# Vulcanisation of Natural Rubber by p-Quinone Dioxime Dibenzoate

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Quinoid vulcanisation of natural rubber by p-quinone dioxime dibenzoate could effectively be accelerated by metal oxides such as zinc oxide (ZnO) and litharge (PbO). The scorch safety and the aged properties were also markedly improved. Stearic acid accelerated quinoid vulcanisation but it also reduced the crosslinking efficiency. The combination of ZnO, PbO, stearic acid and a small amount of peroxide in the quinoid system showed minimum thermal reversion.

Vulcanisation is a process of linking the flexible long-chain molecules into a threedimensional elastic network by various chemical bridges. Through successive improvements from conventional to efficient vulcanising (EV) systems, sulphur vulcanisation has remained the preferred method of crosslinking natural rubber (NR) for over 130 years. The non-sulphur crosslinking agents of organic peroxides, bisazodicarboxylates, bismaleimides, phenol formadehyde resins, boranes, quinones and their oximes have also been used to cure NR<sup>1,2</sup> but none of them has ever been used on a major scale industrially.

Quinone dioxime and its derivatives have never been used alone to vulcanise NR commercially despite their successful applications in butyl rubber. Good heat resistant properties are reported for quinoid cures of butyl rubber<sup>3</sup> and SBR<sup>4,5.</sup> The scorch problem is the primary drawback in the quinoid-NR system which uses red lead (Pb<sub>3</sub>O<sub>4</sub>) as oxidant. Recently, there are some indications<sup>6</sup> that some simple metal oxides can also activate p-quinone dioxime dibenzoate (DGMF) to form quinoid-NR vulcanisates satisfactorily. This paper reports on a detailed study of the suitability of various oxides as activators for quinoid vulcanisation of NR.

The quinoid vulcanisation mechanism is not yet fully established. Early workers<sup>7</sup> proposed a nitrone crosslink structure but recent studies<sup>8,9,10</sup> favour an anil crosslink in the quinoid-butyl system. It is believed<sup>6</sup> that the quinoid crosslinking reactions of NR are similar to those of butyl rubber.

#### EXPERIMENTAL

### Materials

Natural rubber (SMR 5);  $Pb_3O_4$ (BDH); PbO (Anchor Chemicals); ZnO (Durham); MgO (Merck); TiO<sub>2</sub> (ICI); Silica (Vulkasil S., Bayer); Dicumyl peroxide (Dicup R, Hercules), Saret 500 (Sartomer Company) and *p*-quinone dioxide dibenzoate (DGMF, The Rubber Regeneration Company) were all used without further purification. Based on nitrogen analysis, the purity of DGMF was 89%. In actual formulations and calculations, the impurity of DGMF was appropriately corrected.

# Preparation of Vulcanisates

The mixes were prepared on a two-roll laboratory mill at  $60^{\circ}C - 75^{\circ}C$ . The com-

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pounded stocks were vulcanised at 160°C in a steam-heated press for different cure times.

#### Determination of Chemically Combined Nitrogen

Vulcanisates were extracted with a mixture of methyl ethyl ketone and benzene in the ratio of 3:2 for five days. The nitrogen analysis was determined by a semi-micro Kjedahl procedure<sup>11</sup>.

To account for the nitrogen content of the naturally occurring proteins in NR, two parts of dicumyl peroxide cured NR was used as a control. The extracted peroxide-cured vulcanisate was subjected to a similar nitrogen analysis. It was found that the amount of residual nitrogen in the extracted NR vulcanisates was 0.34%. Thus, the chemically combined quinoid nitrogen in the vulcanisate was obtained by deducting 0.34% from the total combined nitrogen in the extracted quinoid vulcanisate.

The combined DGMF in rubber vulcanisate  $(N_c)$  was calculated from the combined quinoid nitrogen and the nitrogen content of added DGMF. As the detailed structure of the quinoid crosslink has not been fully established, the chemically combined quinoid nitrogen in rubber network could only be expressed in general as the combined dinitrocompounds  $(N_d)$  in moles per gramme rubber hydrocarbon.

