6
Optimum Cure Time	5.25	5.35	6.25	7.00
Cure Rate	6.78	7.47	8.79	9.48

**Table 20**  
**Effect of Ricon® S-203 at High Concentration**  
**Formulation E (Peroxide Cure)**

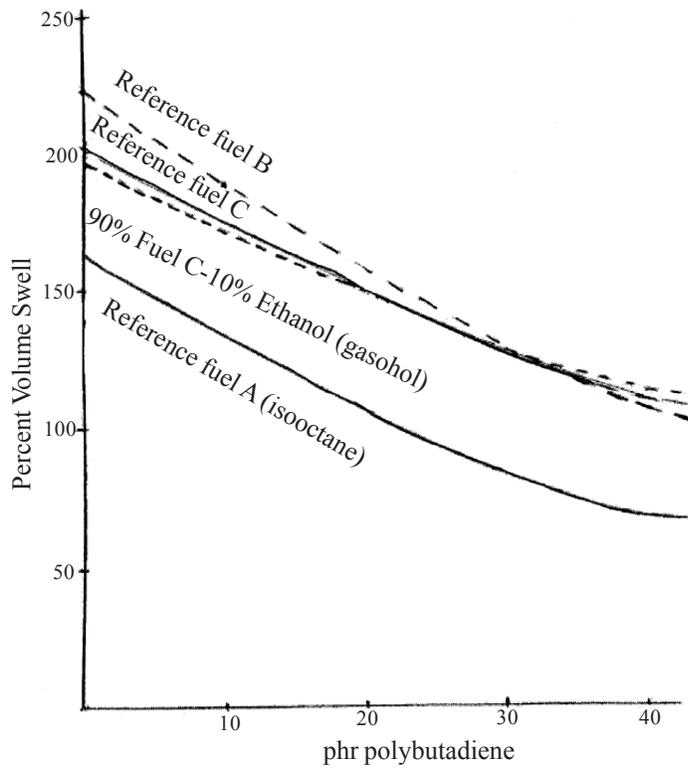
Properties:	Concentration:				
Unaged-Cured 10 Minutes 166°C (330°F)	0 phr	10 phr	20 phr	40 phr	60 phr
Tensile MPa	7.9	7.2	8.0	5.3	5.1
Ultimate Elongation %	350	220	210	50	30
100% Modulus, MPa	1.9	3.2	4.1	--	--
200% Modulus, MPa	4.0	6.4	7.9	--	--
300% Modulus, MPa	6.6	--	--	--	--
Hardness, Shore A	65	72	79	86	91

**Solvent, Oil, Fuel and Chemical Resistance**

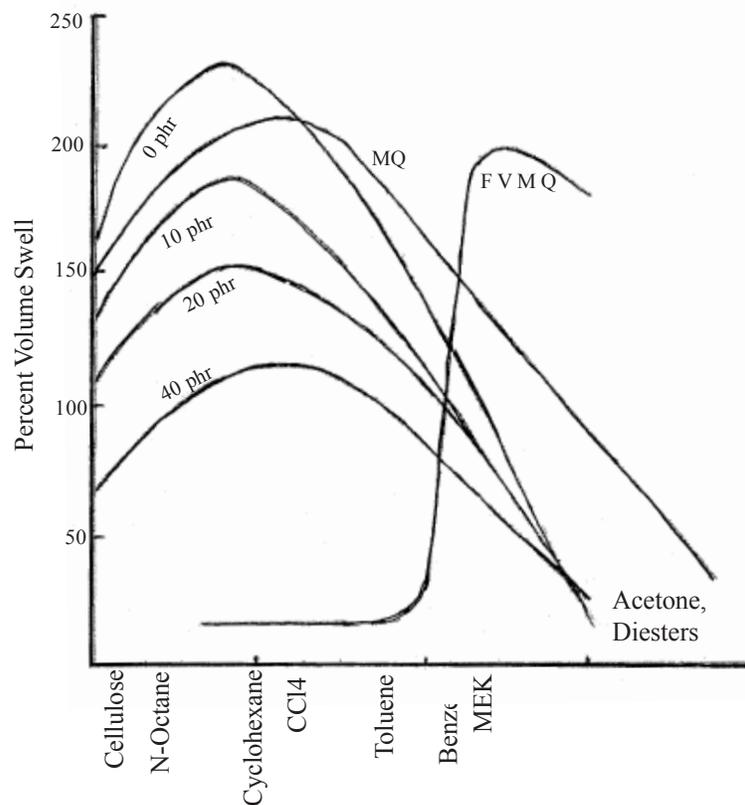
Silicone type VMQ elastomers containing LPB resins are considerably more resistant to swelling than are silicones without LPB resins. This fact may lead to improved compounds for us in such applications as fuel hoses, oil resistant seals, carburetor gaskets, etc. In addition, these compounds may be more highly filled than typical silicone formulations. The cost savings can be considerable when compared to fluorocarbon

