

Current and Future Trends of Accelerators and Antidegradants for the Tire Industry

Sung W. Hong[†]

Uniroyal Chemical Company, Inc. Spencer Street TSSC Building Naugatuck, Connecticut 066770

(Received May 21, 1999)

ABSTRACT : Rubber chemicals such as accelerators, antidegradants, vulcanizing agents, processing agents and retarders are very important to the production and protection of tires and rubber goods.

The use of accelerators and antidegradants are evaluated in various tire components. This paper will focus on how to vulcanize tires economically and maintain the physical properties of each tire component without severe degradation due to oxygen, heat and ozone. Also, new non-nitrosoamine accelerators and non-staining antiozonants will be discussed. Lastly, the future requirements of antidegradants and accelerators in the tire industry will be reviewed.

Tires have been vulcanized with Sulfenamides as primary accelerators and either Guanidine's or Thiurams as secondary accelerators to achieve proper properties at service conditions. However, interior components such as the carcass can be vulcanized with Thiazoles as a primary accelerator to cure faster than the external components. Using the combination of Sulfenamide with secondary accelerators in a tire tread compound and the combination of a Thiazole and Guanidine in a carcass compound will be presented with performance data. Uniroyal Chemical and another Rubber Chemical Manufacturer have developed, "Tetrabenzyl Thiuram Disulfide," (TBzTD) as a non-Nitrosoamine accelerator, which could replace Nitrosoamine generating Thiurams. This new accelerator has been evaluated in a tread compound as a secondary accelerator. Also, Flexsys has developed N-t-butyl-2-benzothiazole Sulfenamide (TBSI) as a non-Nitrosoamine accelerator which could replace 2-(Morpholiniothio)-benzothiazole (MBS), a scorch delayed Sulfendamide accelerator. TBSI has been evaluated in a Natural Rubber (NR) belt skim compound vs. MBS. An optimum low rolling resistant cure system has been developed in a NR tread with Dithiomorpholine (DTDM). Also, future requirements for developing accelerators will be discussed such as the replacement of DTDM and other stable crosslink systems.

Antidegradants are divided into two different types for use in tire compounds. Internal tire compounds such as apex, carcass, liner, wire breaker, cushion, base tread and bead compounds are protected by antioxidants against degradation from oxygen and heat due to

[†]대표저자(e-mail : Sung-Hong@uniroyalchemical.coe)

mechanical shear. The external components such as sidewall, chafer and cap tread compounds are protected from ozone by antiozonants and waxes. Various kinds of staining and non-staining antioxidants have been evaluated in a tire carcass compound.

Also, various para-phenylene diamine antiozonants have been evaluated in a tire sidewall compound to achieve the improved lifetime of the tire. New non-staining antiozonants such as 2, 4, 6-tris-(N-1, 4-dimethylpentyl-p-phenylene diamine) 1, 3, 5 Trizine (D-37) and unsaturated Acetal (AFS) will be discussed in the tire sidewall to achieve better appearance.

The future requirements of antidegradants will be presented to improve tire performance such as durability, better appearance and longer lasting tires.

Keywords : accelerators, antidegradants, vulcanizing agents, processing agents, retarders.

I. Introduction

Rubber chemicals are very important in the role to economically produce tires and other rubber goods while maintaining properties at service conditions. Tire manufacturers try to develop better performance and long lasting tires using stable crosslinking systems and antidegradants. This special performance tire would provide more profits than the conventional commodity tire. Therefore, continuous efforts have been made to produce run flat tires by Michelin and Goodyear. Most tire manufacturers produce high performance/speed rated low aspect ratio tires and 80,000 mile tires. Bridgestone and Hankook Tire produce sponge tread tires for ice traction. Also, another approach is to produce tires economically so that they can compete with pricing from lower cost imports for maintaining or increasing conventional tire market shares. The low cost tires can be developed by a simplified design, however, proper selection of rubber chemicals is one of the several approaches which tire manufacturers can produce tires with lower production costs by reducing the vul-

canization times. Such as higher temperature cures with less reversion and thinner gauge with sufficient antidegradant protection. This concept can be also applied to higher performance and new concept tires for producing tires economically.

1. Accelerators

All the rubber products have tried to minimize cure times for improving productivity. A choice of suitable accelerators for compounding must be selected depending upon processing requirements. Usually, organic accelerators are divided into certain groups based on chemical composition of each accelerator. Each group is then classified as either a primary or a secondary accelerator depending upon the group activity in rubber compounds. The thiazoles, sulfenamides are known to yield a classical curemeter vulcanization curve, with an adequate scorch time and therefore, are classified as primary accelerators. The thiurams, dithiocarbamates and guanidine's yield scorch curemeter curves when used alone and are classified as secondary accelerators. In tire compounding,

only primary accelerators or a combination of primary accelerators with secondary accelerators have been used. The secondary accelerators are used as activators or kickers for the primary accelerators. There is another secondary accelerator, aldehyde amines.

Usually, for tire compounds, ultra fast accelerators are not recommended, because of scorch problems in the larger batches. Therefore, sulfenamide, thiazole and guanidine type of accelerators have been used. However, a lower cost cure system has been developed with an activator such as TMTD for a kicker. The amount of TMTD or other thiuram accelerator should be used below 0.2 phr or 2.0 phr level, because of scorch problems. Cure systems for tread, sidewall, carcass, bead filler/apex and belt skim compounds will be discussed by using existing and new accelerators. The detailed information of various accelerators are shown in Table 1.

Table 1. Classification and Chemical Groups of Accelerators What is Mean¹⁰

Chemical group	Classification	Vulcanization rate
Thiazoles(MBT, MBTS, ZMBT)	Primary	Medium-Fast
Sulfenamides(CBS, TBBS, MBS, DCBS, TBSI, DIBS, OBTS, Curite 18, ESVE)	Primary	Fast after delayed action
Thiurams(TMTD, TMTM, TBTD, TETD, TBzTD)	Secondary	Fast
Dithiocarbamates (ZMDC, ZEDC, ZBDC, ZBzDC)	Secondary	Very fast
Aldehyde amines	Secondary	Fast
Guanidine's (DPG, DOTG)	Secondary	Medium

Table 1(CONTINUED). Various Accelerators

Primary accelerators	Chemical name
Thiazoles	
MBT	2-Mercaptobenzothiazole
MBTS	Dibenzothiazyl disulfide
ZMBT	Zinc Salt of 2-Mercaptobenzothiazole
Sulfenamides	
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide
TBBS	N-t-butyl-2-benzothiazyl sulfenamide
MBS	2-(Morpholiniothio) Benzothiazole
DCBS	N, N, dicyclohexyl-2-benzothiazole sulfenamide
TBSI	N-T-butyl-bis-2-benzothiazole sulfenamide
ESVE	N-cyclohexyl bis (2-benzothiazole) sulfenamide
OBTS	N-Oxydiethylene-2-benzothiazole sulfenamide
Curerite 18	Thiocarbamyl sulfenamide
Secondary accelerators	Chemical name
Thiurams	
TBTD	Tetrabutyl thiuram disulfide
TMTD	Tetramethyl thiuram disulfide
TMTM	Tetramethyl thiuram monosulfide
TETD	Tetraethyl thiuram disulfide
TBzTD	Tetrabenzyl thiuram disulfide
Dithiocarbamates	
ZMDC	Zinc N-Dimethyl dithiocarbamates
ZEDC	Zinc N-Diethyl dithiocarbamates
ZBDC	Zinc N-Dibutyl dithiocarbamates
ZBzDC	Zinc N-Dibenzyl dithiocarbamates
Guanidines	
DPG	N, N'-diphenyl guanidine
DOTG	N, N'-diotolyl guanidine

