

Quinoid Vulcanisation of Natural Rubber

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Quinoid-cured natural rubber (NR) by p-dinitrosobenzene, quinone dioxime and dibenzo quinone dioxime with and without red lead was studied. The quinoid crosslinks were thermally stable. Their tensile strength were comparable to those of EV vulcanisates. The structures of the crosslinks for the quinoid-NR vulcanisates were more complicated than that of butyl. Quinoid crosslinking efficacy depended not only on the concentrations of the curing agent and oxidant but also the cure time. The vulcanisation mechanism is also discussed.

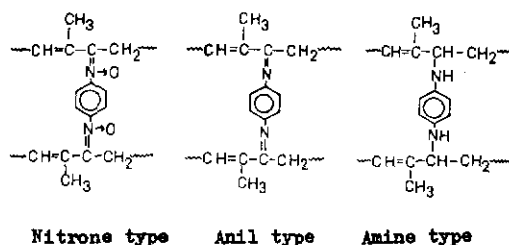
The vulcanisates obtained by the treatment of unsaturated rubbers with p-quinone dioxime (known as GMF) and its derivatives such as dibenzo GMF (DGMF) have been referred to as 'Quinoid-cured compounds'. The quinoid-cured butyl vulcanisates are noted for their excellent thermal stability and for their application in cable insulation and tyre curing bags^{1,2}. The mechanism of quinoid vulcanisation has been the subject of discussion in several papers³⁻⁶.

Quinone dioxime and its derivatives have never been used alone to vulcanise NR commercially despite their successful applications in butyl rubber. The scorch problem with its consequent processing difficulties has been the primary drawback in the quinoid curing NR system. It is therefore not surprising to find that very little work has been published about this system^{7,8}. However, NR⁹ or blends of NR with cis-1,4-polybutadiene¹⁰ had been satisfactorily co-vulcanised by DGMF with an appropriate accelerated sulfur system. This co-vulcanisation system not only minimises the scorch problem but also improves the physical properties of the vulcanisates.

Natural rubber has many active sites as a result of the many double bonds in comparison with butyl rubber of low unsaturation. Thus, acceptable formulations for quinoid-cured butyl rubber would not be

suitable when used with NR. The differences may relate not only to the rate of crosslink formation but also to the chemical nature of the quinoid crosslinks.

The nature of quinoid crosslink has not been clearly understood. The crosslink may consist of either a nitron or an anil or an amine or even a mixture of these as shown below:



EXPERIMENTAL

Materials

Natural rubber (pale crepe), red lead (Riedel-Dehaven), p-dinitrosobenzene (DNB) and GMF (Tokyo Kasei ICI), and DGMF (The Rubber Regeneration Co., UK) were all used without further purification. Based on nitrogen analysis, the purities of DNB, GMF and DGMF were found to be 71%, 92%, 89% respectively. In the actual formulations, the weights of the impurities were allowed for and had been corrected for these reagents. The

COMMUNICATION 627

amounts of these reagents shown in the compounding recipes were all based on 100% purity.

Preparation of Vulcanisates

Compounding was done on a two-roll laboratory mill following basically the same procedure as outlined in ASTM D15-70, except that the mill was constantly cooled by running water in order to avoid scorching on the mill. Vulcanisation was carried out in a compression mold under an electrically heated press at different cure times and temperatures.

Determination of Chemically Combined Nitrogen

About 4 g of the vulcanisate was accurately weighed and extracted with a mixture of methyl ethyl ketone and benzene in a ratio of 3:2. The extraction was first performed at room temperature in a soxhlet cup for two days followed by continuous extraction for another five days at 90°C. This pre-extraction at room temperature was to minimise post-vulcanisation.

The extracted solution was transferred to a Kjeldahl flask and concentrated to about 5 millilitres. The residue solvents were driven off by air to avoid any decomposition. The dried extract was then digested with concentrated sulfuric acid in the presence of the mixed catalysts of potassium sulfate, copper sulfate and selenium in a ratio of 15:2:1. After a clear solution was obtained, it was made alkaline by addition of sodium hydroxide solution. The liberated ammonia was steam-distilled and trapped in 2% boric acid. The solution was then titrated with 0.01N sulfuric acid.