rubber and fluorosilicone elastomers, which may otherwise be required for such applications. Resistance to hydrolysis by steam is improved by silicone LPB blends. Data on volume swell is given for a variety of materials in Table 21 and Figure 6. Data for fuel swell is shown in Figure 5. Swell can be reduced even more by compounding with carbon filled silicone LPB blends.

**Figure 5**  
 Fuel Swell characteristics of silicone - LPB blends  
 Swelled 166 hours at 23 °C ± 2 °C ASTM D-471



**Figure 6**  
 Volume Swell in solvents - ASTM 471



**Table 21**

Volume Swell Data for Various Solvents and Aqueous Solutions (166 hrs at 23 +/-2°C)				
<u>Reagent</u>	<u>0</u>	<u>10</u>	<u>20</u>	<u>40</u>
<b>Aqueous</b>				
Water	.5	.5	.6	.8
Water (95°C)	2.7	1.8	.3	.2
50% Ethylene Glycol	.5	1.0	.4	--
-50% Water (104°C)				
<b>Acid Solutions</b>				
10% Hydrochloric	-2	-1.2	-.7	-.9
Conc. Hydrochloric	5	9	16	15
10% Sulfuric	.9	.8	.8	.6
5% Acetic	.1	.7	0	.2
Glacial Acetic	1.3	1.4	3	1.2
<b>Alkali Solutions</b>				
10% Ammonium Hydroxide	2	3	4	2
10% Sodium Carbonate	1.9	1.1	.1	.1
<b>Solvents and Fluids</b>				
Acetone	21	20	20	23
MEK	159	58	54	35
Methylene Chloride	128	110	85	97
Ethanol	5	8	6	5
Methanol	.4	.3	.4	.6
Toluene	159	124	120	97
Isoctane (Fuel A)	163	125	110	66
Ref. Fuel B	202	185	151	111
Ref. Fuel C	222	188	156	106
90% Fuel C – 10% Ethanol	198	167	152	116
90% Fuel C – 10% Methanol	218	179	152	115
Ethyl Acetate	88	62	60	44
Tetrahydrofuran	157	124	104	107
Ethylene Glycol	.9	.7	.6	1.2
140 Solvent	122	109	91	88
<b>Oils</b>				
Mineral Oil	11	12	10	20
ASTM #1 (1)	26	19	4	6
ASTM #3 (1)	34	37	32	27
Silicone Oil SF 96 (2)	18	15	13	6
Hydraulic Fluid (2)	1.1	1.4	1.6	1.7
Skydrol 500 (2)	14	20	13	20
(1) 70 hrs at 150°C				
(2) 70 hrs at 100°C				

**Heat Resistance**

Ricon® Resins, when thoroughly cured, are very heat resistant materials. They begin to “crack” at 415 °C when heated under nitrogen. They will yellow and carbonize when heated above 230 °C in the presence of air. Molded parts of Ricon® will maintain up to 85% of original flexural strength when heated in an air oven for 6000 hours at 204 °C. Silicone-LPB blends are also very heat resistant as might be expected from

the resistance of each material separately. The following test data was obtained on Silicone-LPB blends (formulation E) without addition of antioxidant. S-201 and S-203 are now compounded with an antioxidant, which gives improved resistance to yellowing and decomposition while heating. Silicone resins without added LPB show better resistance to long term heat aging than blends with LPB, but the blend materials are still impressive.

