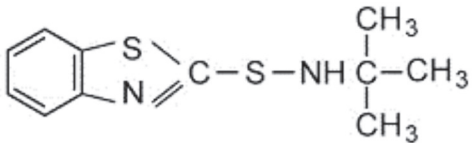
Ram Charan

OVERVIEW OF NZ IN REPLACING MOZ

N-tert.Butyl-Benzothiazyl Sulfenamide–TBBS-Vulkacit NZ is the sulphenamide family accelerator which is being widely used in the rubber industry as the versatile curing accelerator known for their delayed action as well as faster cure rate during the vulcanisation of rubber compound based on sulfur curing.

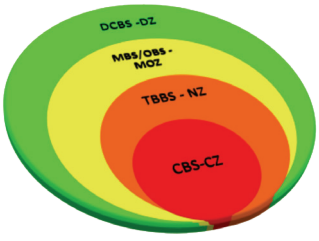
TBBS



Among the sulphenamide family, the following trend pattern will be observed in their characteristic of curing behaviour of Suflur curing system.

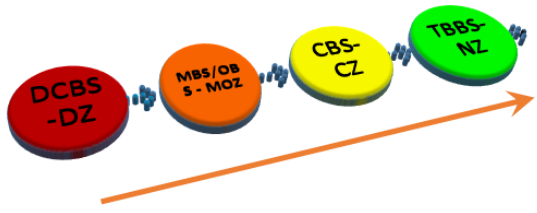
1. SCORCH SAFETY – **Longer the better**

CBS – VULKACIT CZ < **TBBS – VULKACIT NZ** < MBS – VULKACIT MOZ < DCBS – VULKACIT DZ



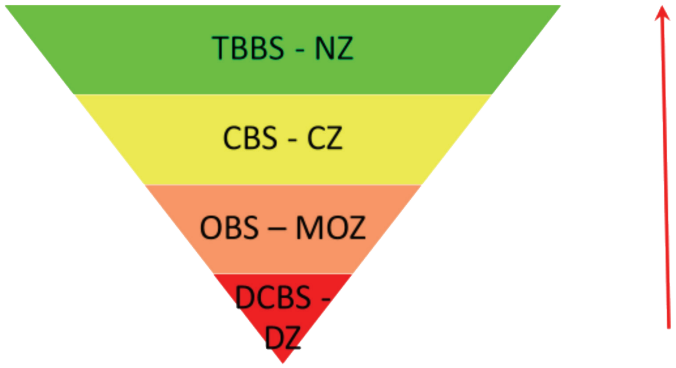
2. CURE RATE – **Faster is better**

TBBS-VULKACIT NZ > CBS – VULKACIT CZ > OBS – VULKACIT MOZ > DCBS – VULKACIT DZ



3. CROSS-LINK DENSITY: **Higher is Better**

DCBS – VULKACIT DZ < OBS – VULKACIT MOZ < CBS – VULKACIT CZ < **TBBS – VULKACIT NZ**



In Tread application - Higher cross-link density is expected to give better Modulus / Mileage. In general moulded rubber goods, it gives better compression set property as well….

HOW TO DESIGN COMPOUND WHEN SWITCHING FROM MOZ TO NZ

General modifications being followed as the industrial practice are

1. Reducing the dosage of NZ by 10% against MOZ (eg. If MOZ is used as 1.2 phr, reduce the same to approx. 1.05 phr)
2. Increase the retarder Vulkalent G by 0.1 phr (Eg. If G is used as 0.1 phr, increase to 0.2 phr)

Please find below the study results of a typical NR based tread formulation in the laboratory condition as follows, which gives the properties almost similar to MOZ.