The amount of the extractable nitrogen (N_f) was calculated from the following simple equation:

$$N_f = \frac{NV}{1000 W}$$

where N_f = mole of extractable nitrogen per gramme rubber (mole/g RH);

V = volume of sulfuric acid used (ml) with N normality;

W = weight of vulcanisate which had been corrected for non-rubber and was expressed as weight of rubber (g RH).

To account for the extractable nitrogen due to the naturally occurring proteins in NR, two parts of di-cumyl peroxide was used to cure NR and the vulcanisate was subjected to the similar extraction. Only a negligible amount of nitrogen was extracted from this peroxide cured NR vulcanisate. Thus, it was assumed that the extractable nitrogenous substances from the quinoid-NR vulcanisates were derived from the free quinoid compounds. The chemically combined quinoid nitrogen in the vulcanisate (N_c) was calculated from the difference between the total amount of nitrogen of the added quinoid curing agent in the formulation (N_t) and that of the extractable nitrogen of the free quinoid compounds (N_f), i.e.

$$N_a = \frac{N_c}{2} = \frac{N_t - N_f}{2} \text{ (mole/g RH)}$$

As the detailed quinoid structure of the crosslink has not been fully established, the chemically combined quinoid nitrogen was expressed in general as the amount of combined dinitrocompounds (N_a).

Stress-Strain Measurements

All the dumbell shaped specimens were of 0.35 cm width and 0.127 cm thick. The stress-strain measurements were performed by means of an Instron tensile tester (model 1026) with a cross-head speed of 5 cm per minute at room temperature (25°C).

Determination of Crosslink Density¹¹

One end of a dumbell test specimen was fixed and the other end was attached to a

weighing pan. Elongation was effected by successively adding weights to the pan at 3-min intervals. The elongation was measured by a cathetometer. The weight added was chosen such that it would roughly cause 10% increment in elongation.

At low and moderate extension, a linear plot of $F/A_0 (\lambda - \lambda^{-2})$ against λ^{-1} was obtained according to the Mooney-Rivlin's equation¹¹

$$F/A_0(\lambda - \lambda^{-2}) = 2C_1 + 2C_2\lambda^{-1}$$

where F , A_0 and λ were force applied, original cross-sectional area of the test specimen and extension ratio respectively.

Constants C_1 and C_2 were obtained from the intercept and the slope of the plot respectively. C_1 was corrected for non-reinforcing particulate fillers by applying the equation

$$C_{1, RM} = C_1 (1 + 2.5V_f + 14.1V_f^2)^{-1}$$

where V_f is the total volume fraction of fillers in the rubber vulcanisate. $C_{1, RM}$ is the C_1 value of the rubber matrix (RM) which included the rubber network diluted by any rubber-soluble material. $C_{1, RM}$ was further corrected for the presence of soluble extra-network materials as:

$$C_{1, RH} = C_{1, RM} \times (1 - V_f)/V_{RH}$$

in which $C_{1, RH}$ is the elastic parameter C_1 of the rubber hydrocarbon component of the network. V_{RH} is the volume fraction of rubber hydrocarbon in the vulcanisate and is the insoluble NR in a hot mixture of methyl ethyl ketone and benzene in a ratio of 3:2.

The chemical crosslink density ($1/2 M_{c, chem.}$) was calculated from $C_{1, RH}$ using the following relationship¹¹ deduced by Mullins and Watson.

$$C_{1, RH} = (\rho RT/2 M_{c, chem.} + 0.78 \times 10^6) (1 - 2.3M_{c, chem.}/\bar{M}_n) \text{ dyne cm}^{-2}$$

where ρ is the density of NR hydrocarbon (0.915 g per millilitre at 25°C); \bar{M}_n is the number-average molecular weight of rubber after compounding; $M_{c, chem.}$ is the number-average molecular weight of chain segments between chemical crosslinks, R is the gas constant and T is the absolute temperature.

