

**1,2 Polybutadiene Coagents  
For Improved Elastomer Properties**

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## ABSTRACT

There is an increased demand for elastomers with better heat resistance, decreased swell in oil and solvents, improved compression set and longer working life. There are also new demands for “clean” elastomer compounds which do not have toxic additives such as lead, cadmium, selenium or by-products of sulfur donors such as nitrosoamines. Vulcanization with peroxides can provide many of these needed improvements in properties. To achieve the best results in peroxide cured elastomers coagents are generally needed. This paper discusses data comparing 1,2-polybutadiene coagents with other well known coagents and attempts to clarify how the compounder or engineer can use this data to choose the right coagent for particular applications. Emphasis is on using coagents to improve elastomers for demanding environments.

## INTRODUCTION

Peroxide can be used to cure many elastomers and the use of peroxides is growing due to demand for “clean” compounds and for improved performance in severe environments. Peroxides are often not used in such elastomers as NR, SBR or CR due to formation of hard, brittle and often useless products. However, by careful application of the appropriate coagent, useful compounds of these elastomers have been achieved and are now in daily commercial use.

Peroxides are commonly used to cure other elastomers such as EPDM, EPM, NBR, HNBR, CPE, EVA, various fluoropolymers, silicones etc., with or without coagents. It is generally accepted that coagents provide needed compounding flexibility for design of rubber compounds with this range of elastomers. For most elastomers, simple peroxide cure without a coagent is not sufficient because the cure rate may be too slow or too scorchy. The degree of crosslinking may be either too high or too low, or the cost of peroxide curative may be too high, or needed properties may not be achieved. Some improvements can be made in the compounds by the use of plasticizers, fillers, and rubber blends, but the compounding change which can bring about the most striking benefits is the use of the correct coagent for the particular application under consideration. There is both a general lack of good information and a lot of misinformation about

coagents which can confuse the compounder setting about to use this technique to improve rubber compounds. This paper will concentrate on applications in EPDM.

It has been known for many years that a co-curing agent or coagent is a necessary additive to peroxide cured EPDM formulations to increase crosslinking and improve mechanical and physical properties. Coagents accomplish this by interacting with the polymer during the crosslinking reaction. This interaction increases the number or rate of the crosslinks being formed and often will result in increased efficiency in the use of peroxide.

All coagents are similar with respect to how they work. They all contain di or polyunsaturation and have a readily extractable hydrogen in the alpha position to the unsaturated bonds<sup>1,2,3</sup>. This hydrogen then reacts with the peroxide to form free radicals. This free radical reaction takes place more readily with the coagent than with the rubber polymer and in the presence of coagents few rubber free radicals are formed directly from peroxide.

The performance and efficiency of all coagents are not alike. Researchers have classified coagents as either Type I or Type II depending on their effect on the curing characteristics of the rubber. Type I coagents generally form more reactive free radicals which increase both the rate of cure and the state of cure of the system. Type II coagents have less reactive and more stable free radicals and increase primarily the state of cure of the elastomer. Most coagents are either low or moderate viscosity liquids. For compounding into elastomers the liquid coagents are often conveniently handled in dispersed form on solid carriers such as fumed silica.

Type I coagents are polar molecules and many are relatively low in molecular weight. Since free radicals of this type are very reactive, Type I coagents have a tendency to react at the very first site possible and cause coupling or homopolymer-ization in addition to elastomer crosslinks<sup>2,3</sup>. The effect of this reaction may be a scorchy cure, which can compromise physical properties, but also results in homopolymer chain formation which become distributed throughout the rubber matrix. Also as a result of the polarity of these

coagents, they often have limited compatibility with many rubber compounds and can bloom from the uncured stock. Due to this compatibility factor, Type I and some Type II coagents can not be used at high levels in rubber compounds. Coagents of this type are typically acrylates, methacrylates and one example of a bismaleimide.

Type II coagents are relatively low polarity molecules and form more stable free radicals resulting in less scorchy compounds. These low polarity coagents have better compatibility with many elastomers, which allows them to be used in many compounds at higher loading levels<sup>3</sup>. This property of low polarity coagents is an advantage to the compounder in that he can effectively use more of the coagent to increase specific properties of the elastomer. The more stable free radicals of Type II coagents also improve scorch safety and exhibit less homopolymerization within the elastomeric matrix. Therefore, the rubber matrix is truly crosslinked by carbon to carbon bonds involving the elastomer. High vinyl 1,2-polybutadiene, allyl esters of cyanurates, isocyanurates and aromatic acids such as mellitic are examples of Type II coagents.

Coagents show differences in toxicity and these differences are important to the compounder<sup>4</sup>. The rubber industry is becoming more aware of toxicity factors needed to promote a safe working environment for employees and the general public. The molecular weight of the coagent is one important factor useful in the estimation of potential toxicity. As a rule of thumb, the higher the molecular weight of the coagent, the lower the volatility of the molecule. 1,2-polybutadiene coagents have molecular weights in the range of 1800 to 4000, depending on the type and grade. A comparison of molecular weight and volatility information is given in Table 1. Since the factors which make one compound toxic where another is not is a complex subject largely ruled by biochemical factors.

Confining the discussion to coagents commonly used in the rubber industry, it is known that heated acrylate and methacrylate esters can release acrylic and methacrylic acid, under conditions where there is ester exchange or saponification occurring. Similarly releases of allyl alcohol can be expected from allyl esters such as TAC and TAIC. This is a concern for formulating most rubber compounds with coagents since conditions leading to ester decompositions could be present.