2. Antidegradants

Polymers have been degraded by either ozone or oxygen. Usually, external components such as the sidewall and tread have been exposed by

protection of antiozonants, while antioxidants protect the internal components from oxidation failure due to oxygen and heat by mechanical shear. Therefore, antidegradants are divided into antiozonants and antioxidants as follows:

2.1. Antiozonants

The commercially available antiozonants are the organic group of p-phenylenediamines. The p-phenylenediamines (PPD) are divided into three classes, depending on the nature of substituents, R and R', which are attached to the Nitrogen atoms of PPD molecules. In one class, R is a phenyl (aryl) substituent and R' is the alkyl group. This unsymmetrical N-alkyl-N'-aryl PPD's are most widely used in the tire industry. This is due largely to the excellent dynamic ozone protection they provide. In general, these unsymmetrical antiozonants tend to provide the best balance with regards to protection from ozone, oxygen and flexing including crack formation.^{1,2} In a second class, both R and R' are alkyl groups. Symmetrically substituted dialkyl PPD are very reactive with oxygen and ozone. They provide extremely good static ozone resistance and possess very good solubility in diene rubbers. However, dialkyl PPD's are not very effective for long term protection from ozone or oxygen induced cracking due to their high reactivity and relatively high volatility.^{5,6} In a third class, both R and R' are large aryl groups. These symmetrical diaryl PPD's are very good antioxidants, they are generally slow to migrate in rubber compounds. Therefore, they are only moderately effective antiozonants and have very limited solubility in rubber compounds

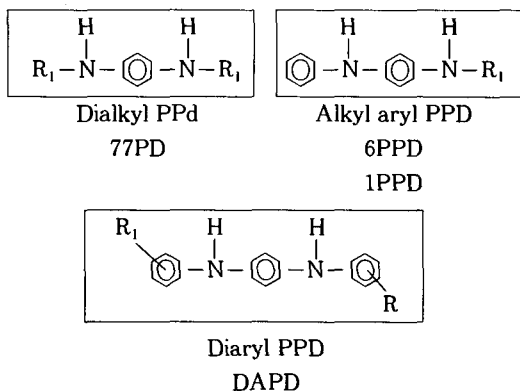
(1.0 phr is the maximum limit in NR/BR compounds).^{8,9}

The ultimate objective is to develop non-staining and non-discoloring antiozonants for a better appearance sidewall. Uniroyal Chemical has developed 2, 4, 6 tris (N-1, 4-dimethylpentyl-p-phenylenediamino)-1, 3, 5 Triazine (TAPDT) as a non-staining antiozonant and Bayer has developed unsaturated Acetal (AFS). TAPDT has a very higher molecular weight chemical (MW 693) and is a slow migrating antiozonant. Therefore, in accelerated testing, it would perform well in an ozone environment. However, it will also provide longer term protection in NR/BR black sidewall.^{9,12} However, AFS is only good with EPDM and halobutyl compounds, but not for SBR, BR and NR compounds. The details of antiozonants are shown in Table 2.

2.2 Antioxidants

Usually, antioxidants have been used for internal components of tire for preventing degradation, due to oxygen and heat generation by mechanical flexing and shear. However, non-staining and non-discoloring antioxidants have been added to both the white sidewall and cover strip for preventing discoloration and for improving flex fatigue. Staining antioxidants have been used internal components such as carcass, belt skim, bead filler/apex, breaker cushion, liner and etc.. There are two types of primary antioxidants which have been used for the tire components. They are hindered phenols and secondary aryl amines. The secondary antioxidants consist of various trivalent phosphorous and divalent sulfur containing compounds. They are

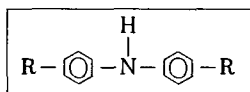
Table 2. Change to Figure or Scheme
Staining Antiozonants



NON-Staining antiozonants

TAPDT : 2,4,6-Tris-(N-1,4-dimethylpentyl-p-phenylenediamino)-1,3,5 Triazine
 AFS : Bis-(1,2,3,6-tetrahydrobenzaldehyde)-pentaerythrityl acetal

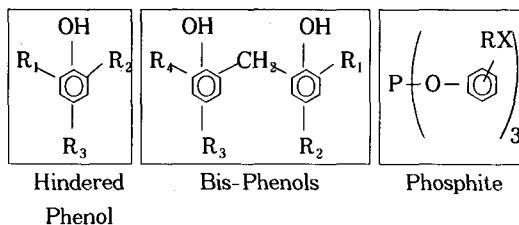
Table 3A. Figure or Scheme
Staining Antiozonants



Amine Type of Antioxidant

ADPA : Diphenylamine/Acetone Condensation Product
 ODPa : Octylated Diphenylamine
 TMQ : 2,2,4 Trimethyl-1,2-dihydroquinoline

Table 3B. Change it to Figure or Scheme



SP : Styrenated Phenol
 o-MBp14 : 2,2' methylene bis-(4-methyl-6-tert-butyl phenol)
 TNPP : tris(nonylphenol) phosphite

phosphites and thioester antioxidants. These antioxidants are used for stabilizing polymers, but not for tire compounds.⁷ The details of antioxidants are shown in Table 3A and 3B.

In this paper, existing and new accelerators and antidegradants are evaluated in the tire tread, sidewall, belt skim, carcass and bead filler/apex for improving process and property. Also, future needs of rubber chemicals for the tire industry will be discussed.

II. Tire Components

Pneumatic tires usually contain a variety of rubber compositions, each designed to contribute some particular factor to the overall performance. Rubber compounds are designed for a specific function and have different physical property requirement such as hardness, elongation, modulus, hysteresis, flex properties and aged physical properties. The method of construction for pneumatic tires also varies among the tire companies. Usually, the simplest construction using the minimum number of components is the most favorable approach. However, the durability, handling, riding and performance requirements force tire companies into developing more sophisticated construction for improving performance tires. The most common construction of the passenger radial tires is shown in Figure 1. The major tire components are tread, sidewall, carcass body ply, wire breakers, liner, bead filler, chafer, bead and breaker cushion.^{3,4}

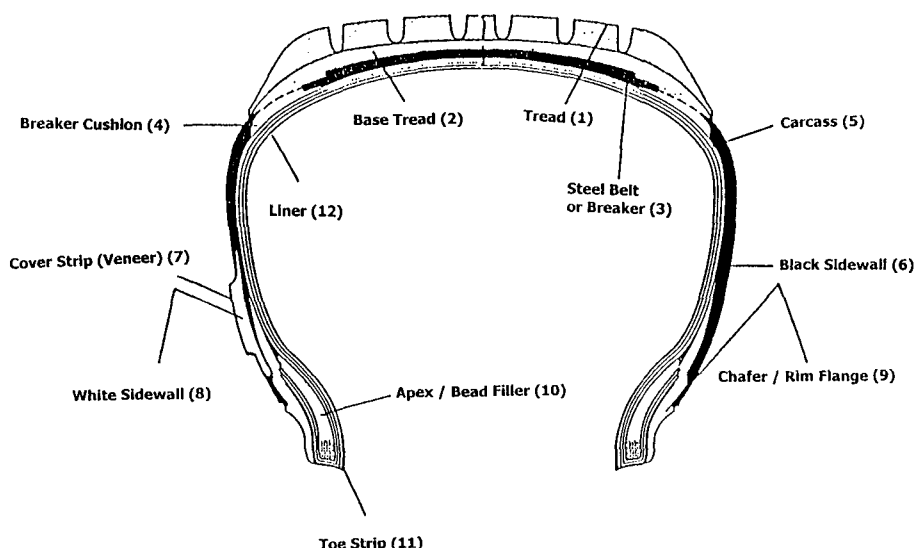


Fig. 1. Cross section of a passenger tire.

