

Studies on Secondary Accelerator Systems for Natural Rubber Retread Compounds

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I. INTRODUCTION

With the introduction of synthetic yarns for the construction of carcass of automotive tyres, the life of carcass has increased considerably and the tyres can be retreaded five or six times before the fabric loses its strength. This has led to the rapid growth of retread compound manufacturing industry. The performance requirements of the retread compounds has already been described in detail.¹ Thus, the retread compound should have high abrasion resistance, good tear resistance and crack growth resistance, low heat build up, high flex fatigue resistance and wet skid resistance, better ageing properties etc. It should also have very good scorch safety and tackiness, reduced tendency for blooming and reasonably fast cure rate. To achieve these requirements sulphenamide type accelerators are mainly recommended for retread compounds.² It is reported that among the sulphenamides, DCBS gives the maximum scorch safety and storage stability for the retread compounds.³ But later works showed that DCBS gives only lower level of chemical crosslinks in natural rubber compounds at all cure temperatures compared with other sulphenamides like CBS, TBBS and MOR.⁴ Since

it has already been established that lower crosslink density gives lower physical properties for the vulcanizates,⁵ use of DCBS accelerator in retread compounds can give only lower physical properties even though the storage properties are better. The optimum cure time of the compounds containing DCBS accelerator is very long compared with that of other sulphenamide accelerators. In this era of energy shortage and polymer shortage, the need of the day is to develop products having maximum service properties expending minimum quantity of energy in the manufacturing process. The present work reports the results of the study conducted at the Rubber Research Institute of India for developing retread compounds having good shelf life, shorter curing cycle and with good service properties.

II. EXPERIMENTAL DETAILS

(i) Selection of cure system

The advantages of using synergism in accelerators has been established long back.⁶ With a view to developing synergistic accelerator systems suitable for natural rubber retread compounds, secondary accelerators like DPG, TMT and ZDC were used in retread compounds in combination

with primary accelerators like MBTS, CBS, TBBS, MOR and DCBS. For comparison, control compounds with primary accelerator alone were also prepared using conventional tread formulation. In compounds containing secondary accelerator, the total level of the accelerator combination was kept the same as that of the primary accelerator in the conventional compound. But the dosage of sulphur was reduced taking into consideration the fact that a higher degree of crosslinking for a given level of sulphur can be achieved using secondary accelerators.⁷ In a selected group of compounds containing secondary accelerator, the effect of retarder was also studied so as to keep up the storage stability of the compounds. N-cyclohexyl thiophthalimide (NCTP) was the retarder used since reports show that this retarder has less effect on rate and state of cure and has higher stability during processing and curing operations, compared with other retarders.⁸ The formulations of the control compounds and those of the compounds containing secondary accelerators are given in tables 2 to 7. All the compounds were prepared from the same masterbatch (table-1) so as to avoid variations in compounding.

(ii) Tests conducted

The compounds were prepared and stored at atmospheric temperature (approx. 30°C) for three months and then moulded to prepare samples for various tests. The scorch time of the compounds were determined at intervals of 30 days for a period of three months. The cure time of the compounds at 150°C were determined after one day and ninety days of preparation of the compounds. Properties like modulus, tensile strength, elongation at break, tear strength, abrasion resistance, rebound resilience, compression set, hardness, heat build up and retention of tensile properties after ageing at 70°C for 66 hours were determined. The test results are given in tables 9 to 14. After evaluating the properties, compound CTR containing TBBS as primary accelerator, TMT as secondary accelerator and retarder NCTP, was selected for assessing the service performance. Conventional compound (NO. E) with DCBS as accelerator was used as the control. These compounds were extruded at 85-90°C in a 6" extruder to give 50-64-14 size tread for jeep tyres. Two cushion gum compounds suitable for the above treads were also prepared. The formulations of the cushion gum compounds are given in table 8. The storage stability of the extruded compounds and cushion gums are given in table 15.