Table 1

Comparison of Molecular Weight and Boiling Points of Coagents				
Coagent	Type	Molecular Wt.	Boiling Point	Volatility
TMPTMA	I	338.4	>200 °C/ 1mm	Moderate
EGDMA	I	198.2	83°C/ 1mm	High
HVA-2	I	268.3	195°C mp	Moderate
ZDA	I	235.4	>250°C mp	Low
70% 1,2 PBD/S	II	2400	>300°C/ 1mm	Low
70% 1,2 PBD	II	2400	>300°C/ 1mm	Low
90% 1,2 PBD	II	3200	>300°C/ 1mm	Low
TAC	II	249.3	110°C mp	Moderate
TAIC	II	249.3	149°C/ 4mm	Moderate
TATM	II	330.3	175°C/ 0.1mm	Moderate

An observation which led to the decision to undertake the studies resulting in this paper is that compounders routinely start with 2-3 phr of TMPTMA or TAC coagents in developing new peroxide cured elastomers, whereas they were likely to begin with 6-10 phr of 1,2-polybutadiene resin (PBD). Elongation at break and compression set development with PBD was as good or better than TMPTMA at 2-3 phr levels, but not quite as good as TAC under similar conditions. EPDM compounds could be made using higher levels of PBD at 20-30 phr to impart oil swell and high temperature resistance to EPDM compounds used in downwell oil well and process steam applications whereas TAC and TMPTMA were not suitable for these applications due to compatibility problems such as blooming and extraction in oil and hot water. PBD coagents provided good physical properties under conditions of very long term heat aging whereas there were inconsistencies in short term heat aging which made PBD appear to be less suitable than TMPTMA, TAC and TAIC.

This paper is a comparative study of the most common commercially used coagents in the market today. The following work will evaluate Type I and Type II coagents and show the performance of both types in EPDM. The authors hope that this data will be used as a compounding tool for engineers and compounders to choose the best coagent for their particular application. Since a comparative study of coagents is a very large undertaking, the subjects covered in this paper is only a fraction of the total field where coagents are used. Even in the area of coagents for EPDM there is much work yet to be done.

## **EXPERIMENTAL**

Nordel 1040 was selected for the control EPDM due to previous work performed comparing coagents<sup>6</sup>. The coagent and peroxide were added prior to testing by mixing several small batches and then combining them to form a homogeneous mass. All test plaques were molded from the same batch of each coagent. All cure times were adjusted to bring the respective cures to  $T_{90}$  for each coagent.

The commonly used coagents known to be in industrial use were selected for testing. Type I coagents include trimethylolpropane trimethacrylate (TMPTMA), ethylene glycol dimethacrylate (EGDMA), zinc diacrylate (ZDA) and N,N'-meta-phenylene dimaleimide (HVA-2). The Type II list includes high 1,2-polybutadienes (PBD) ranging from 70% to 90% vinyl content, a new high vinyl 1,2-polybutadiene/styrene copolymer coagent, triallyl cyanurate (TAC), triallyl isocyanurate (TAIC) and triallyl trimellitate (TATM). The triallyl trimellitate material may no longer be in commonly used in the rubber industry. A number of other materials are commercially used as coagents in the wire and cable industry and have not been included here.

A large EPDM masterbatch was prepared off site to provide for a consistent formulation for use in this study. The peroxide and coagents were mixed into this masterbatch on a two roll lab mill at a temperature of 125°F (52°C). Formulations were sheeted and allowed to cool to room temperature for 24 hours then sampled for testing. Appendix I contains the appropriate ASTM methods and test equipment used in this study. Figure 1 shows the fixture needed to run the Ford Laboratory Compression Set test, which may not be familiar to all rubber compounders. Formulation used for this study are shown in Table 2.

In addition to the above testing, this study was completed by performing Deterioration in an Air Oven ASTM-D 573-88 and Effects of Liquids-ASTM D 471-91. Test liquids used to determine volume swell were ASTM # 1 and ASTM # 3 oils. Toluene was used for swelling the elastomers to equilibrium for determination of the relative crosslink density.

A careful log of mill time, temperatures and observations was kept on the compounding work. This approach allowed for consistent and reliable data to be generated. The material balances were determined for all compounds and found to be satisfactory.