### Determination of Chemical Crosslink Density

The chemical crosslink density  $[2M_{c}, \text{ chem}]^{-1}$  was calculated<sup>6</sup> from  $C_{1,RH}$  using the Mullins and Watson's relationship<sup>12</sup>:

$$C_{1, RH} = \left(\frac{PRT}{2M_c, \text{ chem}}\right) + 0.78 \times 10^6 \left(1 - \frac{2.3M_c, \text{ chem}}{M_n}\right)$$
  
dynes cm<sup>-2</sup>

where  $\rho$  is the density of NR hydrocarbon (0.915 g per millilitre at 25°C);  $\overline{M}_n$  is the molecular weight of rubber hydrocarbon in the mix;  $C_{1,RH}$  is the elastic parameter pertinent to the rubber hydrocarbon in the vulcanisate. The molecular weight of the rubber hydrocarbon,  $\overline{M}_n$  was determined from the intrinsic viscosity in benzene at 25°C according to the following relationship<sup>13</sup>:

$$[\eta] = 2.29 \times 10^{-7} \ \overline{M}_n^{1.33}$$

The tensile strength<sup>14</sup>, elongation at break, modulus at 300%, hardness<sup>15</sup>, resilience<sup>16</sup> and compression set<sup>17</sup> were determined using standard methods.

#### RESULTS AND DISCUSSION

#### Effect of Oxides on DGMF-NR Vulcanisation

Natural rubber can be vulcanised by DGMF alone but at a very slow reaction rate<sup>6</sup>. In the presence of the oxidising agents such as  $Pb_3O_4$  or Dicup R, the rate of quinoid vulcanisation increased significantly. It was found that zinc oxide or litharge (PbO) could also activate DGMF to produce good quinoid vulcanisates at a reasonable rate. But other metal oxides, namely, magnesium oxide, titanium dioxide and silica did not show any significant effect on DGMF-NR vulcanisation<sup>18</sup>.

The quinoid curing agent which was chemically combined in the rubber network might exist as dinitro- or/and polynitro-crosslinks, intramolecular crosslinks and as pendent groups of dinitrocompounds<sup>6</sup>. As there is still no reliable way to differentiate them, the term 'crosslinking efficiency parameter (E)' is used to describe the average number of the combined dinitro-compounds per chemical crosslink, *i.e.*  $E = N_d/X_c$ , where  $N_d$  is the number of moles of dinitrocompounds per gramme of rubber network and  $X_c$  is the chemical crosslink density. A low value of E represents a high crosslinking efficiency and less structural complexity.

The effect of various oxides on DGMF-NR vulcanisation at  $160^{\circ}$ C is shown in *Table 1*. When Pb<sub>3</sub>O<sub>4</sub> was replaced by PbO at the same molar ratio of oxide/ DGMF, the scorch time was improved from 18 min to 30 minutes. By doubling the molar ratio of PbO to DGMF, the Mooney scorch time was reduced only slightly to 25 min and its rheometric cure rate was similar to that of the  $Pb_3O_4/DGMF$  system (equimolar ratio). However, it was evident that the  $Pb_3O_4/DGMF$  system produced a higher chemical crosslink density and it had a better crosslinking efficiency (E = 2.9) than the PbO/ DGMF system (E = 4.9). The low crosslinking efficiency for the latter system could be due to the formation of some azoxy bridge crosslinks and pendent groups<sup>9</sup>.