\bar{M}_n was determined from the intrinsic viscosity in benzene according to the following relationship¹²:

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

RESULTS AND DISCUSSION

Characteristics of Cure

It is known that p-dinitrosobenzene (DNB) is a fast curing agent for butyl rubber³, but GMF or DGMF will not cure the rubber without an oxidising agent^{5,6}. In contrast to butyl rubber, NR could be vulcanised by either GMF or DGMF alone at a very slow rate. Four hours were required for the optimum cures for both systems containing 2.4 p.h.r. GMF and 5.5 p.h.r. DGMF. Although both systems contained about the same molar concentrations, GMF-NR yielded much higher crosslink density than DGMF-NR as shown in *Figure 1*.

When the oxidising agent (Pb_3O_4) was added to GMF-NR, the compounded stocks cured (hardened) slowly even at room temperature but not for the DGMF/ Pb_3O_4 system. *Figure 2* shows the relative extent of vulcanisation (P) for DNB, GMF/ Pb_3O_4 and DGMF/ Pb_3O_4 . It was calculated from the shawbury curometer traces using the following equation:

$$P = \frac{1}{a_t} - \frac{1}{a_0} \bigg/ \frac{1}{a_\infty} - \frac{1}{a_0}$$

where a_0 = width of the trace at the widest part
 a_t = width of the trace at time t
 a_∞ = width of the trace at the narrowest part.

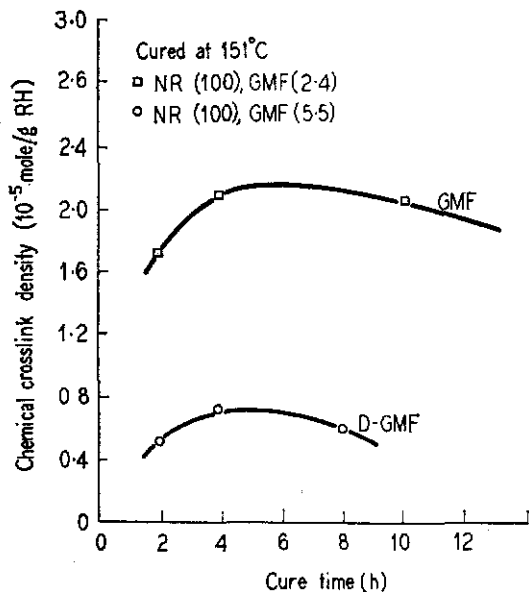


Figure 1. Curing curves for GMF- and DGMF-NR vulcanisation.

Natural rubber with DNB or GMF/ Pb_3O_4 was too scorchy giving almost no induction period for vulcanisation. Scorch caused the uneven flow of the compound under compression molding, thus resulting in rough surfaces on the vulcanisates. On the other hand, the vulcanisation curve for DGMG/ Pb_3O_4 was quite satisfactory because there was a short delay before fast vulcanisation took off.

Structural Features

At the optimum cures, the combined dinitrocompounds were 38% and 82% for the non-oxidant DGMF and GMF respectively. These dinitrocompounds could be in the form of either dinitrones, or dianils or diamines or even a mixture of them. The non-oxidant GMF was more reactive than DGMF. Its ability to cure butyl rubber in the presence of channel black¹³ had been attributed to the oxidation of GMF to form DNB by some oxygen absorbed on the surfaces of the carbon particle, probably in the form of peroxide. It is also speculated that GMF might have first been oxidised