Figure 1

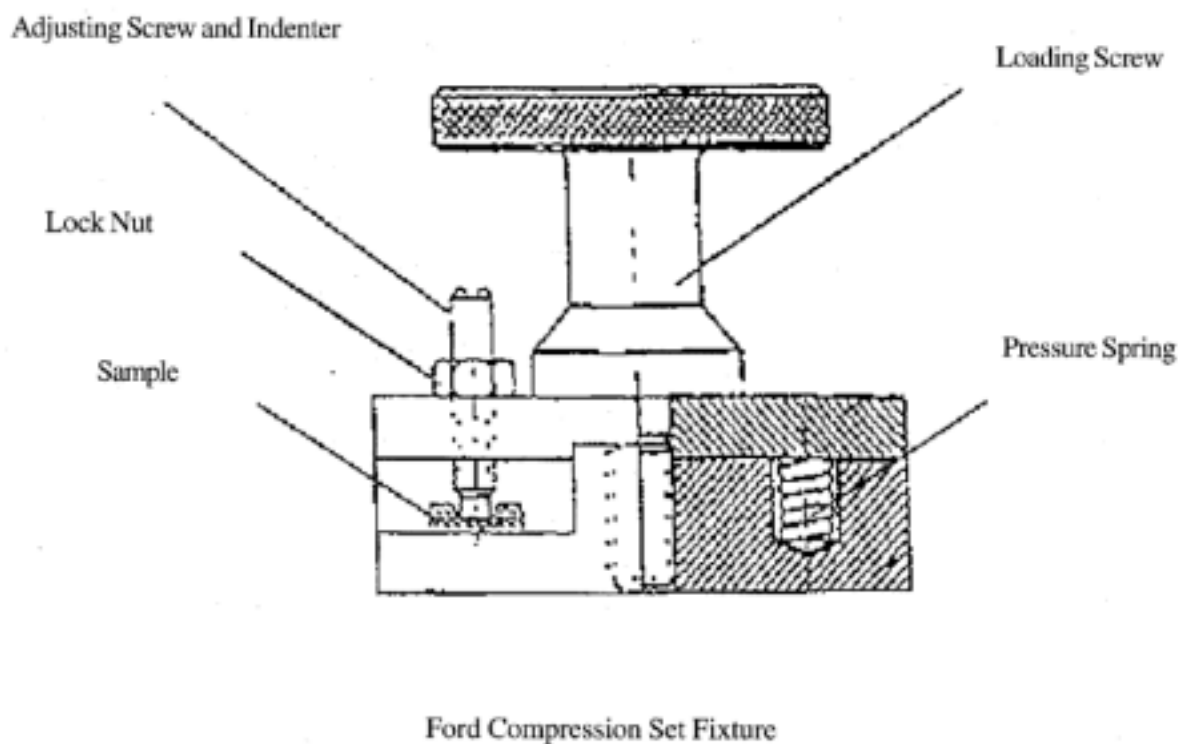


Table 2

Coagent Test Formulation phr	
EPDM (Nordel 1040)	100.00
N660 Carbon Black	50.00
Zinc Oxide	5.00
AgeRite Resin D	0.50
	155.25

## RESULTS AND DISCUSSION

The first study conducted for this work was a peroxide comparison of t-butylperoxydiisopropyl-benzene (Vulcup) and dicumyl peroxide (Dicup) for the selection of the best peroxide. The masterbatch according to the formulations in Table 2 were cured with each of the peroxides. Rheometry demonstrated that the t-butylperoxydiisopropyl-benzene produced

a higher maximum torque of 38.8 dNm compared to 32.8 dNm maximum torque of the dicumyl peroxide. The minimum torque, scorch times and cure times at 90% cure were approximately the same. Curing the formulas at a higher temperature of 177°C demonstrated the same results Tables (3 and 4) Therefore t-butylperoxydiisopropyl benzene was the chosen peroxide for this study.

Table 3

<b>Rheometer Data, ASTM D 2084</b>					
Range: 100%		Clock: 40 min		Speed: 100 cup	
Die: Micro		Arc: 1°		Temperature: 160°C	
Compound	Initial Visco. dNm	Min. Torque dNm	Max. Torque dNm	Scorch Time Min.	T <sub>90</sub> min.
Dicup 40 KE	16.4	12.3	32.8	2.1	18.1
Vulcup 40 KE	19.2	13.8	38.8	2.2	19.9

Table 4

<b>Rheometer Data, ASTM D 2084</b>					
Range: 100%		Clock: 40 min		Speed: 100 cup	
Die: Micro		Arc: 1°		Temperature: 160°C	
Compound	Initial Visco. dNm	Min. Torque dNm	Max. Torque dNm	Scorch Time Min.	T <sub>90</sub> min.
Dicup 40 KE	15.8	11.6	33.2	1.2	6.3
Vulcup 40 KE	15.8	12.2	45.4	1.1	11.8

A head to head comparative study was made between TMPTMA, PBD and the control at 2 phr concentration for the coagents using the standard Nordel 1040 compound shown in Table 2. Data from this study confirmed that the PBD (Ricon 154 in this compound) while being less scorchy than the TMPTMA gave unaged physical properties having

a lower ultimate elongation (Eb) of 255% vs. 300%. Compression set was better after aging 168 hours at 150°C (34.4% vs. 37.8% for the ASTM D 395 Method and 58.8% vs 65.5% for the Ford method - Table 5). This work confirms other data showing that PBD can compare favorably with TMPTMA at low use levels.

Table 5

<b>Rheometer Data, ASTM D 2084</b>						
Range: 100%		Clock: 40 min		Speed: 100 cup		
Die: Micro		Arc: 1°		Temperature: 160°C		
Coagent	Phr	Initial Visco dNm	Min. Torque dNm	Max. Torque dNm	Scorch Time Min.	T <sub>90</sub> min.
Control	---	14.7	11.0	40.9	2.2	28.2
TMPTMA	2.0	14.7	12.2	44.2	1.6	36.6
90% 1,2 PBD	2.0	14.7	12.1	45.3	2.0	39.2
<b>Unaged Physical Properties ASTM D 412</b>						
<b>Press Cure @160°C Cure to T<sub>90</sub></b>						
Coagent	Tensile Strength (MPa)	Modulus @100% (MPa)	Die C Tear (KN/m)	Ult. Elong (%)	Shore Rebound Resil.	Shore A Hard. points
Control	15.8	2.4	37.1	310	43	73
TMPTMA	16.9	2.9	44.3	300	46	69
90% 1,2 PBD	16.6	3.6	42.4	255	45	70
<b>Compression Set</b>						
<b>168 hrs. at 150°C</b>						
Coagent		ASTM D 395 Method		Ford Method		
Control		38.1		63.4		
TMPTMA		37.8		65.5		
90% 1,2 PBD		34.4		58.8		



Direct comparisons of coagents are difficult due to many complicating factors such as compatibility and the differing response of physical properties to concentration changes. Three physical properties offer the best chance of comparative analysis.

These are ultimate elongation, 100% modulus, and crosslink density. In an attempt to produce correlations using ultimate elongation as the primary property, compounds were developed with each coagent which resulted in an ultimate elongation of 200%. In a few cases, this resulted in the use of levels of coagent which would not ordinarily be used in commercial practice for that particular coagent (such as TMPTMA at 11 parts). One hundred per cent modulus (100%) was determined for each system, but the size of the data base precluded direct comparison of this property since not enough data points were available. Estimates of crosslink density are also available since swell data

at equilibrium in toluene is considered a good indicator for the property.