**Table 22**  
**Heat Resistance Of Silicone – LPB Blends (No Antioxidants Used)**

Temp.	Time	PHR 1,2-PBD	% Wt. Loss	% Linear Shrinkage	Hardness Durometer	Tensile % Loss (Gain)	Ultimate Elongation
200°C	166 hrs.	0	2.5	1.2	+5	14	+13
		10	3.6	2.9	+11	(6)	-37
		20	3.4	3.8	+9	(0.2)	-42
		40	2.3	4.2	+13	(16)	-68
250°C	166 hrs.	0	3.7	2.5	+6	17	-22
		10	7.8	5.2	+9	(22)	-48
		20	10.6	6.1	+12	6	-61
		40	11.1	5.8	+13	0	-75
300°C	166 hrs.	0	7.7	4.1	+19	71	-94(weak)
		10	12.6	6.6	+21	78	-97(brittle)
		20	16.7	9.3	+18	57	-95(brittle)
		40	22.6	10.2	+16	10	-88(brittle)

**Low Temperature Properties**

1,2-LPB resins do not significantly reduce the excellent low temperature properties of silicone elastomers until rather high concentrations of LPB resins are used.

Ricon® 104 is recommended for PMQ and PVMQ elastomers due to improved compatibility. Data on one series of compounds is given in Table 23.

**Table 23**  
**Formulation B Low Temperature Torsion Test, ASTM D-1053**

Temperature in °C at which Relative modulus is Equal to:	Compound Identification Based on Parts RICON® S-203			
	0	10	20	40
RM = 2	-58.0	-61.5	-57.5	-13.0
RM = 5	-61.0	-64.5	-60.5	-56.0
RM = 10	-68.5	-69.0	-76.0	-73.5
Twist (degrees) at				
Room Temperature	158	153	151	145
Thickness of sample, mm	2.03	1.96	1.85	1.85
Width of sample, mm	2.5	2.5	2.5	2.5

**Reinforcing Fillers and High Concentrations of LPB Resins**

Since it has long been known that Ricon® polybutadiene resins compounded as molding compounds are strengthened by rubber grade reinforcing carbon, silicone-LPB blends were tested to discover whether reinforcing carbon could be incorporated into these blends. Compounds like those presented in Table 24 do have increased tensile strength. Other properties are also changed as expected by the addition of the carbon filler. Low cost compounds can be made using

this technique and are very resistant to heat and swell by hydrocarbons. These materials can be made very hard or reasonably elastic, but they must necessarily be harder than most silicone rubbers. These materials should be very attractive for applications where the swelling characteristics or cost of silicone rubber has heretofore limited or prohibited use. These materials resist steam, hot water, and automotive coolants far better than most silicone elastomers. This is undoubtedly due to a different type of bridging structure between elastomer chains. Typical test recipes are shown in Table 26.