III. Accelerators and Antidegradants in Tire Components

1. Tread

One of the principal components of the rubber composition in tires is the tread. It must be tough and resilient to minimize cures and tears as well as to protect the tire body from bruising impact. Most passenger treads contain Styrene-Butadiene Rubber (SBR), cis-Polybutadiene (cis-BR) or high vinyl content Polybutadiene (HVBR) and Natural Rubber (NR). Three types of performance properties include high wear resistance, good wet/dry traction and low rolling resistance. It is, therefore, important to select the appropriate polymer blends to develop a tread with the overall performance.¹¹

• Experimental

Two different types of tread compounds have been evaluated. One group has two lower roll-

ing resistant compounds, which have been cured with TBBS/DPG/sulfur and the other has two high performance treads with semi-EV cure systems (higher level of TBBS with lower levels of sulfur for less reversion at a high temperature cure), which are shown in Table 4A and 4B. Usually, tread compounds have been protected with antiozonants/wax and antioxidants. 6PPD and TMQ were added to these compounds for the protection from ozone cracking and oxidation due to heat and shear. In order to determine the level of antidegradants, the optimization work has been carried out, which is shown in Table 5A, 5B and 5C. Solution SBR (S-SBR), HVBR or a high vinyl content S-SBR was used to develop lower rolling resistant treads, the blends of higher styrene content SBR and lower styrene content SBR were utilized to develop higher performance speed rated tire treads. One of the higher performance treads contains emulsion SBR and the other

Table 4A. Low Rolling Resistant Treads

Ingredients	A-4	A-5
Duradene 711	70.0	
Duradene 723	30.0	
NS 112		60.0
NS 116		40.0
N-234	55.0	55.0
OIL	20.0	20.0
Zinc Oxide	3.0	3.0
Stearic Acid	1.5	1.5
6PPD	1.0	1.0
TMQ	1.0	1.0
WAX	0.5	0.5
TBBS	1.0	1.0
DPG	0.4	0.4
Sulfur	1.75	1.75

Table 4B. High Performance Tread

Ingredients	A-6	A-7
E-SBR 1712	55.0	
E-SBR 1721	82.5	
D-750		55.0
TO-591		82.5
N-234	85.0	85.0
Aromatic OIL	27.3	27.3
Zinc Oxide	3.0	3.0
Stearic Acid	1.0	1.0
6PPD	1.0	1.0
TMQ	1.0	1.0
WAX	0.5	0.5
TBBS	1.8	1.8
Sulfur	1.0	1.0

Table 5A. Tread Recipe

	A(0-3)
S-SBR	70.0
HVBR	30.0
N-234 Black	55.0
Aromatic OIL	20.0
Zinc Oxide	3.0
Stearic Acid	1.5
6PPD	Varied
WAX	0.5
TMQ	1.0
TBBS	1.0
DPG	0.4
Sulfur	1.8

consists of solution SBR. All four compounds were measured for Mooney Viscosity at 100°C, Mooney Scorch at 132°C, curometer at 177°C, physical properties including what does it stand for MTE, tear, abrasion and viscoelastic properties at various temperatures. With these compounds, P175/70R-14 experimental tires were built for evaluating rolling resistance, wet/dry traction and wear.

• Results and Discussion

1) Accelerations and Antidegradants

The optimized cure system and antidegradants level would provide proper protection from ozone and oxidation and proper properties with a cure system. Especially, lower rolling resistant treads would require more sulfur with lower levels of accelerators for lower rolling resistance, while high performance tread would need a less reversion cure system with higher levels of accelerators and lower levels of sulfur.

2) Lower Rolling Resistant Treads

For lowering rolling resistant treads, two different types of solution SBR's are used for improved wear, rolling resistance and traction. Usually, lower styrene content SBR (less than 18.5% styrene) would provide not only lower rolling resistance, but would also improve wear resistance. However, it does not provide traction, especially wet traction. Therefore, it is necessary to blend the SBR with high Tg polymers such as HVBR or with a higher vinyl content SBR for improved traction. Higher styrene content SBR would increase the rolling resistance significantly. Therefore, it is not recommended for rolling resistant treads.

The first group contains (S-SBR)/HVBR, of

Table 5B. Physical Properties

	A-0	A-1	A-2	A-3
S-SBR	70	70	70	70
HVBR	30	30	30	30
6PPD		1	2	3

Physical Properties AT R. T.-Cured 10' at 177°C

Tensile, MPa	22.5	21.9	20.8	22.0
Elongation, %	550	570	560	570
300% Modulus, MPa	9.2	8.8	8.5	8.4
Shore a Hardness	65	64	64	63
Tear, DIE C, kN/m	64.8	69.5	65.3	63.0

Physical Properties after Aged 2 Weeks at 70°C

Tensile, MPa	15.5	20.4	20.7	21.7
% Retention	69	93	100	99
Elongation, %	410	460	490	500
% Retention	74	80	88	88
300% Modulus, MPa	13.5	11.2	10.3	10.5
% RETENTION	146	127	121	125
Shore a Hardness	71	70	69	69
Die C Tear, Kn/M	50.5	68.2	63.3	63.14
% Retention	77	98	97	100

Table 5C (CONTINUED). Monsanto Flex Fatigue

Title	A-0	A-1	A-2	A-3
S-SBR	70	70	70	70
HVBR	30	30	30	30
6PPD		1	2	3

Unaged				
KC TO Failure Average of 6 Samples	338	412	460	456

Aged 3 Days at 100°C				
KC TO Failure Average of 6 Samples	15	41	62	68

70/30 the other group contains chemically modified solution SBR, which can bind chemically with carbon black and high vinyl content SBR (Table 4A). No significant differences in Mooney Viscosity, curometers and unaged physical properties between these compounds were

Table 6. Rheometer

	A-4	A-5	A-6	A-7
ML 1+4 @ 100°C	67	62	64	65
MS AT 132°C	21	24.5	26.5	27.0

Curemeter at 177°C

ts ₂	2.16	2.21	2.49	2.51
t ₉₀	4.50	4.60	4.42	4.70
ML	4.7	4.3	4.4	4.5
MH	28.8	29.0	25.3	26.9

Physical Properties-Cured at 177°C

Tensile, MPa	21.5	23.5	18.5	21.5
Elongation, %	520	530	500	480
300% Modulus, MPa	10.1	9.9	21.0	14.0
Shore a Hardness	63	64	68	70
Tear DIE C, kN/m	65.5	68.7	59.5	57.5
Picco Abrasion Index	115	125	92	94