Rheometry for each compound is shown in Table 6. The column labeled phr (parts per hundred) indicates that the Type I acrylates need approximately 2 to 6 times the amount of Type II coagent to meet the elongation criteria. HVA-2 did not require such a large quantity to achieve this elongation. It was observed that the Type I coagents had scorch times which were significantly less than that of the Type II coagents. Therefore the Type II coagents have a larger margin of scorch safety. This effect is generally typical of a Type I coagent due to the higher reactivity of the free radicals formed, resulting in a faster onset of cure and shorter cure time. Ricon 100 (high vinyl 1,2-polybutadiene/styrene copolymer) obtained the best scorch safety of all the coagents at 2.5 minutes and one of the faster cure times of 27.7 minutes.

Table 6

<b>Rheometer Data, ASTM D 2084</b>						
Range: 100%		Clock: 40 min		Speed: 100 cup		
Die: Micro		Arc: 1°		Temperature: 160°C		
Coagent	Phr	Initial Visco dNm	Min. Torque dNm	Max. Torque dNm	Scorch Time Min.	T <sub>90</sub> min.
Control	---	14.7	11.0	40.9	2.2	28.2
<u>Type I</u>						
EGDMA	11.0	13.6	9.7	50.2	1.4	27.3
TMPTMA	12.0	14.1	10.4	53.3	1.3	27.2
HVA-2	1.0	17.0	11.8	48.3	1.7	26.2
ZDA	6.0	15.8	10.4	55.7	1.7	24.2
<u>Type II</u>						
70% 1,2 PBD/S	10.0	13.0	9.1	44.1	2.5	27.7
70% 1,2 PBD	7.5	15.8	11.7	51.2	2.1	29.4
90% 1,2 PBD	5.0	16.4	11.5	50.0	2.3	29.2
TAC	2.0	15.8	11.7	52.2	2.1	29.4
TAIC	2.0	16.1	11.4	48.8	2.1	29.8
TATM	2.5	15.3	10.6	49.3	2.2	29.2

**ROOM TEMPERATURE TESTING:**

Room temperature physical data was collected after curing to T<sub>90</sub> conditions (Table 7). All compounds did show an adequate comparative baseline with an elongation range of 200% +/- 5%. The data demonstrates that all coagents exhibited increased 50% and 100% moduli, decreased tear strength and

ultimate elongation, which demonstrates increased crosslink density. The 70% high vinyl 1,2-PBD (Ricon 150) showed the most improvement in 50% and 100% moduli. 70% high vinyl 1,2-PBD improved the 100% modulus from 2.4 Mpa to 5.25 Mpa, an 118% increase.

Table 7

Coagent	Tensile Strength (MPa)	Modulus @ 50% (MPa)	Modulus @ 100% (MPa)	Die C Tear (KN/m)	Ult. Elong (%)	Shore Rebound Resil.	Shore A Hard. points
Control	15.8	1.4	2.4	37.1	310	43	73
<u>Type I</u>							
EGDMA	14.4	2	4.2	36.6	205	42	74
TMPTM	15.7	1.8	4.4	36.6	205	42	77
HVA-2	11.3	1.5	3.5	34	200	45	73
ZDA	17.3	2.1	4.7	35	205	45	76
<u>Type II</u>							
70% 1,2 P	13.3	1.7	3.9	35.4	200	45	73
70% 1,2 P	15.5	2.1	5.3	27.7	195	43	75
90% 1,2 P	15.4	2.1	4.6	31.9	200	44	73
TAC	14.3	1.5	3.2	31.2	205	46	73
TAIC	13.5	1.7	3.6	28.9	200	42	74
TATM	14.8	1.9	4.8	32.6	205	44	72

This data agrees with the tear strength data which would be expected to decrease with increasing crosslinking. 70% high vinyl 1,2-PBD generated the lowest Die C tear of 27.7 (kN/m), decreasing the tear strength 25% from the control. Both the modulus and tear properties are indications that there is increased crosslinking. The tensile strength data is difficult to conclude since this property has a bell-shaped curve relationship to crosslinking density. A study was not conducted to optimize the tensile strength for each of the coagents. All Shore rebound and Shore hardness values tested within approximately the same range. The exception was TMPTMA with a Shore A of 77 compared with 73 for the control. Of the Type II coagents the 70% 1,2-PBD/Styrene copolymer was the highest at a Shore A hardness of 75.

#### COMPRESSION SET:

ASTM Method B compression set testing and the Ford Laboratory compression set testing in harsh conditions of 150°C for 168 hours were performed. The design of the Ford compression set apparatus introduces additional shear forces into the sample and causes three dimensional creep possibilities whereas the shear forces in ASTM method B only allows one