(iii) Curing of the Retreads

For curing the retread compounds after applying it on the tyre, the oldest method of giving five to six minutes cure for every 1/32 inch thickness of the tread is still followed.⁹ Nikolov¹⁰ introduced the formula $P = 0.25C - 3.25$ (where P is the distance of the cure front in 32nds of an inch and C is the cure time at 298°F) for curing retread compounds. The above two methods do not take into consideration of the rate of cure of the compounds and assume that heating of the compound is from one side only. Using numerical methods Hills¹¹

Table 1. Composition of the Masterbatch

Ingredients	Weight (gms.)
Natural Rubber	100
Zinc Oxide	3.5
Stearic Acid	2.0
Phenyl-β-Naphthyl Amine	1.0
N-(1,3-dimethyl butyl)-N' Phenyl p-phenylene diamine	1.0
HAF Black	50.0
Aromatic Process Oil	5.0

Table 2. Conventional Retread Compounds

Masterbatch (gms.)	Accelerator (gms.)	Sulphur (gms.)	Compound No.
162.5	MBTS 0.6	2.5	A
162.5	CBS 0.6	2.5	B
162.5	TBBS 0.6	2.5	C
162.5	MOR 0.6	2.5	D
162.5	DCBS 0.6	2.5	E

has shown that for a 1" thick slab of filled stock at 70°F the time taken for the central portion to attain the temperature of the heating surface (300°F) is about forty minutes when heated from both sides. During moulding of retread compounds where the thickness of the tread is only about 1/4" and heating takes place from three sides due to the presence of tread patterns, it is expected that the actual time taken for the bottom portion of the tread to attain the surface temperature of the mould may come to about thirty five minutes. Hence if the retread compound is having fast rate of cure, it may get cured within a period of 35 to 45 minutes at 150°C. Considering these factors, the retread compound CTR was moulded at 60 psi steam pressure and 120 psi air pressure for 45 minutes in jeep tyre moulds. The control compound E was moulded under the same conditions giving 85 minutes cure, adopting the conventional method. The service performance of the retreaded jeep tyres was evaluated, and the results obtained are given in table 16.

III. RESULTS & DISCUSSIONS

(i) Conventional Mixes

Table 9 gives the test results of the conventional retread com-

pounds. From the table, it is seen that retread compounds containing CBS, TBBS or MOR give higher tensile strength, tear strength, hardness and cure rate index compared with the compound containing DCBS accelerator. These compounds also give better resistance to abrasion, lower heat build up and lower cure time compared with the compound containing DCBS. The scorch time and shelf life of the compound with DCBS were better than those of the compounds containing other sulphenamides accelerators. Thus retread compound with DCBS accelerator gives comparatively lower physical properties which are most essential for the better performance of the retread material.

(ii) Effect of Secondary Accelerators

The properties of the compounds containing secondary accelerator DPG are given in table 10. From the table, it is seen that the tensile properties are better with MOR-DPG system where as TBBS-DPG system showed better tear strength and retention of tensile strength after ageing. DCBS-DPG system showed lower tensile strength, elongation at break, tear strength and hardness. The cure rate index of all the compounds containing DPG was higher compared with that of the conventional mixes. But all

the compounds with DPG showed loss of activity of the accelerator system as evidenced by increased cure time and less decrease in scorch time after storing the compounds for three months.

In the case of compounds containing TMT as secondary accelerator, combination of MOR with TMT gave higher tensile strength, tear strength, rebound resilience, hardness and cure rate, better abrasion resistance and lower heat build up. TMT in combination with DCBS gave the shortest scorch time. TBBS-TMT system gave better resistance to ageing. As in the case of compounds with secondary accelerator DPG, compounds containing TMT also showed loss of activity of the accelerator system during storage as evidenced by increased cure time and in certain cases increased scorch time after 3 months.

Among the compounds with secondary accelerator ZDC, combination of MOR and ZDC gave better tensile strength and abrasion resistance. Better tear strength was shown by CBS-ZDC system. The scorch time, tensile strength, elongation at break and tear strength of the DCBS-ZDC system were lower compared with other sulphenamide-ZDC systems. During storage, loss of activity of the accelerator system was more pronounced with DCBS-ZDC combination, compared with other sulphenamides.

Among the three secondary accelerators used in this study, compounds containing TMT were found to give higher modulus, tensile strength, tear strength and hardness, lower heat build up and faster cure rate. But the scorch time of the compounds containing TMT was lower after storing for a period of three months.

(iii) Effect of Retarder

Use of retarder in conventional system has increased the modulus but reduced the tensile strength in certain cases. Tear strength was

lowered only in the case of compounds containing MOR accelerator. There was only marginal increase in cure time of all the compounds but the increase in scorch time was appreciable. Addition of retarder NCTP in compounds containing TMT as secondary accelerator increased the ageing resistance, abrasion resistance, hardness and compression set resistance, but there was slight decrease in tensile strength and elongation at break. Tear strength was higher for compounds containing MBTS and DCBS. The change in cure time of the compounds was not appreciable. The scorch time and shelf life were increased considerably in the case of compounds containing sulphenamides. The cure rate index was higher and retention of cure rate was also better after storage for three months.