FORMULATION		Phr	Phr	Phr	Phr
Natural rubber		100.00	100.00	100.00	100.00
Renacit 11		0.20	0.20	0.20	0.20
Zinc Oxide		5.00	5.00	5.00	5.00
Stearic Acid		3.00	3.00	3.00	3.00
Carbon Black N330		45.00	45.00	45.00	45.00
Elasto 710		8.00	8.00	8.00	8.00
Vulkanox 4020/LG		2.00	2.00	2.00	2.00
Vulkanox HS/LG		1.00	1.00	1.00	1.00
Antilux 654		1.00	1.00	1.00	1.00
Master Batch Wt		165.20	165.20	165.20	165.20
COMPOUND NO		**1**	**2**	**3**	**4**
Master Batch		165.20	165.20	165.20	165.20
Vulkacit MOZ/LG		1.20	-	0.60	-
Vulkacit NZ/EGC		-	1.00	-	0.50
Vulkalent G		0.10	0.20	0.10	0.15
Sulphur		1.60	1.60	2.20	2.20
ODR @ 150°C	ASTM - D 2084				
Min. Torque		4.43	5.08	5.05	4.98
Max. Torque		57.19	56.259	54.67	55.85
TS2		6.78	6.93	6.01	6.22
TC90		14.66	13.89	17.05	17.71
Mooney Scorch @ 1200C	ASTM D 1646-94	52.4	46.98	50.92	48.9
ODR @ 160°C	ASTM - D 2084				
Min. Torque		4.16	4.68	4.78	4.72
Max. Torque		55.15	54.49	52.37	53.72
TS2		3.66	3.89	3.27	3.39
TC90		8.55	8.13	9.5	9.71
ODR @ 170°C	ASTM - D 2084				
Min. Torque		4.04	4.57	4.67	4.69
Max. Torque		53.23	53.44	50.02	51.65
TS2		2.1	2.18	1.95	1.98
TC90		4.97	4.9	5.59	5.59
Cure time@150°C, Mnts.	**ASTM D 3182/89**	**20**	**20**	**25**	**25**
Tensile Strength, MPa	ASTM D 412-92/A	30.7	30.3	28.3	28.9
Elongation at break, %	ASTM D 412-92/A	625	625	605	635
COMPOUND NO		**1**	**2**	**3**	**4**
100% Modulus, MPa	ASTM D 412-92/A	1.7	1.8	1.7	1.8
300% Modulus, MPa	ASTM D 412-92/A	8.6	8.4	8.2	8.3
Tear strength, N/mm	ASTM D 624	76	76	82	91
Hardness, IRHD	ASTM D1415-88	58	58	58	58
Hardness, SH A	ASTM D2240-90	55	56	56	56

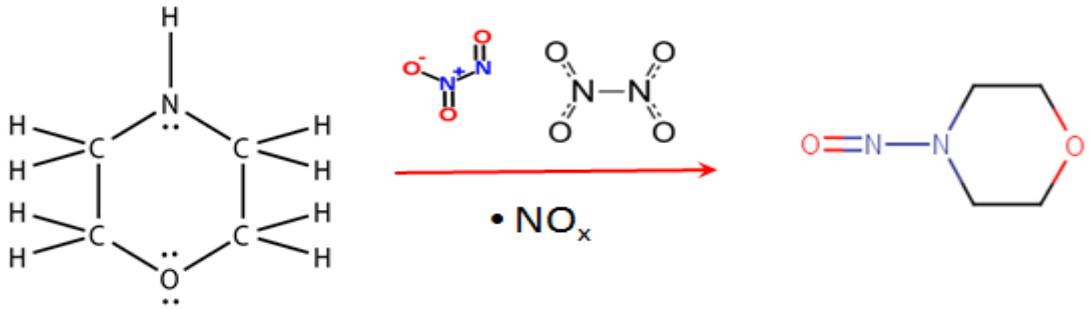
FORMULATION		Phr	Phr	Phr	Phr
Specific gravity	IS 3400 PART 9	1.088	1.088	1.089	1.092
DIN Abrasion Index, %	ISO/DIS 4649/95 PART3	98.5	100.1	101.3	98.4
GOODRICH HEAT BUILDUP	ASTM - D 623-93/ A				
Rise in temp.after 25 Mnts.°C		11	9	10	8
Permanent set, %		5	4.79	6.68	6.5
Hot Air Ageing @ 70°C/5 days	**ASTM D 573-88**				
COMPOUND NO		**1**	**2**	**3**	**4**
Tensile Strength, MPa	ASTM D 412-92/A	30.1	29.3	28.8	28.2
Elongation at break, %	ASTM D 412-92/A	585	580	575	520
100% Modulus, MPa	ASTM D 412-92/A	2.1	2.1	2.1	2.3
300% Modulus, MPa	ASTM D 412-92/A	10.3	10.1	10	11
Tear strength, N/mm	ASTM D 624	76	88	92	80
Hardness, IRHD	ASTM D1415-88	59	60	59	60
Hardness, SH A	ASTM D2240-90	57	58	57	58
DIN Abrasion Index, %	ISO/DIS 4649/95 PART3	98.5	100.9	96.6	94.7
GOODRICH HEAT BUILDUP	ASTM - D 623-93/ A				
Test piece 17.8mm dia, 25.5mm ht.Preload					
0.98 Mpa, Frequency 30Hz, Chemb. Temp.100°C, Stroke 5.71mm					
Rise in temp. after 25 Mnts.°C		14	11	12	12
Permanent set, %		4.21	3.9	5	5.15