Table 7. Viscoelastic Properties

	A-4	A-5	A-6	A-7
Cured at 177°C				
Rheometer Values at 10 Hz				
Tangent Delta				
at 0°C	0.21	0.20	0.40	0.55
at 25°C	0.18	0.16	0.31	0.35
at 50°C	0.16	0.13	0.25	0.22
at 75°C	0.14	0.11	0.22	0.20
at 100°C	0.12	0.09	0.20	0.18

Table 8. Tire Test Results

	A-4	A-5	A-6	A-7
Tire Wear Test, Miles	55,000	62,000	35,000	42,000
Rolling Resistance (Lower=Better)	100	95	126	126
Traction (Higher=Better)				
DRY, 40 MPH	98	99	121	125
WET, 60 MPH	85	87	108	112

measured (Table 6). However, significant improvements in abrasion resistance and the tangent delta value at 75°C with chemically modified S-

SBR (Table 7). These results have been confirmed with the tire test results for rolling resistance, wet and dry traction and wear test, which are shown on Table 8.

3) High Performance Treads

Two different model compounds for high performance treads have been developed, using both high Tg emulsion SBR and solution SBR blended with low Tg SBR's (Table 4B). Both compounds were tested for Mooney Viscosity and Scorch, curometers and physical properties such as MTE, Die C Tear and Shore A Hardness (Table 6). Also, tangent delta values at 0°C and 75°C were measured along with Picco Abrasion. Identical physical properties were measured however, Tangent Delta values and abrasion results indicated significant differences between emulsion and solution SBR treads. Clearly, solution SBR tread is superior in wear and traction, while it provides lower rolling resistance over emulsion SBR tread, which is shown in Tables 7 and 8.

• Conclusion

1) 1/1 TMQ/6PPD would provide sufficient ozone protection for treads.

2) Lower rolling resistance and improved wear resistance has been achieved with chemically modified solution SBR's, compared to solution SBR.

3) Improved wear resistance and traction has been obtained with high Tg solution SBR, compared to high Tg emulsion SBR. Also, slight reduction of rolling resistance was achieved with solution SBR.

2. Sidewall

Typically, tire sidewall packages consist of three components: (1) breaker cushion, which protects wire adhesion to rubber under the wire breaker, (2) black sidewall, which provides good flexing, good cut growth resistance, ozone cracking resistance and abrasion resistance, especially in Europe and (3) chafer or rim flange, which would have stiffer compounds which would provide stability to the radical ply tires and abrasion resistance for bead chafing. Both sidewall and rim flange are exposed to the outside environment. Therefore, both components must be protected from ozone or oxidation cracking. Typically, 2.5 to 4.0 phr of alkyl aryl paraphenylene diamine such as 6PPD or IPPD are used in combination or blended wax for static and dynamic ozone cracking resistance in the sidewall and rim flange. The sidewall contains NR and cis-BR for improving lower cut growth resistance, lower hysteresis for lower running temperature for improved flex fatigue resistant properties, also for lowering the modulus for improvement in flexing. Usually, 2.0 to 4.0 phr of 6PPD has been used for the sidewall for protection from ozone cracking and to improve flex fatigue and aged physical properties, including aged cut growth resistance. TBBS or CBS have been used for a primary accelerator. The secondary accelerator does not require to cure faster because the sidewall gauge is much thinner than the tread thickness.

• Experimental

Five compounds were mixed by varying the amounts of antiozonants and wax (Table 9).

Table 9. Black Sidewall

	B-0	B-1	B-2	B-3	B-4
NR	55.0	55.0	55.0	55.0	55.0
CIS BR	45.0	45.0	45.0	45.0	45.0
N-660 Black	30.0	30.0	30.0	30.0	30.0
N-375 Black	20.0	20.0	20.0	20.0	20.0
Zinc Oxide	3.0	3.0	3.0	3.0	3.0
Stearic Acid	1.5	1.5	1.5	1.5	1.5
Naphthenic OIL	7.0	7.0	7.0	7.0	7.0
6PPD		2.0	2.5	3.0	4.0
WAX		4.0	3.0	1.5	1.0
TBBS	1.0	1.0	1.0	1.0	1.0
80% oiled Insoluble Sulfur	2.0	2.0	2.0	2.0	2.0

Mooney Viscosity, aged and unaged physical properties, static and dynamic ozone cracking test and outdoor dynamic flexing have been tested for the evaluation of these five compounds by curing them for 10 min at 160°C.

• Results/Discussion

All the aged physical properties have significantly been improved with the addition of 2.0 phr or more 6PPD. Also, with the addition of wax, static ozone cracking resistance improved. However, dynamic flexing is directly proportional to the amount of 6PPD, which is shown in Tables 10 and 11.

• Conclusion

1) Static ozone protection is directly proportional to the amount of wax, but not to the amount of antiozonant.

2) Dynamic ozone protection and flex fatigue properties can be improved by increasing the amount of antiozonant.

3. Carcass

Tire body or carcass rubber compounds must

Table 10. Physical Properties

	B-0	B-1	B-2	B-3	B-4
6PPD		2.0	2.5	3.0	4.0
WAX		4.0	3.0	1.5	1.0
ML -1+4 at 100°C	49	45	46	48	48
MS at 132°C, 3 Point Rise Time	21.0	22.7	21.5	19.2	19.0
Cured 10' at 160°C					
Tensile at R. T., MPa	19.2	19.9	18.9	19.3	19.0
Elongation, %	540	580	560	550	540
300% Modulus, MPa	8.60	8.26	8.23	8.60	8.70
Shore a Hardness	52	51	52	52	52

Aged 2 Weeks at 70°C, % Retention

Tensile	67	82	91	95	96
Elongation, %	62	76	81	82	83
300% Modulus	150	130	130	130	130
Hardness Points Change	+8	+8	+8	+7	+7
Tear, DIE C	75	83	90	95	100

Table 10(CONTINUED). Ozone Cracking Test

	B-0	B-1	B-2	B-3	B-4
6PPD		2.0	2.5	3.0	4.0
WAX		4.0	3.0	1.5	1.0

Static Ozone Cracking-Bent Loop(Hours), 50 PPHM at 40°C

O.K.		4	4	4	4
VVS		6	6	6	6
VS				96	72
S					
C	6				

Dynamic Ozone Flexing, 25% Extension, 50 PPHM at 40°C

Hours to Crack	8	24	24	72	144
----------------	---	----	----	----	-----

*Outdoor Dynamic Flexing

KC to Failure	Not Tested	16951	Not Tested	Not Tested	39560
---------------	------------	-------	------------	------------	-------

*Nagatuck, CT-Continuous Flexing-Aged 6 Months Prior to Testing.

form strong bonds to the adhesive coated

(Resorcinol Formaldehyde Latex Dipped) fabric. Usually, polyester, rayon or nylon fibers are used to make cords for tire carcass, except for steel monople tires. Carcass strength and durability should be adequate enough to insulate the tire cords and hold them in their paths. The carcass compounds must, however, be soft enough to permit a slight change in the cord angles when the tire is flexed. The body rubber serves as insulation between the fabric plies. Outstanding fatigue resistance required of the carcass compounds in order to withstand cyclic deformation. Previously, suflendamide type of accelerators had been used for carcass compounds. However, amines in accelerators had a tendency to degrade polyester cords. Therefore, MBTS and MBS has been used along with DPG as a kicker and modulus developer. MBS delays scorch for improved processing, because it is a sulfenamide type of accelerator.