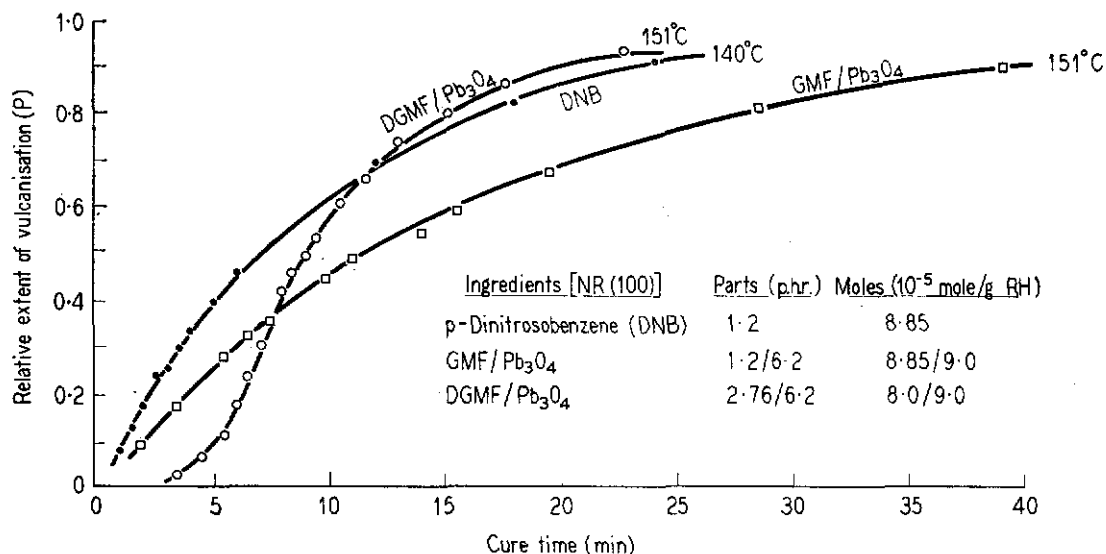


Figure 2. Extent of vulcanisation of NR by DNB, GMF/ Pb_3O_4 and DGMF/ Pb_3O_4 .

to DNB by some kind of organic peroxides which were present in the NR system or formed during compounding. Similarly, the formation of DNB through similar oxidation of DGMF might also take place perhaps with a much slower rate. The nature of this type of oxidation is not clear yet and will be subjected to further investigation.

Besides the oxidants, metal oxides could also increase the reactivity of GMF or DGMF towards rubber molecules. It was found that the combined dinitrocompounds in the DGMF-NR system were markedly increased from 38% to 70% by the effect of 1.4 p.h.r. zinc oxide or 3.7 p.h.r. lead oxide. Furthermore, its optimum cure time was tremendously reduced and the crosslink density was boosted three-fold. Table 1 shows some of the structural features

of the vulcanisates under the influence of metal oxides and red lead (Pb_3O_4). There is no doubt that red lead was superior to the metal oxides in affecting crosslink formation in the DGMF-NR system. The function of red lead was to oxidise DGMF to DNB. But it is not clear about the interaction between metal oxide and DGMF.

Tables 2, 3 and 4 list the detailed formulations and the structural features for the systems DNB, GMF/ Pb_3O_4 and DGMF/ Pb_3O_4 . When the concentrations of the curing agents were plotted against the combined dinitrocompounds, a linear relationship was established as shown in Figure 3. The slopes indicate that only 68% of DNB was ever combined with the rubber molecules, while as high as 86% of GMF or DGMF was used up in crosslinking formation. The combined dinitrocompounds

TABLE 1. EFFECT OF METAL OXIDES ON THE STRUCTURAL FEATURES OF DGMF-NR VULCANISATES

Feature	Sample			
	A ₀	A ₁	A ₂	A ₃
Pale crepe (g)	100	100	100	100
DGMF (g)	5.51	5.51	5.51	5.51
(mole/g RH, 10 ⁻⁵)	15.9	15.9	15.9	15.9
ZnO (g)	-	1.40	-	-
PbO (g)	-	-	3.70	-
Pb ₃ O ₄ (g)	-	-	-	12.4
Oxides/DGMF (molar ratio)	0	1.08	1.04	1.13
Optimum cure time (min)	240	25	20	12
X _c (mole/g RH, 10 ⁻⁵)	0.71	2.51	2.56	4.34
N _d (mole/g RH, 10 ⁻⁵)	6.04	11.3	11.0	13.9
C _N (%)	38	71.0	69.2	87.4
E = N _d /X _c	8.5	4.5	4.3	3.4

All compounds were cured at 151°C.

N_d = mole of the combined dinitrocompounds per gramme of rubber network

C_N (%) = percentage of combined dinitrocompounds in rubber network

X_c = chemical crosslink density from C_{1RH}

E = crosslinking efficacy, i.e. the average number of combined dinitrocompounds per crosslink

increased slowly with the increase of the molar ratio of Pb_3O_4 /GMF or Pb_3O_4 /DGMF until it reached the maximum at equimolar

ratio. No significant changes in the combined dinitrocompounds were further observed for the ratio greater than one.