The Mooney scorch time could be further increased to 68 min by using zinc oxide to activate DGMF, except that the cure rate was slower. The ZnO/DGMF system produced the same chemical cross-

Item	Sample							
item	1	2	3	4	5			
Pb <sub>3</sub> O <sub>4</sub>	12.0	~~~~			_			
РьО	-	3.9	7.8	_	_			
ZnO		-	_	1.4				
Dicup R	- 1	_	_	_	0.8			
Oxide/pure DGMF (molar ratio)	1.13	1.13	2.26	1.13	0.09			
$\overline{\mathrm{M}}_{\mathrm{n}}$ (g/mole) $\times 10^{-5}$	2.08	2.02	2.02	1.97	1.97			
Mooney scorch at 120°C (T <sub>5</sub> ) min	17.7	30.2	25.3	68.0	14.3			
Rheometer cure rate <sup>b</sup> (160°C) min	1.1	2.0	1.3	10.3	5.0			
Maximum cure time (160°C) min	6	6	6	21	16			
N <sub>c</sub> (%)	62.88	67.50	69.11	68.90	50.25			
$N_{d}$ (mole/g rubber hydrocarbon) $\times 10^{5}$	9.70	10.41	10.65	10.61	7.74			
$X_c = [2M_c, chem]^{-1} (mole/g rubberhydrocarbon) X 105$	3.38	1.95	2.18	2.16	2.21			
$E = N_d / X_c$	2.9	5.3	4.9	4.9	3.5			

TABLE 1. EFFECT OF OXIDES ON CURE/CHARACTERISTICS OF DGMF-NR VULCANISATES<sup>a</sup>

<sup>a</sup>SMR 5 (100); commercial DGMF (6) = pure DGMF (5.34); oxides as indicated

<sup>b</sup>Cure rate = optimum cure time  $(t_{90})$  - scorch time  $(t_2)$ 

 $N_c$  = Percentage of added DGMF combined in rubber network

- N<sub>d</sub> = Moles of the combined dinitrocompounds per gramme of rubber network
- $X_c$  = Chemical crosslink density from C1RH
- E = Crosslinking efficiency *i.e.* the average number of the combined dinitrocompounds per chemical crosslink

link density and crosslinking efficiency as compared to the PbO/DGMF system.

Using 0.8 p.h.r. Dicup R as activator, the quinoid system had scorch time shorter than that oxidised by Pb<sub>3</sub>O<sub>4</sub>. Its crosslinking efficiency (E = 3.5) was slightly inferior to the Pb<sub>3</sub>O<sub>4</sub>/DGMF system but it was better than those of both PbO/DGMF and ZnO/DGMF systems (E = 4.9).

#### Effect of Mixed Oxides on DGMF-NR Vulcanisation

The results in *Table 2* show the effect of the mixed oxides on the quinoid vulcanisation system. Addition of ZnO to Pb<sub>3</sub>O<sub>4</sub>/DGMF improved both Mooney scorch and crosslinking efficiency. Even when half the amount of Pb<sub>3</sub>O<sub>4</sub> was substituted by ZnO, the chemical crosslink density and the crosslinking efficiency still remained unchanged. Similarly, ZnO also markedly increased the crosslinking efficiency in the peroxide/DGMF system by boosting its chemical crosslink density.

Total elimination of the oxidising agent, Pb<sub>3</sub>O<sub>4</sub>, in the quinoid system was achieved by using a combination of PbO and ZnO. The mixed metal oxides/DGMF system not only exhibited good scorch safety but it also produced a comparable chemical crosslink density. Its crosslinking efficiency was also improved significantly from E = 4.9 for either the PbO/DGMF or ZnO/DGMF system to E = 3.8.

#### Effect of Stearic Acid on Oxides-DGMF-NR Vulcanisation

Addition of stearic acid to the oxides/ DGMF system shortened the Mooney scorch time considerably and the cure rate