• Experimental

Two compounds were evaluated with MBTS/DPG and MBS/DPG cure systems respectively (Table 11). Mooney Viscosity, Mooney Scorch at 132°C, Curometer at 177°C, unaged and aged physical properties, DeMattia and flex fatigue to failure have been measured (Tables 12 and 13).

• Results/Discussions

MBS/DPG cure system provided scorch safety, however, it may have a problem due to slow curing for the optimum vulcanization as an internal component. All the physical properties included flex fatigue, showed no differences between cure systems. Therefore, one of the cure systems can adopt a carcass compound for either polyester or other cords.

Table 11. Recipe for Carcass Compound

Ingredients	MB	C-1	C-2
NR	60		
CIS BR	20		
SBR	20		
N-660 Black	50		
Naphthenic OIL	15		
Zinc Oxide	3		
Stearic Acid	1		
TMQ	1		
Tackifying Resin	2		
Resorcinol Resin	2		
HMMM		2.0	2.0
MBTS		1.0	
MBT			1.0
DPG		0.25	0.25
80% Insoluble Sulfur		3.0	3.0

Table 12. Processing Properties

	C-1	C-2
MBTS	1.0	
MBS		1.0
ML 1+4 @ 100°C	49	50
MS @ 132°C, 3 PT. Rise Time	11.0	18.0
Curometer @ 177°C		
ML N-M	0.39	0.38
MH N-M	2.91	2.83
ts ₁ , Minutes	0.97	1.5
ts ₂ , Minutes	1.13	1.85
tc ₅₀	1.75	2.61
tc ₉₀	3.02	5.01

• Conclusion

1) MBTS/DPG cure systems provide a faster cure system. The internal components such as carcass, apex and base tread should require a faster cure system.

2) MBS/DPG cure systems provide scorch safety over MBTS / DPG cure systems.

3) All the physical properties indicated no significant differences between the cure systems.

Table 13. Physical Properties

	C-1	C-2
MBTS	1.0	
MBS		1.0
ML 1+4 @ 100°C	49	50
MS @ 132°C, 3 PT. Rise Time	11.0	18.0
Curometer @176°C		
Tensile @ R. T. MPa	20.2	21.5
% Elongation	480	550
300% Modulus, MPa	9.5	8.5
Shore a Hardness	57	55
Tear, DIE C, kN/m	49.7	53.0

% Retention After Aging 2 Weeks at 70°C

Tensile	78.1	81.0
% Elongation	71	70.0
300% Modulus	137	140
Tear, DIE C	77	75
Hardness, Point Changes	+6	+7

Demattia Flexing-Unaged KC to Failure

	405	527
--	-----	-----

Flex Fatigue Failure(100%) KC to Failure-Unaged

	215	230
--	-----	-----

Aged 70 Hours @ 100°C-KC to Failure

	23.0	22.0
--	------	------

4. Bead Filler/Apex

In both passenger and truck radial ply tires, a stiff lower sidewall construction is very important for handling performance. The stiffness controls the tire's movement at elevated speeds to provide improved handling and cornering. Tire manufacturers continue to develop higher hardness bead filler compounds for radial tires. The current bead filler compounds are highly filled with carbon black with an increased

amount of crosslinking density (tight cure).

Previously, 4, 4'-Dithiodimorpholine (DTDM) was used along with sulfenamide accelerators and a high level of sulfur is needed to achieve a higher level of total crosslinking density which would increase hardness. DTDM generates Nitrosmorpholine, therefore, Tetra benzyl thiuram disulfide (TBzTD) has replaced DTDM as a sulfur donor.

The highly filled bead filler compound will cause problems in processing the extension due to a higher Mooney Viscosity. Several resin manufacturers have developed phenolic hardening resins (Novolac) to meet the tire manufacturers requirements such as lower Mooney Viscosity and higher hardness. The typical bead filler compounds consists of either 100% NR or NR / SBR 1904. SBR 1904 contains a higher amount of styrene resin, which would provide a higher hardness at room temperature. However, at elevated temperatures, the styrene resins became soft, which would have a problem for higher speed handling.

• Experimental

Three compounds were evaluated, using 100% NR compound with Novolac Resin cured with methylene donor as shown in Table 14. Mooney Viscosity at 100°C, Mooney Scorch at 132°C, unaged and aged physical properties, cured for 10 minutes at 177°C and DeMattia Flex have also been tested.

• Results/Discussion

Using Novalac Resin and a lower level of carbon black, lower Mooney Viscosity values have been achieved for improved processing. Improved heat aged properties and DeMattia flex

Table 14. Bead Filler/Apex

	D-0	D-1	D-2
NR	100.0	100.0	100.0
Phenol Formaldehyde Resin	10.0	10.0	10.0
N-351 Black	55.0	55.0	55.0
Aromatic OIL	5.0	5.0	5.0
Zinc Oxide	10.0	10.0	10.0
Steraic Acid	2.0	2.0	2.0
Phenolic Resin Tackifier	2.0	2.0	2.0
TMQ		1.0	
DAPD			1.0
Methylene Donor	2.0	2.0	2.0
TBBS	0.60	0.60	0.60
TBzTD	0.25	0.25	0.25
CPT (Vulcanized Inhibitor)	0.25	0.25	0.25
80% Oiled Insoluble Sulfur	5.0	5.0	5.0

Table 15. Physical Properties

	D-0	D-1	D-2
TMQ		2.0	
DPPD			2.0
ML -1+4 at 100°C	49	51	52
MS at 132°C, 3 Point Rise Time	15.9	16.3	15.1
Cured 10' at 177°C			
Tensile at R. T., MPa	15.7	16.2	17.7
Elongation, %	370	350	450
200% Modulus, MPa	8.1	8.3	9.7
300% Modulus, MPa	13.1	13.7	13.4
Shore a Hardness	84	85	87
Tear, DIE C, kN/m	39	40	37

Aged 2 Days at 100°C, % Retention

Tensile at R. T.	49	59	74
Elongation, %	26	31	27
Shore a Hardness	+6	+5	+1
Tear, DIE C	52	61	62

Aged 2 Weeks at 70°C, % Retention

Tensile	61	73	77
Elongation	31	40	33
Shore a Hardness	+5	+5	+1
Tear, DIE C	59	65	71

Demattia Flex			
KC to Failure	8.0	11.7	83.5

properties were measured with the addition of antioxidants. However, DAPD provided superior performance over TMQ, which is shown in Table 15.

• Conclusion

1) Both DAPD and TMQ improved heat aged properties over the compound with antioxidants, aged 100°C and 75°C respectively. However, at 100°C, DAPD is superior in performance to TMQ.

2) Significant flex improvement was obtained with DAPD.

3) TBzTD/TBBS cure system provides sufficient scorch safety for processing.