(iv) Performance of Retreads

The scorch times of the extrudates containing DCBS accelerator and TBBS-TMT-NCTP combination system were comparable. The shelf life of the extruded compound with DCBS accelerator was slightly better than that containing secondary accelerator TMT. The service performance of the compounds with TBBS-TMT-NCTP system was better than that of the compound with conventional accelerator DCBS.

IV. CONCLUSIONS

1) Among the sulphenamide accelerators used for this study, compounds containing DCBS gave comparatively lower physical properties.

2) Out of the three secondary accelerators tried in this work, TMT gave better physical properties to the vulcanisates.

Table 3. Retread Compounds with Secondary Accelerator DPG

Masterbatch (gms.)	Accelerator system (gm)		Sulphur (gms.)	Compound No.
	Primary	Secondary		
162.5	MBTS 0.4	DPG 0.2	2.0	AD
162.5	CBS 0.4	DPG 0.2	2.0	BD
162.5	TBBS 0.4	DPG 0.2	2.0	CD
162.5	MOR 0.4	DPG 0.2	2.0	DD
162.5	DCBS 0.4	DPG 0.2	2.0	ED

Table 4. Retread Compounds with Secondary Accelerator TMT

Masterbatch (gms.)	Accelerator system (gm)		Sulphur (gms.)	Compound No.
	Primary	Secondary		
162.5	MBTS 0.5	TMT 0.1	2.0	AT
162.5	CBS 0.5	TMT 0.1	2.0	BT
162.5	TBBS 0.5	TMT 0.1	2.0	CT
162.5	MOR 0.5	TMT 0.1	2.0	DT
162.5	DCBS 0.5	TMT 0.1	2.0	ET

Table 5. Retread Compounds with Secondary Accelerator ZDC

Masterbatch (gms.)	Accelerator system (gm)		Sulphur (gms.)	Compound No.
	Primary	Secondary		
162.5	MBTS 0.55	ZDC 0.05	2.0	AZ
162.5	CBS 0.55	ZDC 0.05	2.0	BZ
162.5	TBBS 0.55	ZDC 0.05	2.0	CZ
162.5	MOR 0.55	ZDC 0.05	2.0	DZ
162.5	DCBS 0.55	ZDC 0.05	2.0	EZ

3) Use of retarder NCTP in combination with sulphenamides containing TMT as secondary accelerator decreased the tensile strength but improved ageing resistance and helped to keep up the faster cure rate and shelf life of the compounds.

4) TBBS-TMT-NCTP combination gave compound having better service performance compared with that containing DCBS accelerator. This new system required about 40 minutes less time for curing the retread compared with the conventional accelerator system.

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VI. ABBREVIATIONS

1. MBTS — Dibenzothiazyl disulphide.
2. CBS — N-Cyclohexyl-2-benzothiazyl sulphenamide.
3. TBBS — Benzothiazyl-2-tert-butyl sulphenamide.
4. MOR — Benzothiazyl-2-sulphene morpholide.
5. DCBS — Benzothiazyl-2 dicyclohexyl sulphenamide.
6. DPG — Diphenyl guanidine.
7. TMT — Tetramethyl thiuram disulphide.
8. ZDC — Zinc-N-diethyl dithiocarbamate.
9. NCTP — N-cyclohexyl thiophthalimide.

Table 6. Conventional Retreads with Retarder NCTP

Masterbatch (gms.)	Accelerator (gms.)	Retarder NCTP (gm.)	Sulphur (gm.)	Compound No.
162.5	MBTS 0.6	0.125	2.5	AR
162.5	CBS 0.6	0.125	2.5	BR
162.5	TBBS 0.6	0.125	2.5	CR
162.5	MOR 0.6	0.125	2.5	DR
162.5	DCBS 0.6	0.125	2.5	ER

Table 7. Retreads with Secondary Accelerator TMT & Retarder NCTP

Masterbatch (gms)	Accelerators system (gm)		Retarder NCTP (gm)	Sulphur (gm)	Compound No.
	Primary	Secondary			
162.5	MBTS 0.5	TMT 0.1	0.25	2.0	ATR
162.5	CBS 0.5	TMT 0.1	0.25	2.0	BTR
162.5	TBBS 0.5	TMT 0.1	0.25	2.0	CTR
162.5	MOR 0.5	TMT 0.1	0.25	2.0	DTR
162.5	DCBS 0.5	TMT 0.1	0.25	2.0	ETR