As expected on the behaviour of the sulphenamide accelerator family of NZ & MOZ, the results based on the NZ is confirming on the same viz. reduction in the Tc90 relatively in this study which confirms the increase in the rate of cure, (Please note here the retarder dosages has been increased to match with the scorch time of MOZ), Also the heat build-up is reduced in NZ based batches.

WHY MOZ NEEDS TO BE REPLACED?

MBS is suspected to give the carcinogenic effect and the amines (morpholine amine - secondary amine – known to give the carcinogenic effect, as it is easily get nitrosated and forms nitrosomorpholine which is mutagenic/carcinogenic in several species study → can cause tumours, heptacellular carcinoma, sarcomas of the liver and lungs…) liberated from MBS is listed in the carcinogenic generating chemical.

Also in MBS the free amine (morpholine amine – a secondary amine) present in the accelerator is found to be about 0.4% on the weight of MBS and this content is expected to increase if MBS is not stored properly and exposed to Heat & Humidity – moisture and also the rate of nitrosation is max. around pH of 3.4 and the rate



of reaction with the gaseous nitrogen oxides viz. N_2O_3, N_2O_4, NO_X, will take place at all pH and is maximum around 7, in the presence of moisture – says a study….

The following amines are suspected to give carcinogenic effect as per TRGS 552 classification of Carcinogenic materials:

N-Nitroso-di-n-butylamine CAS-No. 924-16-3 N-Nitroso-diethanolamine	N-Nitroso-diethylamine CAS-No. 55-18-5
((2,2'-Nitrosoimino) -bisethanol) CAS-No. 1116-54-7	N-nitroso-diisopropylamine CAS-No. 601-77-4
N-nitroso-dimethylamine CAS-No. 62-75-9	N-Nitroso-di-n-propylamine CAS-No. 621-64-7
N-Nitroso-ethylphenylamine CAS-No. 612-64-6	N-Nitroso-methylethylamine CAS-No. 10595-95-6
N-Nitroso-methylphenylamine CAS-No. 614-00-6	N-Nitroso-morpholine CAS-No. 59-89-2
N-Nitroso-piperidine CAS-No. 100-75-4	N-Nitroso-pyrrolidine CAS-No. 930-55-2

The following amines are considered to be safe as per TRGS 552….

N-nitroso-methyl-tert-butylamine CAS-No. 2504-18-9	N-nitroso-dibenzylamine CAS-No. 5336-53-8
N-nitroso-dicyclohexylamine CAS-No. 947-92-2	4- (N-nitroso-methylamino) -pyridine CAS-No. 16219-99-1
N, N'-dinitroso-pentamethylentetramin CAS-No. 101-25-7	3- (N-nitroso-methylamino) -pyridine CAS-No. 69658-91-9
N-nitroso-proline CAS-No. 7519-36-0	N-nitroso-diallylamine CAS-No. 16338-97-9
N-nitroso-n-butyl-tert-butylamine CAS-No. 31820-20-9	N-nitroso-ethyl-tert-butylamine CAS-No. 3398-69-4

VULKACIT / VULKANOX / ANTILUX are the brand name of **LANXESS & RHEINCHEMIE**

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