5. Steel Belt Compound

Tire compounders continue to develop better performance steel belt skim compounds which require high unaged and aged adhesion to brass coated wire, stiffness for less movement for tread block. This stiffness and better adhesion will provide better handling, improved heat aging and dynamic flexing. This compound is of utmost importance to tire durability. Usually, 100% natural rubber with high levels of sulfur is used along with Cobalt salt, resorcinol resin and methylene donor as bonding agents to enhance adhesion. These raw materials also control cut formation and also control cut formation and prevent moisture from attacking the adhesion. The stiffness of the tread/belt package is directly correlated with the tire handling performance and riding performance. The stiffer package is better for handling and the softer package provides a better ride. The belt angles are therefore set between 20° and 26° for opti-

Table 16. Belt Skim Compound

	E-0	E-1	E-2	E-3
NR	100.0	100.0	100.0	100.0
Black N-330	55.0	55.0	55.0	55.0
Zinc Oxide	7.0	7.0	7.0	7.0
Stearic Acid	1.0	1.0	1.0	1.0
Naphthenic OIL	6.0	6.0	6.0	6.0
Cobalt Naphthenate	1.0	1.0	1.0	1.0
Resorcinol	2.0	2.0	2.0	2.0
6PPD		1.0	2.0	3.0
HMMM	2.0	2.0	2.0	2.0
DCBS	0.7	0.7	0.7	0.7
80% Insoluble Sulfur	5.0	5.0	5.0	5.0

mum performance for tires. Lower angles will provide a stiff tread/belt with a higher belt angle making the tread/belt softer.

6PPD or TMQ are usually used in belt skim compounds. If flex fatigue and heat aged properties must be improved, 6PPD is the antioxidant of choice. However, if only heat aged properties should be improved, then only TMQ must be added to the belt skim compound.

However, the selection of TMQ for various suppliers is very important, because a higher level of monomer in TMQ would migrate out to the surface causing a tack problem.

Excessive amounts of primary amines in the TMQ convert insoluble soluble sulfur.

The soluble sulfur would crystallize on the surface of the belt causing a tack problem too. Therefore, 6PPD has been used in this evaluation.

Also, most belt skim compounds require slow curing accelerators, such as DCBS, TBSI, MBS and ESVE for developing a copper sulfide layer for improved adhesion. DCBS accelerator has been used in this evaluation.

• Experimental

Four compounds were evaluated by varying the amount of 6PPD, which are shown in Table 16. Mooney Viscosity at 100°C, curometer at 160°C, unaged/aged physical properties, dynamic flexing, tack measurement and unaged/aged wire adhesion by using ASTM pull out test were measured.

• Results/Discussion

No significant differences in Mooney Viscosity, Mooney Scorch and Curometer results and unaged physical properties were measured among the four compounds. However, significant improvements for aged physical properties, flex fatigue and aged adhesion were achieved with the addition of 6PPD, as expected, which

Table 17. Physical Properties

	E-0	E-1	E-2	E-3
6PPD		1.0	2.0	3.0
ML - 1 + 4 at 100°C	55	53	52	52
MS at 132°C, 3 Point Rise Time	11.5	12.0	11.0	11.0
Curometer at 160°C				
ts ₂	2.62	2.58	2.55	2.53
tc ₉₀	9.50	9.39	9.10	9.05
ML, N.M	0.64	0.60	0.60	0.59
MH, N.M	5.20	5.10	5.09	5.05
Cured 16' at 160°C				
Tensile at R. T., MPa	21.4	21.5	21.7	21.5
Elongation, %	360	370	380	380
300% Modulus, MPa	15.6	14.9	14.8	14.5
Shore a Hardness	74	72	70	70
Tear, DIE C, kN/m	63.0	61.0	64.0	62.0
Aged 2 Weeks at 70°C				
Tensile at R. T., MPa	17.0	19.1	21.0	20.5
Elongation, %	200	260	280	280
300% Modulus, MPa	17.0	15.1	14.4	14.8
Shore a Hardness	85	84	82	82
Tear, DIE C, kN/m	29.0	32.0	35.0	36.0

Table 18. Dynamic Flexing

	E-0	E-1	E-2	E-3
6PPD		1.0	2.0	3.0
Flex Fatigue to Failure				
Unaged(KC)	23.0	64.0	110.0	109.0
Aged 24 Hours at 100°C, (KC)	0.5	12.5	39.0	40.0
Tel Tak at R. T.				
Unaged	28	25	31	19
Aged 3 Days at 40°C	15	8	7	5

Table 19. Wire Adhesion

	E-0	E-1	E-2	E-3
6PPD		1.0	2.0	3.0
Unaged				
Pull Force(N)	359	366	345	352
Coverage(%)	90	100	100	90
Aged(2 Days/100°C)				
Pull Force(N)	290	310	330	315
Coverage(%)	90	90	90	90
Aged 2 Weeks/70°C				
Pull Force(N)	210	265	285	274
Coverage(%)	60	90	100	100

are shown in Table 17, 18 and 19.

• Conclusion

1) Heat aged properties have been improved with the addition of 1.0 phr or more of 6PPD.

2) By increasing the amount of 6PPD to 2.0 phr, significant improvements on flex fatigue properties was achieved.

3) By the addition of 6PPD, aged tack has been reduced significantly and aged adhesion has been improved.

IV. Future Trends/Needs

1. Accelerators

1.1 High Temperature Cure Accelerators

Every tire manufacturer has tried to increase

productivity for reducing the cure cycle by raising the cure temperature. However, there is a limitation due to severe reversion at an elevated temperature (above 170°C), which would lead to poor cured physical properties, including viscoelastic properties. Previously, B. F. Goodrich Chemical Company developed N Oxydiethylene Sulfenamide (OTOS) for a high temperature cure accelerator in SBR tread. They recommended the combination of MBS with OTOS which would minimize reversion when tires were cured at 177°C. However, both OTOS and MBS generate Nitrosamine which would cause a health issue in tire manufacturing plants or tire warehouses. Nitrosamine which would cause a health issue in tire manufacturing plants or tire warehouse. Rubber chemical manufacturers have tried to develop the replacements of OTOS. Up to now, there is no alternative to OTOS. Uniroyal Chemical and other rubber chemical manufactures have developed tetra benzyl thiuram disulfide (TBzTD) for replacing TDTM,

Table 20. Recipe

	F-0	F-1	F-2
SBR 1712	82.4	82.4	82.4
SBR 1500	20	20	20
CIS BR	20	20	20
N-339 Black	85	85	85
Aromatic OIL	27.3	27.3	27.3
Zinc Oxide	3	3	3
Stearic Acid	1.0	1.0	1.0
6PPD	1.0	1.0	1.0
TMQ	1.0	1.0	1.0
WAX	0.5	0.5	
TBBS	1.25	1.00	1.00
TBzTD		0.25	0.50
Sulfur	1.75	1.75	1.50

Nitrosamine generating accelerators. TBzTD can generate Nitrosamine chemically, however due to the higher molecular weight, it is very stable at the curing temperature. Therefore, Nitrosamines cannot be detected under curing temperatures. TBzTD is used as a secondary accelerator for developing high temperature curing

systems for tire compounds, especially in tread. TBzTD has been evaluated in SBR/BR tread. It did not provide a scorchy problem and at the same time it reduces reversion, hysteresis and it provides a faster cure system, which is shown in Tables 20, 21 and 22.