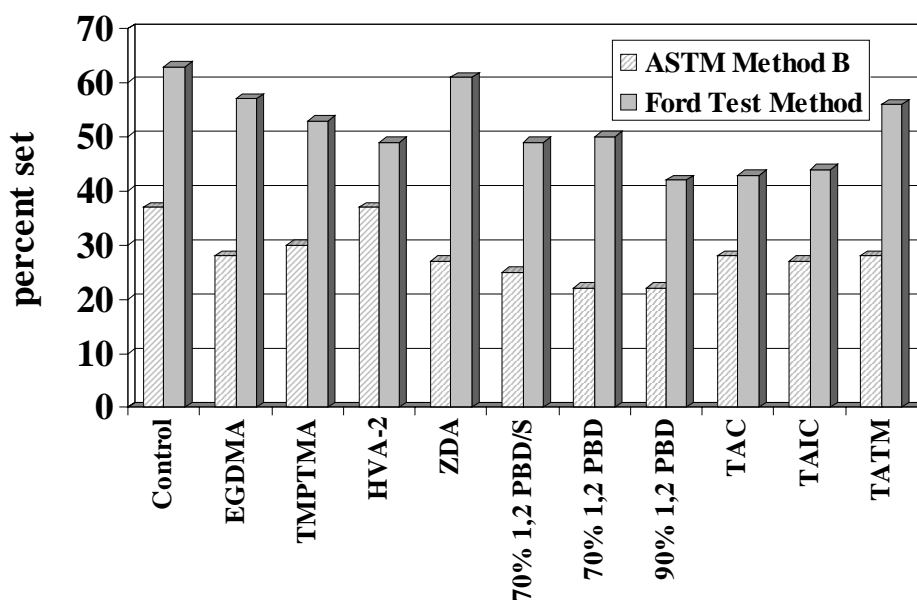
dimensional creep to occur. For this reason, the Ford compression set data represents a more severe test in compression set terms. The data obtained (Figure 2) reflects that the Type II coagents are superior especially in the Ford method. The 90% high vinyl 1,2-PBD outperformed all other coagents in this property. This product recorded a 22.94% and 3.03% compression set for the ASTM and Ford methods, respectively.

The Type I coagent, ZDA, performed very well in unaged and aged physical properties shown in Tables 6 and 7, but it produced the highest compression set in both types of compression test. This is probably due to the formation of an ionic type of crosslink rather than carbon-carbon bond crosslinks which results in poor performance at the severe conditions of the compression set testing. Homopolymer networks formed due to the tendency of Type I coagents to homopolymerize may be responsible for the lesser performance of these types of coagents in the compression set tests. These homopolymers can soften at the Tg for the particular homopolymer network involved, causing decreased performance in compression set<sup>2,3</sup>.



Figure 2

## Compression Set 168 hours at 150 C



### SOLVENT AND OIL SWELL TESTING:

Fluid swell testing in toluene was used to determine crosslink density for each of these compounds. This test was performed for 22 hours and 46 hours at room temperature to determine the time the test specimens needed to reach equilibrium. Results showed that equilibrium had already been reached at 22 hours. As shown in Figure 3, there is little variance in the Type II coagents, indicating that the crosslink density of each material had reached a similar value. This correlates very well with ultimate elongation which was designed to be equal for all test compounds. Except for 1,2-PBD/S, which had a slightly lower value for this test, all measured values were practically identical. These values represent tight crosslinking of the rubber chains. Type I coagents present a less clear picture. While TMPTMA and ZDA promote tight crosslinking with respect to toluene swell, the HVA-2 and EGDMA are rather poor in this respect. It is not altogether clear why this should be so. However, HVA-2 is used at a low concentration in these compounds; the same thing cannot be said for EGDMA.

Fluid swell tests were performed in both ASTM reference oils #1 (paraffinic oil) and #3 (aromatic oil).

Samples were allowed to swell for 168 hours at 150°C. Results from Tables 8 and 9 reveal that all the coagents decrease the percent volume swell relative to the control and favor the Type II coagents in both oils. It is interesting to note that the fluid swell properties of all the coagents with the mild exception of TAC in ASTM #1 oil correspond remarkably with the swell data observed with toluene. The data recorded for ASTM #3 oil is very different. Despite the fact that ASTM #3 oil is an aromatic oil and toluene is an aromatic solvent, the relative swell for the respective coagents are dissimilar. For ASTM #3 oil, there appears to be a strong correlation between actual quantities of coagent used rather than crosslink density as determined by toluene swell data. HVA-2 is again poor, but as was pointed out before, relatively little of the material was used. The exception to this observation is the EDGMA swell data. EDGMA is poor in all fluid swell tests, thus it should not be used for this purpose in EPDM. 1,2-PBD at levels of 20-30 phr has proved successful in reducing oil swell under the harsh environments of down hole use for EPDM cable formulations. Coagents such as TMPTMA, TAC, and TAIC are not compatible with EPDM at these levels and are thus not useful in this application.

Figure 3

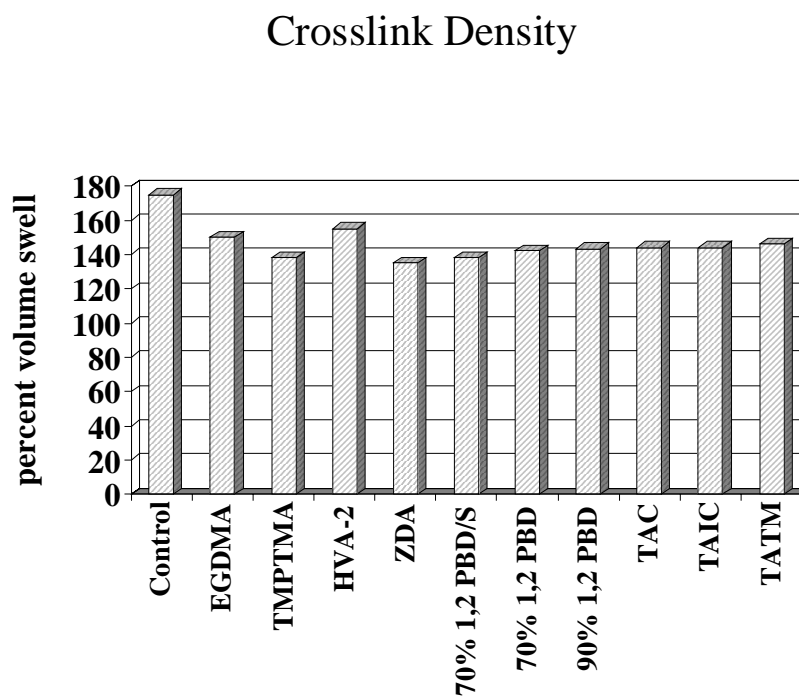


Table 8

Oil Swell in ASTM Oil #3 168 hrs. @ 150°C

Coagent	% Length	% Mass	% Volume
Control	26.5	92.2	115.1
<u>Type I</u>			
EGDMA	24.3	75.9	94.9
TMPTMA	22.0	70.6	88.3
HVA-2	22.5	75.5	94.2
ZDA	22.8	67.2	85.0
<u>Type II</u>			
70% 1,2 PBD/S	19.9	65.7	81.4
70% 1,2 PBD	20.7	66.8	82.9
90% 1,2 PBD	20.3	68.9	85.3
TAC	21.6	71.3	97.2
TAIC	22.2	68.6	84.7
TATM	21.6	71.6	89.1