Itom	Sample							
item	1	2	3	- 4	5	6		
Pb <sub>3</sub> O <sub>4</sub>	10.0	10.0	5.0		_	_		
PbO	- 1	••••		3.2	3.2	_		
ZnO	- 1	1.2	2.4	2.4	_	2.4		
Dicup R	-	40	_		0.80	0.80		
Oxide(s)/pure DGMF (molar ratio)	1.13	2.26	2.82	3.40	1.25	2.35		
$\overline{M}_{n}(g/mole) \times 10^{-5}$	2.07	2.02	1.94	1.97	2.07	2.15		
Mooney scorch at 120°C (T <sub>5</sub> ) min	22.3	48.7	21.9	24.6	18.0	12.3		
Rheometer cure rate (160°C) min	1.8	2.5	2.3	4.1	6.1	9.0		
Maximum cure time (160°C) min	6	8	10	12	25	23		
N <sub>c</sub> (%)	61.91	61.13	68.54	69.47	76.48	76.63		
$N_d$ (mole/g rubber hydrocarbon) X 10 <sup>5</sup>	7.95	7.85	8.80	8.92	9.82	9.84		
$X_c = [2M_c, chem]^{-1} (mole/g rubber)$	:							
hydrocarbon) X 10 <sup>5</sup>	2.63	3.05	3.03	2.35	2.20	4.10		
$\mathbf{E} = \mathbf{N}_{\mathbf{d}} / \mathbf{X}_{\mathbf{c}}$	3.0	2.6	2.9	3.8	4.5	2.4		

TABLE 2. EFFECT OF MIXED OXIDES ON CURE/CHARACTERISTICS OF DGMF-NR VULCANISATES<sup>a</sup>

<sup>a</sup>SMR 5 (100); commercial DGMF (5) = pure DGMF (4.45); oxides as indicated

was accelerated. It also increased the amount of the combined dinitrocompounds in the rubber network. However, the chemical crosslink density progressively decreased with increments of stearic acid as shown in *Table 3*. Hence, the crosslinking efficiency (E) was adversely affected by the addition of stearic acid.

## Technological Properties of Quinoid Vulcanisates

The technological properties of the quinoid gum vulcanisates are summarised in *Table 4*. Results showed that  $Pb_3O_4/DGMF$  vulcanisates had the best tensile strength but their properties after three days ageing at 100°C were inferior in comparison with vulcanisates using other activator systems. The Dicup R/DGMF vulcanisate exhibited the lowest compression set, but had poor tensile strength.

The retention of tensile strength of the quinoid vulcanisates after ageing was markedly improved by the use of PbO, ZnO and stearic acid. In particular, the quinoid vulcanisate containing both PbO and ZnO (Compound 5) retained 68% of the initial tensile strength after ageing for three days at  $100^{\circ}$ C, whereas the Pb<sub>3</sub>O<sub>4</sub>/ DGMF vulcanisate retained only 11% of the initial tensile strength. Their aged elongation and modulus remained almost unchanged. This mixed metal oxides/ DGMF system retained the tensile strength in spite of the lack of any antioxidant additive in the mix. When 0.4 p.h.r. Dicup R and 2 p.h.r. stearic acid were further added to the mixed oxides/ DGMF system (Compound 9), the unaged strength was marginally improved but there was a slight adverse effect on the aged properties.

Item	Sample							
	1	2	3	4	5	6		
ZnO	1.4	2.4	2.4	2.4				
РЬО	-	_	_	_	3.9	3.2		
Dicup R	_	_	_	_	_	_		
Stearic acid	_	1.0	2.0	4.0	_	2.0		
Oxide/DGMF (pure molar ratio)	1.13	2.26	2.26	2.26	1.13	1.13		
$\overline{M}_n$ (g/mole) $\times 10^{-5}$	1.97	2.10	1.90	1.89	2.02	2.16		
Mooney scorch at $120^{\circ}C(T_5)$ min	68.0	30.1	22.7	17.8	30.2	20.5		
Rheometer cure rate (160°C) min	10.3	5.3	4.0	2.9	<b>2.0</b>	1.5		
Maximum cure time at (160°C) min	21	14	11	10	6	7		
N <sub>c</sub> (%)	68.90	79.20	80.40	79.52	67.5	79.91		
N <sub>d</sub> (mole/g rubber hydrocarbon) × 10 <sup>5</sup>	10.61	10.17	10.33	10.21	10.40	10.26		
$X_c = [2M_c, chem]^{-1}$ (mole/g rubber								
hydrocarbon) × 10 <sup>5</sup>	2.16	1.75	1.85	1.58	1.95	1.33		
$\mathbf{E} = \mathbf{N}_{\mathbf{d}} / \mathbf{X}_{\mathbf{c}}$	4.9	5.8	5.6	6.5	5.3	7.7		