VII. REFERENCES

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Table 8. Cushion Gum Compounds for Retreads CTR & E

Ingredients	For CTR	For E
Natural Rubber	100	100
Zinc Oxide	3.5	3.5
Stearic Acid	1.5	1.5
CBS	0.7	0.7
TMT	0.1	—
Phenyl β-Naphthyl amine	1.0	1.0
N-Cyclohexyl thiophthalimide	0.4	0.15
C. I. Resin	2.0	2.0
SRF Black	30.0	30.0
Pine Tar	7.5	7.5
Sulphur	2.0	2.25

Table 9. Properties of Conventional Retread Compounds

Properties	A		B		C		D		E	
	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %
Modulus 300% (kg/cm ²)	80	124	105	111	110	112	102	112	91	112
Elongation at break (%)	636	95	622	91	588	92	625	91	602	95
Tensile strength (kg/cm ²)	232	99	275	93	267	94	268	95	242	99
Tear strength (kg/cm)	89		105		113		188		95	
Abrasion resistance (loss in cc/hr)	1.62		0.68		0.65		0.88		1.11	
Hardness (Shore A)	56		60		61		60		59	
Heat build up at 122°F ($\Delta T^{\circ}F$)	34		34		27		32		38	
Compression set (%)	36		37		40		42		36	
Rebound resilience (%)	54		54		59		56		55	
Cure time at 150°C (Minutes) 1st day	12		11		12		14		22	
90th day	13		13		12		13		21	
Scorch time at 120°C (Minutes) 1st day	18		29		34		40		44	
90th day	14		17		23		28		34	
Cure rate index : 1st day	11.4		13.8		13.3		10.8		5.5	
90th day	9.1		10.3		11.4		11.1		6.3	

b. a. — before ageing
r. a. a. — retention after ageing

Table 10. Properties of Retread Compounds with Secondary Accelerator DPG.

Properties	AD		BD		CD		DD		ED	
	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %
Modulus 300% (kg/cm ²)	77	113	92	103	88	113	87	103	90	106
Elongation at break (%)	678	92	691	95	628	98	668	93	625	90
Tensile strength (kg/cm ²)	256	92	260	95	254	99	269	89	250	93
Tear strength (kg/cm)	98		112		118		105		89	
Abrasion resistance (loss in cc/hr)	1.36		0.73		0.78		1.12		1.05	
Hardness (shore A)	51		56		58		58		51	
Heat build up at 122°F ($\Delta T^{\circ}F$)	34		34		36		36		36	
Compression set (%)	60		45		42		43		38	
Rebound resilience (%)	50		54		54		54		54	
Cure time at 150°C (Minutes) 1st day	8		10		10		9		20	
90th day	13		14		14		13		21	
Scorch time at 120°C (Minutes) 1st day	16		26		34		29		26	
90th day	15		18		22		23		37	
Cure rate index : 1st day	21.1		16.7		16.7		16.7		9.3	
90th day	10.0		10.9		10.3		9.8		6.4	

b. a. — before ageing
r. a. a. — retention after ageing

Table 11. Properties of Retread Compounds with Secondary Accelerator TMT.

Properties	AT		BT		CT		DT		ET	
	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %
Modulus 300% (kg/cm ²)	91	110	100	114	99	113	113	104	97	106
Elongation at break (%)	662	94	655	92	620	94	621	91	600	91
Tensile strength (kg/cm ²)	279	88	288	92	266	96	293	85	245	94
Tear strength (kg/cm)	130		156		149		194		101	
Abrasion resistance (loss in cc/hr)	1.33		1.02		0.82		0.74		1.01	

Table 11. (Contd.)

Hardness (shore A)	57	57	59	59	57
Heat build up at 122°F ($\Delta T^{\circ}F$)	32	31	32	31	34
Compression set (%)	54	53	53	54	55
Rebound resilience (%)	54	53	53	55	54
Cure time at 150°C (Minutes) 1st day	6	8	9	7	13
90th day	10	12	12	11	18
Scorch time at 120°C (Minutes) 1st day	19	24	27	26	14
90th day	13	12	13	14	16
Cure rate index : 1st day	28.6	22.2	19.1	22.2	10.0
90th day	13.3	10.9	10.9	10.9	7.3
b. a. — before ageing					
r. a. a. — retention after ageing					

Table 12. Properties of Retread Compounds with Secondary Accelerator ZDC.