**Table 24****Effect of Ricon® S-203 and N 550 Carbon Formulation F (peroxide cure)**

Compound #1, #2, and #3 Cured 5 Minutes @ 166 °C

Compound #4 and #5 Cured 8 Minutes @ 166 °C

Compound #6 and #7 Cured 10 Minutes @ 166 °C

Properties	Concentration:						
Compound	#1	#2	#3	#4	#5	#6	#7
Unaged	0 phr	10 phr	10 phr	20 phr	20 phr	40 phr	40 phr
		S-203	S-203	S-203	S-203	S-203	S-203
			10 phr		20 phr		40 phr
			Carbon		Carbon		Carbon
Tensile, Mpa	5.5	5.1	6.6	6.7	5.9	5.4	6.0
Ultimate Elongation	290	180	220	160	110	120	40
100% Modulus, Mpa	1.93	2.90	3.38	3.86	5.38	4.96	--
Hardness, Shore A	62	80	76	80	85	85	92
Compression Set	39.6	28.2	32.5	33.0	31.6	32.5	33.9
Rheometer Data							
Model: MPV Range: 100							
Clock: 12 Min Speed: 900 cpm							
Die: Micro Arc: 1°							
Temperature: 166 °C							
Minimum Viscosity, dNm	22.4	13.4	18.4	9.0	14.5	3.4	10.0
Scorch Time	.70	.90	.85	1.20	1.30	2.35	1.75
Maximum Torque, dNm	53.4	66.9	81.0	78.3	101.3	*	99.8
Optimum Cure torque, dNm	50.3	61.5	74.7	71.4	92.6	*	90.8
Optimum Cure Time	3.00	4.25	4.90	5.50	6.90	*	6.70
Cure Rate	10.76	12.71	12.31	12.83	12.36	17.37	14.44
*Invalid Cure – Compound Split in Rheometer							

**Injection and Extrusion Molding**

Silicone and Ricon® combinations can be successfully molded by most techniques. Hot air cures with 2,4-dichlorobenzoyl peroxide have not been successful due to lower cure temperature. These materials may be cured very rapidly at higher temperatures (175 °C or higher) using appropriate peroxide catalysts. Ricon® Resins cure rather slowly below 150 °C which can be an advantage when using these materials for injection or extrusion molding since barrel temperatures can be quite high without causing scorch.

**Handling**

Ricon® Resins are tacky, highly viscous liquids. They are easily pourable when warmed and can be heated to 150 °C without decomposition. Care should be exercised not to over heat these resins since at temperatures above 190 °C, cure may become auto-

catalytic. Ricon® Resins are non-toxic and have low odor. Ricon® can be milled into unfilled silicone gum stocks easily up to 5-7.5 phr, but higher levels are difficult to mill. They can be handled on a two-roll mill if special care is taken to keep the liquid polybutadiene from contacting the roll surface, since contact causes the band to become unstable and break up. Silicone-Ricon® blends from 20 phr and up are very soft and sticky. If fillers are not used, it is necessary to scrape the compound from the roll with a nylon spatula. Refrigeration of the mill or alternate mixing equipment such as sigma blade mixers or extruders may help solve this problem. Compounds containing fillers are easier to mill since the filler reduces the tackiness of the mix. Normally it is necessary to alternate filler and resin to get successful compounding. Dry liquid concentrates on Microcel E are commercially available, but are not always desirable for silicone elastomer compounding.

## Conclusions

The data presented in this paper clearly shows that 1,2-polybutadienes are effective coagents for EPDM and EPM. These non-toxic and non-odorous resins are now available. When used with peroxide vulcanization catalysts, property enhancement results at low levels of 1,2-polybutadiene. There are additional benefits in that the resin serves as a non-extractable plasticizer, which improves handling characteristics and decreases energy consumption. When cured using additive levels of 20-30 phr, hard but highly heat and hydrocarbon resistant materials are obtained.

These materials have been tested in geothermal and oil well environments and have performed in these carefully designed tests at temperatures up to 315 °C. This is performance much beyond the usual limits for elastomers. Undoubtedly, 1,2-polybutadiene crosslinked EPDM has an important future in geothermal and oil well applications. It is equally likely that other applications requiring resistance to heat, hydrocarbons and chemicals would benefit by using this improved system.

Data presented in this paper also shows that 1,2-polybutadiene resins are effective coagents for peroxide and cured Silicone elastomers in several ways. Small amounts of LPB additive can bring about significant changes in the dynamic properties of Silicone elastomers, as well as useful changes in such physical properties as hardness, elongation and modulus. Larger amounts of LPB additive can bring about very significant reduction in swell in hydrocarbon solvents. In addition, carbon can be used as a reinforcing filler in inexpensive formulations which can perform tasks not previously possible for Silicone elastomers.

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