TABLE 3. EFFECT OF STEARIC ACID ON CURE/CHARACTERISTICS OF OXIDES-DGMF-NR VULVANISATES<sup>a</sup>

<sup>a</sup>SMR (100); commercial DGMF (5) = pure DGMF (4.45), except sample 1 and sample 5 where commercial DGMF (6) = pure DGMF (5.34); oxides and stearic acid as indicated.

Item	Compound								
	1	2	3	4	5	6	7	8	9
SMR 5	100	100	100	100	100	100	100	100	100
DGMF (commercial)	6	6	6	5	5	5	5	5	5
Pb <sub>3</sub> O <sub>4</sub>	-	-	_	10	_		_		
РЬО	7.8	_		-	3.2	_		_	3.2
ZnO	_	1.4	-	_	2.4	2.4	2.4	2.4	2.4
Dicup R	_	-	0.8	_	_	0.8	_	—	0.4
Stearic acid	-	_		—	_	_	2.0	4.0	2.0
Mooney scorch at 120°C	25.3	68.0	14.3	22.3	24.6	12.3	22.7	17.8	14.9
$(1_5)$ min Rheometer cure rate $(160^{\circ}C)$ min	2.0	10.3	5.0	1.8	<b>4.</b> 1	9.9	4.0	2.9	2.7
Maximum cure time (160°C) min	6	21	16	6	12	23	11	10	8
Tensile strength (MPa)	6.0	6.2	3.1	16.6	7.3	13.0	6.5	5.1	8.2
Elongation at break (%)	480	550	500	650	550	560	570	510	530
M 300 (MP <sub>a</sub> )	1.70	1.36	1.11	1.63	1.23	1.75	1.14	1.31	1.51
Hardness (IRHD)	30.2	31.5	28.9	37.7	32.2	35.5	32.0	33.0	33.4
Resilience (%)	77.0	79.9	77.0	84.4	79.0	84.6	75.7	74.0	77.8
Compression set after 24h/70°C (%)	71.8	55.1	34.1	57.9	59.2	37.9	51.0	52.6	55.7
Aged 3 days at 100°C	ł								
(% retention)									
Tensile strength (MP.)	30.8	46.2	29.1	10.5	68	53.7	49.0	74.2	58.1
Elongation at break (%)	79.2	78.2	68.0	58.5	98.2	94.6	82.5	96.1	81.1
M 300 (MPa)	67.0	97.4	71.0	68.7	94.4	84.9	104	89.3	122

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## TABLE 4. TECHNOLOGICAL PROPERTIES OF QUINOID VULCANISATES

#### Effect of Cure Temperature on Maximum Change in Rheometer Torque Values

The suitability of the various oxides/ DGMF systems for use at high temperature vulcanisation was examined. The maximum change in the rheometer torque values was obtained at cure temperatures from 160°C to 190°C. The results are summarised in Figure 1. It was found that the maximum modulus for the Dicup R/ DGMF vulcanisate was quite low but it remained practically the same at all cure temperatures. All the PbO-, ZnO- and Pb<sub>3</sub>O<sub>4</sub>-DGMF systems showed a similar thermal reversion trend except that the latter had a higher modulus at each cure temperature. When ZnO was used in combination with Dicup R, the modulus was markedly increased to a similar level as shown by the Pb<sub>3</sub>O<sub>4</sub>/DGMF system. The synergistic effect of ZnO and PbO on thermal reversion was also noticeable. The modulus at higher temperatures could also



Figure 1. Effect of cure temperature on rheometer torque difference  $(\Delta T)$  for quinoid vulcanisation.

be improved by adding stearic acid. The technological properties of a quinoid system consisting of PbO, ZnO, stearic acid and 0.4 p.h.r. Dicup R could match most of the technological properties of the Pb<sub>3</sub>O<sub>4</sub>/DGMF vulcanisate except in tensile strength; on the other hand it had a better resistance to thermal reversion in terms of modulus change.