Table 9

## Oil Swell in ASTM Oil #3 168 hrs. @150°C

Coagent	% Length	% Mass	% Volume
Control	39.8	107.2	120.8
<u>Type I</u>			
EGDMA	33.7	97.3	117.3
TMPTMA	31.4	61.8	77.4
HVA-2	31.8	83.6	101.5
ZDA	30.8	60.8	76.6
<u>Type II</u>			
70% 1,2 PBD/S	28.5	51.4	64.0
70% 1,2 PBD	30.2	68.1	82.5
90% 1,2 PBD	31.6	84.1	100.8
TAC	29.6	97.0	115.6
TAIC	23.0	89.8	107.7
TATM	30.7	64.8	80.6

**HEAT AGING TESTS:**

Some very interesting results were obtained by heat aging these formulations in air under relatively severe conditions at 150°C for 168 hours followed by cooling to room temperature for 24 hours and measurement of the aged physical properties. These results can be found in Table 10. Table 11 tabulates percent change of the physical properties versus unaged physical properties. It should be understood that moderate changes were anticipated because the cure conditions were normalized to arrive at the  $T_{90}$  cure rather than  $T_{100}$ . The moduli, tear and ultimate elongation data

indicates that all the Type II coagent formulations continued to crosslink. This additional crosslinking produced relatively small percent change in all properties for the 70% 1,2-PBD and the 90% 1,2-PBD, but TAC and TAIC continued to harden and the resulting heat aged compound had relatively large changes in tensile strength, hardness, modulus and ultimate elongation. Changes of similar magnitude were observed with the 1,2-PBD/S copolymer. The Type I coagents performed well in most physical properties but there appeared to be a peak in physical property data followed by a heat induced degradation in properties represented by increasing elongation<sup>6</sup>.

Table 10

## Heat Aged Physical Properties 168 hrs. @ 150°C in air

Coagent	Tensile Strength (MPa)	Modulus @50% (Mpa)	Modulus @100% (MPa)	Die C Tear (KN/m)	Ult. Elong (%)	Shore Rebound Resil.	Shore A Hard. points
Control	15.7	1.6	3	35.6	310	39	72
<u>Type I</u>							
EGDMA	15.5	2.0	4.4	32.9	225	41	75
TMPTMA	13.7	2.0	4.3	32.6	215	40	76
HVA-2	11.4	1.8	3.7	35	205	45	72
ZDA	15.9	2.6	6.1	36.4	185	46	78
<u>Type II</u>							
70% 1,2 PBD/S	12.5	2.0	5.1	26.5	155	44	75
70% 1,2 PBD	14.2	2.1	5.4	27.7	160	44	74
90% 1,2 PBD	13.8	2.4	4.6	29.5	180	44	76
TAC	5.9	1.8	4.4	23.6	125	40	75
TAIC	7.9	2.2	4.8	26.6	140	42	74
TATM	12.8	1.4	3.6	25	200	43	72

Table 11

Coagent	Tensile Strength (% chg)	Modulus @ 50% (% chg)	Modulus @ 100% (% chg)	Die C Tear (% chg)	Ult. Elong (% chg)	Shore bound Re (pt. change)	Shore A Hard. (pt. change)
Control	-1	19.8	25.4	-4.3	0	-4	-1
<u>Type I</u>							
EGDMA	8	-2.1	4.9	-10.1	9.8	-1	1
TMPTM	-12.4	13.5	-4.0	-11	4.9	-2	-1
HVA-2	0.6	19	6.3	3.1	2.5	0	-1
ZDA	-8.1	28.2	29.9	4	-9.8	1	2
<u>Type II</u>							
70% 1,2 PBD/S	-5.7	18.1	31.7	-25.3	-22.5	-1	2
70% 1,2 PBD	-8.4	3	2.5	-8.1	-18	-2	-1
90% 1,2 PBD	-10.4	15.8	0.3	-7.4	-10	0	3
TAC	-59.5	24.8	36.7	-24.2	-39	-6	2
TAIC	-42	27.8	35.7	-7.9	-30	0	0
TATM	-13.2	-28.9	-23.4	-23.1	-2.4	-1	-5

In summary, the severely heat aged compounds from both Types I and II continued to cure as expected by the change from  $T_{90}$  to  $T_{100}$ , but following this Type II coagents continued to crosslink while the Type I coagents underwent some reversion. Small changes in antioxidant content and type can make very large differences in heat age testing in air. Further work and even longer heat aging periods are necessary to clearly delineate the potential differences noted here.