1.2 Stable Crosslink System

Lower rolling resistant tires would require

Table 21. Processing Data

	F-0	F-1	F-2
TBBS	1.25	1.00	1.00
TBzTD		0.25	0.50
Sulfur	1.75	1.75	1.50
Mooney Viscosity at 100°C	50	50	50
Mooney Scorch at 142°C			
3 Point Rise Time	17.8	18.6	17.4
Curometer at 160°C			
t_{s1}	5.6	5.5	5.6
t_{10}	8.5	8.0	7.5
t_{90}	11.6	10.7	9.9
ML	4.9	4.9	4.9
MH	30.3	29.8	29.9
Reversion(Drop)	7.3	2.1	1.0

Table 22. Physical Properties

	F-0	F-1	F-2
TBBS	1.25	1.00	1.00
TBzTD		0.25	0.50
Sulfur	1.75	1.75	1.50
Cure Time at 160°C Minutes	14.0	13.0	12.0
Tensile at R. T., MPa	15.7	16.0	17.2
100% Modulus, MPa	1.7	1.7	1.7
300% Modulus, MPa	8.9	8.8	9.2
% Elongation	510	540	540
Shore a Hardness	65	64	66
Tear DIE C(kN/m)	38.5	36.8	42.0
Goodyear Flex at 100°C			
Temperature Rise(°C)	33.4	32.8	32.8
% SET	15.9	10.6	8.6
Tan Delta at 75°C			

Table 23. Recipes

	G-0	G-1	G-2	G-3
Natural Rubber	100	100	100	100
N-660 Carbon Black	50	50	50	50
Naphthenic OIL	6	6	6	6
Zinc Oxide	4	4	4	4
Stearic Acid	2	2	2	2
TMQ	2	2	2	2
TBBS	1.00	2.00	1.00	2.00
DTDM			1.00	
TBzTD				0.25
Sulfur	2.25	1.20	2.00	1.10

Table 24. Physical Properties

	G-0	G-1	G-2	G-3
TBBS	1.00	2.00	1.00	2.00
DTDM			1.00	
TBzTD				0.25
Sulfur	2.25	1.20	2.00	1.10
Mooney Viscosity at 100°C	48	48	48	48
Mooney Scorch at 160°C				
3 Point Rise Time(Minutes)	23.0	19.0	22.0	21.0
Curometer at 160°C				
ML	2.7	2.6	2.7	2.6
MH	35.0	25.5	35.5	25.0
t_{s2}	3.5	3.3	3.5	3.4
t_{50}	4.3	4.6	4.9	4.2
t_{90}	7.5	5.8	6.2	5.1
Reversion	9.5	2.50	7.50	1.00
Tan Delta at 75°C	0.110	0.120	0.078	0.090

lower hysteresis compounds, especially in the base tread. DTDM has been used to develop a lower hysteresis base tread for lower rolling resistant tires. However, DTDM generates Nitrosamine, as a sulfur donor. This sulfur donor system would provide a monosulfide crosslink system which would be stable. Combinations of mono/poly sulfidic crosslink system would also provide a lower hysteresis. Four base tread compounds were mixed using different cure systems which included DTDM and TBzTD (Table 23).

Tangent Delta values indicated that DTDM and TBzTD would provide a lower hysteresis system, while DTDM had more reversions than both TBzTD and semi EV cure systems (Table 24).

1.3 Non-Nitrosamine Sulfenamide Accelerators

Previously, it was mentioned that MBS, a scorch delayed sulfenamide accelerator generated Nitrosmorpholine which would cause a health problem. Most synthetic tread compounds would adopt TBBS with a pre-vulcanized inhibitor (PVI) for replacing MBS. However, in natural rubber, it was necessary to develop a scorch delayed non-Nitrosamine sulfenamide accelerator to replace MBS. Flexsys has commercialized *t*-butyl bis-(2-Benzothiazole) sulfenamide (TBSI) and Uniroyal Chemical has developed Cyclohexyl bis-(2-Benzothiazole) sulfenamide (ESVE). MBS, TBSI and ESVE have been evaluated in NR compounds (Table 25). Both TBSI and ESVE have slightly shorter scorch safety and shorter elongation, which are shown in Table 26. All other physical properties are equivalent.

Table 25. Processing Data

	J-1	J-2	J-3
NR	100	100	100
N-330 Black	58	58	58
Zin Oxide	8	8	8
Stearic Acid	0.5	0.5	0.5
66PD	2	2	2
Resorcinol	2.5	2.5	2.5
Methylene Donor	2.0	2.0	2.0
MBS	1.0		
TBSI		1.0	
ESVE			1.0
80% Insoluble Sulfur	6.25	6.25	6.25

Table 26. Physical Properties

	J-1	J-2	J-3
Mooney Viscosity at 100°C	74	73	73
Mooney Scorch at 132°C			
3 Point Rise Time	12.6	11.7	12.0
Curometer at 160°C			
MH(Torque)	33.98	36.78	37.3
ML(Torque)	4.27	4.44	4.52
t_{s1}	1.01	0.85	0.88
t_{50}	3.27	3.61	3.15
t_{90}	8.35	7.48	7.61
Tensile at R. T., MPa	24.5	24.7	25.2
% Elongation	460	400	440
300% Modulus	15.0	15.8	16.6
Shore a Hardness	74	73	73

2. Antidegradants

2.1 Antiozonants

2.1.1 Non-Staining Antiozonants

The current available antiozonants such as, dialkyl, alkyl aryl and diaryl PPD are staining and discoloring to brown/yellow, which would make the new tires look old. Rubber chemical manufacturers have tried to develop non-staining and non-discoloring antiozonants whose ozone crack resistance performance in NR/BR

can be equivalent to 6PPD. Bayer Chemical has developed bis (1, 2, 3, 6 tetra hydrobenzaldehyde) pentaerythrityl acetal), for non-staining and non-discoloring antiozonants. However, it did not work for natural rubber, SBR or BR which requires ozone protection the most. Uniroyal Chemical has developed a high molecular weight Triazine base antiozonant (TAPDT). TAPDT provides not only good static ozone protection for NR, SBR and BR, but also provides limited dynamic ozone crack resistance. It is not as good as 6PPD for accelerated dynamic flexing, because TAPDT is an extremely high molecular weight antiozonant which migrates to the surface very slowly. However, three arms of an alkyl group in a molecule has excellent chemical reactions with ozone, so that static protection from ozone cracking would be superior without the addition of wax, like 77PD. In Table 27, static and dynamic ozone cracking test in NR/BR compound has been carried out, using TAPDT, 77PD and DAPD, without the addition of wax. The results indicate that the alkyl group is more reactive than the aryl group antiozonant. Also, TAPDT is a non-staining antiozonant.

2.1.2 Longer Term Protection

Tire manufacturers have developed steel monople truck tires, 80,000 mile passenger radial and farm tires which require a longer term protection sidewall. Previously, 6PPD and DAPD were used to achieve slightly longer term protection. The combination of high molecular weight (TAPDT) and 6PPD would provide longer term protection for static and dynamic flexing which is shown in Table 28.