# Interaction between Metal Oxides and DGMF

It has been established<sup>7</sup> that DGMF is first oxidised by  $Pb_3O_4$  or peroxides to form dinitrosobenzene which is the real crosslinking agent for rubber. However, a good level of quinoid vulcanisation could also be obtained by using metal oxides such as PbO or ZnO as discussed earlier. One would suspect that some kinds of peroxide compounds might be present either in NR or exist as contaminants in these metal oxides to cause this quinoid vulcanisation.

To ascertain the involvement of peroxide compounds in the NR-metal oxides-DGMF systems, a coagent – Saret 500 was used (Table 5). Saret 500 consists mainly of trimethylolpropane trimethacrylate and a nitroso radical capture reagent. It is a coagent for any radical cure system to improve scorch safety and enhance crosslink density. No crosslinking effect by Saret 500 was observed in either PbO/DGMF or ZnO/DGMF system as shown by Monsanto rheographs in Figure 2. In fact, the moduli and strength were

T	Formulation							
Jtem	1	2	3	4	5	6		
SMR 5	100	100	100	100	100	100		
DGMF	5	5	5	5	5	5		
ZnO	2.4	2.4	2.4		· <u> </u>	_		
РЬО	-	-	_	3.2	3.2	3.2		
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0		
Saret 500	-	3.0	3.0	_	3.0	3.0		
Dicup R	-	-	0.4		_	0.4		
Mooney scorch (T5) min	22.7	11.0	8.2	20.5	19.6	17.3		
Rheometer cure rate (160°C) min	4.0	4.3	13.3	1.5	1.9	15.0		
Maximum cure time (160°C) min	11	12	30	7	8	30		
Tensile strength (MP <sub>a</sub> )	6.5	4.0	5.7	4.8	4.2	7.1		
Elongation at break (%)	570	540	510	510	550	520		
M 300 (MP <sub>a</sub> )	1.14	1.11	1.59	1.18	1.01	1.49		
Hardness (IRHD)	32.0	31.0	31.0	30.0	25.3	35.5		
Resilience (%)	75.7	74.2	76.6	68.9	65.1	77.0		
Compression set after 24h/70°C (%)	51.0	54.6	38.2	68.8	73.4	46.1		
Aged 3 days at 100°C(% retention)								
Tensile strength (MPa)	49.0	93.3	87.0	25.8	33.3	16.1		
Elongation at break (%)	82.5	79.6	88.2	74.5	61.8	51.9		
M 300 (MPa)	104	131	113	73.6	75.1	_		

TABLE 5. EFFECT OF SARET 500 ON TECHNOLOGICAL PROPERTIES OF OUINOID-OXIDE NR VULCANISATES



Figure 2. Effect of Saret 500 on Monsanto rheograph for quinoid-oxide NR vulcanisation (range selection: 50, formulations as in Table 5).

somewhat decreased. These indicate that there are no peroxide compounds in the metal oxide/DGMF system to initiate the reaction for Saret 500. When 0.4 p.h.r. Dicup R was incorporated into the systems, the rheographs were distinctively different. The Mooney scorch times were also shortened even with the presence of Saret 500. Both the moduli and strength were higher and the compression sets were lower. This could be attributed to the formation of additional crosslinks by peroxide activated Saret 500 coagent reaction. Two inferences could be obtained from the observations. First, the interactions between DGMF and PbO or ZnO are able to produce dinitrosobenzene. Second, DGMF itself might be able to react with the NR molecule directly in the presence of PbO or ZnO. The metal oxides could facilitate the removal of benzoic acid, a by-product of the reactions. The reaction mechanisms are yet to be investigated.

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