#### PHYSICAL PROPERTIES AT ELEVATED TEMPERATURES:

Physical properties at 100°C (Tables 12 and 13) and at 150°C (Tables 14 and 15) were tested. The test specimens were placed in a pre-heated environmental chamber for 5 minutes to equilibrate. This chamber was able to maintain the specified temperature +/- 0.5 degree for this time period. This data is difficult to interpret based only on a comparison of Type I and Type II considerations. A comparison of the physical properties of Table 12 and Table 14 shows the expected trend that tensile strength and elongation properties decrease for most of the compounds as the temperature at which they are measured increases from 100°C to 150°C. ZDA and 90% 1,2-PBD maintained the best elongation properties. Although the Type I coagents seem to retain a higher percentage of the

original values at 100°C, they are strongly affected by increasing the temperature to 150°C. PBD coagents maintained more consistent results and were less affected by increasing the temperature from 100°C to 150°C. For instance, the 70% vinyl 1,2-PBD showed very little change in all physical properties when compared at 100°C and 150°C. The tensile strength, 50% modulus and elongation values deviated less than 0.5 percent and the tear results only 4.2%. In Type I coagents the properties of the elastomer changes rapidly from 100°C to 150°C.

The final evaluation for this study was a cost vs performance ratio for comparison of the coagents. The main property that benefits from the use of coagents is compression set. Therefore an equation was developed using this property in the normalized compounds previously tested. Cost performance was calculated by using the following expression:

$$\text{Cost Performance} = [(p/tp) * C / (100 - \%cs)]$$

p - PHR of coagent used

tp - total PHR of the formulation

c - average cost of coagent

%cs - Ford % compression set value

Table 16 demonstrates that the Type II coagents are generally more cost efficient per performance than the Type I coagents. The average Type I compound cost per performance is nearly 60% more than the average Type II compound. Of all the coagents, TMPTMA is

the least cost efficient coagent at \$0.0047/%, more than 4 times the least expensive coagent TATM at \$0.0011/% and nearly 3 times higher cost/performance than the 90% 1,2-polybutadiene resin.

Table 12

<b>High Temperature Physical Properties tested at 100°C</b>					
<b>Coagent</b>	<b>Tensile Strength (MPa)</b>	<b>Modulus @ 50% (MPa)</b>	<b>Modulus @ 100% (MPa)</b>	<b>Ultimate Elongation (%)</b>	<b>Die C Tear (KN/m)</b>
Control	6.5	0.9	2.1	20.5	20.5
<u>Type I</u>					
EGDMA	9.6	2.1	3.3	150	23.1
TMPTMA	7.8	1.7	4.8	160	22.1
HVA-2	4.7	1.4	2.9	155	19.4
ZDA	7.2	1.9	4.5	140	16.1
<u>Type II</u>					
70% 1,2 PBD/S	6.4	2.0	3.3	130	16.1
70% 1,2 PBD	4.7	3.3	--	70	14.2
90% 1,2 PBD	4.9	2.3	4.4	100	18.2
TAIC	6.0	2.2	4.9	130	14.5
TATM	5.9	1.5	3.1	155	12.1

Table 13

<b>High Temperature Physical Properties tested at 100°C</b>					
<b>Coagent</b>	<b>Tensile Strength (% chg)</b>	<b>Modulus @ 50% (% chg)</b>	<b>Modulus @ 100% (% chg)</b>	<b>Ultimate Elongation (% chg)</b>	<b>Die C Tear (% chg)</b>
Control	-58.7	-31.0	-15.1	-33.9	-44.8
<u>Type I</u>					
EGDMA	-33.2	5.5	15.2	26.8	36.9
TMPTMA	-50.4	-7.3	-25.0	-22.0	-39.7
HVA-2	-58.2	-7.7	-17.9	-22.5	-42.8
ZDA	-58.4	-6.0	-4.1	-31.7	-54.0
<u>Type II</u>					
70% 1,2 PBD/S	-52.0	14.1	19.4	35.0	54.5
70% 1,2 PBD	-69.6	58.5		-64.1	-52.9
90% 1,2 PBD	-68.0	10.1	7.7	-50.0	-48.5
TAC	68.5	10.8	41.3	-51.2	-50.6
TAIC	-55.5	29.0	-40.3	-35.0	-49.7
TATM	-60.1	-21.1	-35.4	-24.4	-62.9

Table 14

**High Temperature Physical Properties  
tested at 150°C**

<b>Coagent</b>	<b>Tensile Strength (MPa)</b>	<b>Modulus @50% (MPa)</b>	<b>Modulus @100% (MPa)</b>	<b>Ultimate Elongation (%)</b>	<b>Die C Tear (KN/m)</b>
Control	3.9	1.4	3.2	120	17.3
<u>Type I</u>					
EGDMA	6.9	2.8	4.8	85	18.4
TMPTMA	5.5	2.3	---	95	20.3
HVA-2	3.5	1.9	---	85	14.4
ZDA	6.3	1.7	4.2	125	10.5
<u>Type II</u>					
70% 1,2 PBD/S	4.3	2.7	---	75	14.2
70% 1,2 PBD	4.7	3.3	---	70	14.2
90% 1,2 PBD	3.4	1.4	3.6	130	16.6
TAIC	3.6	2.4	---	80	10.5
TATM	4.1	2.0	---	85	14.0

Table 15

**High Temperature Physical Properties  
tested at 150°C**

<b>Coagent</b>	<b>Tensile Strength (% change)</b>	<b>Modulus @50% (% change)</b>	<b>Modulus @100% (% change)</b>	<b>Ultimate Elongation (% change)</b>	<b>Die C Tear (% change)</b>
Control	-75.5	0.0	34.0	-61.3	-53.3
<u>Type I</u>					
EGDMA	-52.3	40.2	14.5	-58.5	-49.8
TMPTMA	-64.6	29.6	---	-53.7	-44.5
HVA-2	-69.6	21.7	---	-57.5	-57.7
ZDA	-63.9	-17.6	-10.2	-39.0	-70.0
<u>Type II</u>					
70% 1,2 PBD/S	-67.4	58.2	---	-62.5	-59.9
70% 1,2 PBD	-69.3	587.7	---	64.1	-48.8
90% 1,2 PBD	-78.2	-32.2	-21.8	-35.0	-53.0
TAC	-77.5	69.6	---	-70.7	-59.0
TAIC	-73.3	39.1	---	-60.0	-63.6
TATM	-72.3	5.7	---	-58.5	-57.0