Properties	AZ		BZ		CZ		DZ		EZ	
	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %
Modulus 300% (kg/cm ²)	82	128	95	117	91	112	95	116	85	117
Elongation at break (%)	650	98	606	94	618	95	620	93	600	92
Tensile strength (kg/cm ²)	247	90	247	93	255	94	257	97	229	97
Tear strength (kg/cm)	106		135		110		119		99	
Abrasion resistance (loss in cc/hr)	1.64		1.14		0.83		0.76		1.16	
Hardness (shore A)	55		56		58		58		57	
Heat build up at 122°F ($\Delta T^{\circ}F$)	36		32		32		32		32	
Compression set (%)	49		51		45		41		41	
Rebound resilience (%)	53		53		54		55		55	
Cure time at 150°C (Minutes) 1st day	9		9		10		10		13	
90th day	11		12		12		12		19	
Scorch time at 120°C (Minutes) 1st day	17		24		28		28		21	
90th day	14		16		18		22		29	
Cure rate index : 1st day	17.1		19.0		19.0		16.7		8.5	
90th day	11.4		10.5		11.1		11.1		6.8	
b. a. — before ageing										
r. a. a. — retention after ageing										

Table 13. Properties of Conventional Retread Compounds with Retarder NCTP

Properties	AR		BR		CR		DR		ER	
	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %
Modulus 300% (kg/cm ²)	95	129	110	117	111	135	107	126	102	127
Elongation at break (%)	612	87	562	90	533	82	570	88	550	88
Tensile strength (kg/cm ²)	249	97	250	99	234	98	251	98	230	98
Tear strength (kg/cm)	129		136		119		109		112	
Abrasion resistance (loss in cc/hr)	1.57		0.77		0.86		0.92		0.88	
Hardness (shore A)	59		61		61		61		61	
Heat build up at 122°F ($\Delta T^{\circ}F$)	34		31		32		31		38	
Compression set (%)	42		38		37		38		37	
Rebound resilience (%)	55		56		58		56		55	
Cure time at 150°C (Minutes) 1st day	13		13		13		15		26	
90th day	12		11		11		12		21	

Scorch time at 120°C (Minutes) 1st day	17	38	39	45	66
90th day	12	23	29	32	49
Cure rate index : 1st day	10.0	13.5	13.2	11.4	5.6
90th day	10.8	13.3	14.3	13.3	7.0
b. a. — before ageing					
r. a. a. — retention after ageing					

Table 14. Properties of Retread of Compounds with TMT & Retarder NCTP

Properties	ATR		BTR		CTR		DTR		ETR	
	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %	b.a.	r.a.a. %
Modulus 300% (kg/cm ²)	94	115	100	120	114	110	114	114	95	111
Elongation at break (%)	610	94	590	95	568	95	560	96	598	92
Tensile strength (kg/cm ²)	253	99	245	108	263	98	259	99	239	99
Tear strength (kg/cm)	138		120		127		132		134	
Abrasion resistance (loss in cc/hr)	1.25		1.06		0.77		0.67		0.98	
Hardness (shore A)	60		61		61		62		59	
Heat build up at 122°F ($\Delta T^{\circ}F$)	34		32		32		32		38	
Compression set (%)	43		38		34		30		36	
Rebound resiliency (%)	54		56		56		56		54	
Cure time at 150°C (Minutes) 1st day	7		9		10		9		12	
90th day	9		9		10		8		15	
Scorch time at 120°C (Minutes) 1st day	18		33		39		35		31	
90th day	12		22		25		21		21	
Cure rate index : 1st day	25.3		23.3		21.5		24.7		14.3	
90th day	14.3		16.7		16.3		22.2		9.3	
b. a. — before ageing										
r. a. a. — retention after ageing										

Table 15. Storage properties of Extruded Compounds CTR and E

Properties	Retread E	Cushion for E	Retread CTR	Cushion for CTR
Scorch time at 120°C (Minutes) 1st day	24	48	24	34
60th day	23	37	20	27
Cure time at 150°C (Minutes) 1st day	20	13.5	8	8
60th day	19	13	8	8
Cure rate index : 1st day	6.2	14.3	22.2	34.5
60th day	6.9	13.1	22.2	33.3

Table 16. Service performance of Retreads CTR and E

Compound No.	Moulding time (Mins.)	Original skid (1/32")	Distance covered (KM)	Present skid (1/32")	Projected mileage (KM)
CTR	45	14.5	1205	12.6	9196
E	85	14.5	1205	12.25	7765