Table 27. Physical Properties

	I-1	I-2	I-3	I-4	I-5
Outdoor Static Exposure Bent Loop, Naugatuck, CT.					
Hours to Crack	78	1874*	1205	1607	1845*
	C	OK	C	C	OK

Ozone Chamber Exposure, 50 PPHM Ozone at 38°C

Bent Loop, Unaged					
Hours to Crack	4	1128	600	1128	1128
	C	OK	C	OK	OK

Bent Loop, Aged 6 Months Prior to Testing

Bent Loop, Unaged					
Hours to Crack	8	1080	24	24	1080
	C	OK	C	C	OK
20% Extension, Unaged	2	1128	888	816	1128
Hours to Crack	C	OK	C	C	OK

20% Extension, Aged 7 Months Prior to Testing

Hours to Crack	4	840	24	24	1080
	C	C	C	C	OK

Dynamic Properties

6PPD		2.0	2.0	4.0	
TAPDT		2.0			4.0
Dapd			2.0		

Outdoor Dynamic Flexing-Naugatuck, CT

Continuous Flexing-Aged 6 Months Prior to Testing

KC to Crack	2609	39560	16951	39560	16951
-------------	------	-------	-------	-------	-------

Intermittent Flexing, 8 Hours to Flex+ 16 Hours of Static Exposure-Aged 6 Months

KC to Crack	2969	33302	28646	31091	23724
-------------	------	-------	-------	-------	-------

2.2 Polymeric Antiozonant (Epdm & Bim)

Recently, the tire manufacturers moved toward the European style, low aspect ratio tires. These low aspect ratio tires have only black sidewall which is very important for the appearance of

Table 28. Static and Dynamic Ozone Testing
Antiozonant Protection-NR/BR Compound*

	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8
TAPDT	2	4						
77PD			2	4				
6PPD					2	4		
DAPD							2	4

Static Ozone Resistance, **50 PPHM Ozone at 38°C

Bent loop, Unaged	480	1014	144	408	8	24	24	24
Hours to Crack	C	S	C	C	C	C	C	C

Dynamic Ozone Resistance, 25% Extension,
50 PPHM Ozone at 38°C

Unaged Samples	48	72	48	192	144	193	48	48
Hours to Crack	C	S	C	C	C	C	C	C

*SMR 5CV (55 PHR), CIS BR (45 PHR), N-660 (50 PHR), ZnO (3 PHR), Stearic Acid (1 PHR), Aromatic OIL (7 PHR), TBBS (1 PHR), Sulfur (2 PHR)

**Static Ozone Testing was Terminated at 1014 Hours.

C=Cracked, S=Slight Cracking

these tires. The producers of EPDM continuously tried to develop black sidewall compounds with a blend of natural rubber and polybutadiene. The most difficult task was to achieve compatibility with other tire components, specifically static and dynamic adhesion to carcass, tread and chafer compounds. In order to obtain this compatibility, ethylene propylene diene terpolymer has been modified and/or the level of unsaturation has been increased to improve co-vulcanization. Also, tri-cure systems have been developed to improve stock to stock adhesion with better co-vulcanization. However, due to the inferior cut growth resistance and poor stock to stock adhesion, a better appearance sidewall with EPDM was not successful. Continuous efforts have been made to improve co-vulcanization with diene rubbers for better stock to

stock adhesion.

Exxon also has promoted brominated isobutylene-co-para-methylstyrene (BIMS) for the tire sidewall.¹³ Laboratory results indicated that promising results were obtained. However, the tire test results were not as good as the NR/BR with antiozonant wax.

2.3 Antioxidants

2.3.1 Longer Term Protection

Tire components would require good flex fatigue properties and good heat aged properties for longer periods of service time. For example, TMQ provides good heat aged properties, but it would not have good flex fatigue properties. Therefore, it is necessary to blend either 6PPD or BLE for improved flex fatigue. This is a continuous effort to develop one antioxidant that would provide both flex fatigue and heat aged properties.

2.3.2 High Temperature Protection

The current available antioxidants would protect cured tire components up to 100°C. In truck or speed rated tires the running temperature exceeds over 100°C. Therefore, it is necessary to develop a high temperature antioxidant for truck and speed rated tires to extend the service time.

2.3.3 Non-Staining/Non-Discoloring

Antioxidants

Phenolic antioxidants will provide non-staining/non-discoloring compounds. However, they do not provide adequate protection for the tire compounds. It is necessary to have performance with amine type antioxidants, but it should not stain and discolor. Continuous efforts have been

made to develop non-staining and non-discoloring amine type antioxidants. Up to now, it has not been successful to commercialize non-staining and non-discoloring antioxidants which would have equivalent performance to amine type antioxidants.

Acknowledgment

The author expresses his gratitude to Uniroyal Chemical Company, a subsidiary of Crompton and Knowles Company to present this paper to the IRC '99 Seoul, Seoul, Korea, April 25 29, 1999. Special thanks to Miss Jill Marnicki for her assistance in arranging and the preparation of this paper.

References

1. S. W. Hong, "Tire Components Protected with Antiozonants/Antioxidants," Automotive Engineering Litigation, Volume No. 5, Chapter No. 7, John Wiley and Sons, Inc., New York, 1993.
2. S. W. Hong, "Stabilization Systems for Radial Tire Components," Presented at the 33rd IISRP Annual Meeting, Cancun, Mexico, May 4 7, 1992.
3. E. G. Kontos, and S. W. Hong, "A Tutorial Introduction to the Rubbers Used in the Tire Industry," Presented at the International Tire Exhibition and Conference, Akron, Ohio, September, 1994.
4. E. G. Kontos, T. J. Brett, and S. W. Hong, "The Modern Passenger Tire, A Composite of Many Synthetic Rubbers," Presented at the 36th IISRP Annual Meeting, Melbourne, Australia, May, 1995.
5. R. A. Mazzeo, et. al., "Functions and Mechanism of Antidegradants to Prevent Polymer Degradation," Tire Technology International, '94.
6. G. Scott, Editor, "Atmospheric Oxidation and Antioxidants," Volume 4, Applied Science Publishers Ltd., London, 1981.
7. G. Scott, Editor, "Developments in Polymer Stabilization," Volume 4, Applied Science Publishers Ltd., London, 1981.
8. S. W. Hong, and R. A. Mazzeo, "Improved Tire Performance Through the Use of Antidegradants," Presented at the International Tire Exhibition and Conference, Akron, Ohio, September, 1996.
9. D. A. Birdsall, and S. W. Hong, "A Novel Slow Migration Antiozonant," Presented at the Tyretex '91 Conference, Berlin, Germany, October, 1991.
10. S. W. Hong, "Improved Vulcanization Systems for Tire Components Through the Use of Various Accelerators," Presented at the Institute of Materials, The Third National Rubber Conference, Durban, South Africa, October, 1997.
11. S. W. Hong, "Polymer Blends for Improved Tire Tread Performance," Presented at the IUPAC MACRO Seoul '96, Seoul, Korea, August, 1996.
12. S. W. Hong, and M. P. Ferrandio, "The Use of TAPDT and Octylated DPA in a Conventional Black Sidewall for Improved Appearance," Presented at the Rubber Division, ACS, Cleveland, Ohio, October, 1997.

13. W. H. Waddell, "Tire Black Sidewall Surface Discoloration and Non-Staining Technology (Review)," Published at Rubber

Chemistry and Technology, Volume 71, July
August, 1998