Table 16

**Cost vs. Performance**

<b>Coagent</b>	<b>\$/ % Recovery after compression</b>
<u>Type I</u>	
EGDMA	0.0037
TMPTMA	0.0047
HVA-2	0.0014
ZDA	0.0029
<u>Type II</u>	
70% 1,2 PBD/S	0.0035
70% 1,2 PBD	0.0024
90% 1,2 PBD	0.0016
TAC	0.0013
TAIC	0.0014
TATM	0.0011



## CONCLUSION

This study showed that all coagents brought about the expected improvements in crosslinking of a particular peroxide cured EPDM formula. The results of these improvement were better physical properties such as modulus and compression set. There were significant differences noted between these coagents, many of which are already well known in the industry. For example, it was not expected that 11 phr of TMPTMA would be necessary to bring about sufficient crosslinking to decrease ultimate elongation to 200% in our test formulation. Since this is more TMPTMA than would be normally used in a typical commercial EPDM application, the commercial utility of this example may not be evident.

Type I coagents provide good physical properties and adequate compression set for those applications not requiring long exposure to high temperatures and fluids. A Type I coagent (ZDA) appears to have very good physical properties in unstressed elastomer, but has poor compression set under conditions used in our tests. Most Type I coagents did not hold up well in the more severe Ford compression set test. Type I coagents cannot be used above certain limiting concentrations for EPDM due to blooming in the uncured state.

The data presented in this study indicates that Type II coagents are generally more effective than Type I coagents for those applications requiring long exposure to heat and fluids. An explanation for this may be due to carbon-carbon crosslinks rather than stiffening of the rubber matrix due to homopolymer chains of coagent from the Type I coagents. It is probable that the homopolymer network in an EPDM matrix softens at the  $T_g$  of the homopolymer fragment. PBD resins are much more compatible with EPDM and can be used up to about 30 phr. Compositions using this high level are somewhat scorchy even though Type II coagents are less scorchy than Type I coagents. Use of high levels of PBD result in hard, creep resistant elastomers which have very good resistance to heat and solvents. In addition to their good performance, PBD coagents have low toxicity and are cost competitive.

In this comparative study, the PBD coagents have been shown to perform well in all areas and in certain environments out perform all the other coagents tested. Examples of these performance areas are compression set and physical properties in hot environments. In industry, liquid high vinyl content 1,2-PBD resins have long been used as coagents in a variety of elastomers in a wide range of applications<sup>7</sup>. As little as 2-3 phr PBD added to EPDM have shown improvement of compression set and physical properties. It should be noted that as much as 30 phr of liquid 1,2-PBD resins can be used in formulations for harsh environments. This loading is typical in many applications such as geothermal and oil well environments to improve heat and hydrocarbon resistance of the elastomer. Cost effectiveness, lack of toxicity and improved properties of peroxide cured EPDM elastomers using PBD as a coagent should permit the compounder to make better rubber compounds for demanding uses.

## REFERENCES

1. "TAC as a Coagent for Free Radical Crosslinking," American Cyanamid Co, Elastomers and Polymer Additive Department
2. Robert C. Keller, "Peroxide Curing of Ethylene-Propylene Elastomers," American Chemical Society, October 6-9, 1987
3. R.E. Drake, Coagent Bulletin: Introduction, April 27, 1992. Ricon Resins, Inc., Grand Junction, Colorado
4. G.T. Perkins, "Peroxide Curing of 'Nordell'," Du Pont Co., Polymer Products Department, July 1987
5. A.R. Hirasuna, G.D. Bilyeu, "Geothermal Elastomers Materials (GEM) Program-Final Report," U.S. Department of Energy, July 1979
6. Hercules Technical Data, "Use of Monomers in Peroxide Cures," Bulletin ORC-110C

Appendix 1  
Test Methods and Equipment

Test	ASTM D#	Equipment
Vulcanization Characteristics Using Oscillating Disk Cure Meter	2084	Techpro Oscillating Disk Curemeter
Measurement of Rubber Properties in Tension	412	GCA/Precision CRE 500 Universal Tester
Tear Resistance (Die C)	624	GCA/Precision CRE 500 Universal Tester
Compression Set Method B	395	Ames 202 Thickness Gauge
Compression Set Ford Method		Ames 282 Thickness Gauge
Determination of swell in Liquids	471	Ames 202 Thickness Gauge Washington Calipers .001”
Standard Temperatures and Atmospheres for Conditioning and Testing	1349	
The Impact Resilience of Rubber by Vertical Rebound	2632	Shore Resiliometer

Appendix 2  
Chemical Name and Suppliers of the Ingredients

Supplier	Compound	Grade
Alcolac	Triallyl Trimaletate	TATM
Akrochem Corp.	Triallyl Cyanurate	Akrosorb 19203
Akrochem Corp.	Triallyl Isocyanurate	Akrosorb 19251
Akrochem Corp.	T-Butylperoxy-Diisopropyl Benzene	Retilox F 40 KEP
Dupont	N, N'-meta-phenylenedimaleimide	HVA-2
H.M. Royal	Dicumyl Peroxide	Perkadox BC 40 KPD
Ricon Resins, Inc.	1,2 PBD	Ricon 150
Ricon Resins, Inc.	1,2 PBD	Ricon 154
Ricon Resins, Inc.	1,2 PBD/Styrene	Ricon 100
Cray Valley	Trimethlopropane Trimethacrylate	SR-350
Cray Valley	Ethylene Glycol Dimethacrylate	SR-206
Cray Valley	Zinc Diacrylate	SR-706
Special thanks to Burton Rubber for supplying the EPDM masterbatch formulation used in this study		