TABLE 2. FORMULATIONS AND THE STRUCTURAL FEATURES OF P-DINITROBENZENE-NR VULCANISATES

Feature	Sample							
	B ₁		B ₂		B ₃		B ₅	
Pale crepe (g)	100		100		100		100	
p-dinitrosobenzene (g)	0.80		1.20		1.60		2.0	
(mole/g RH, 10 ⁻⁵)	5.9		8.85		11.80		14.80	
Cure time (min)	10	20	10	20	20	20	20	20
X_c (mole/g RH, 10 ⁻⁵)	1.05	1.10	1.28	1.31	1.55	1.77	2.02	2.02
N_d (mole/g RH, 10 ⁻⁵)	1.93	3.61	4.57	6.27	8.05	9.69	11.39	11.39
C_N (%)	32.7	61.2	51.6	70.8	68.2	65.5	64	64
$E = N_d/X_c$	1.8	3.3	3.3	4.8	5.3	5.5	5.6	5.6

All compounds were cured at 140°C.

The optimum cure times appeared to be about 20 min for all the vulcanisates.

N_d = mole of combined dinitrosobenzene per gramme of rubber network

C_N (%) = percentage of added dinitrosobenzene being combined in rubber network

E = crosslinking efficacy, i.e. the average number of combined dinitrosobenzene per crosslink

TABLE 3. FORMULATIONS AND THE STRUCTURAL FEATURES OF GMF-PB₃O₄-NR VULCANISATES

Feature	Sample							
	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
Pale crepe (g)	100	100	100	100	100	100	100	100
GMF (g)	2.83	1.19	1.19	1.19	1.19	1.79	2.38	2.98
(mole/g RH, 10 ⁻⁵)	17.3	8.67	8.67	8.67	8.67	13.0	17.3	21.6
Pb ₃ O ₄ (g)	0	3.10	6.20	9.30	12.4	9.30	12.4	15.5
Pb ₃ O ₄ /GMF (molar ratio)	0	0.52	1.04	1.56	2.08	1.04	1.04	1.04
Optimum cure time (min)	240	50	40	30	25	25	25	25
X_c (mole/g RH, 10 ⁻⁵)	2.22	1.46	1.82	1.85	1.91	2.08	2.48	3.06
N_d (mole/g RH, 10 ⁻⁵)	14.25	6.27	6.81	6.85	6.90	11.3	15.0	19.1
C_N (%)	82.4	72.3	78.5	79.0	79.6	86.9	86.7	88.4
$E = N_d/X_c$	6.4	4.3	3.7	3.7	3.6	5.4	6.0	6.2

All compounds were cured at 151°C.

Symbols are identical to those in Table 1.

TABLE 4. FORMULATIONS AND THE STRUCTURAL FEATURES OF DGMF-PB₃O₄-NR VULCANISATES

Feature	Sample										
	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	D ₉	D ₁₀	D ₁₁
Pale crepe (g)	100	100	100	100	100	100	100	100	100	100	100
DGMF (g) (mole/g RH, 10 ⁻⁵)	5.51 15.90	5.51 15.90	5.51 15.90	5.51 15.90	5.51 15.90	2.76 7.98	4.12 11.90	6.88 19.90	1.38 3.99	1.38 3.99	1.38 3.99
Pb ₃ O ₄	2.48	4.96	7.44	9.92	12.40	6.20	9.25	15.45	3.10	6.20	9.30
Pb ₃ O ₄ /DGMF (molar ratio)	0.28	0.46	0.69	0.91	1.13	1.13	1.13	1.13	1.13	2.27	3.40
Optimum cure time (min)	15	15	15	15	12	30	25	12	30	15	10
X _c (mole/g RH, 10 ⁻⁵)	2.80	3.89	4.19	4.29	4.34	2.20	3.29	5.10	1.42	1.44	1.46
N _d (mole/g RH, 10 ⁻⁵)	11.96	12.10	12.50	13.00	13.90	6.41	10.00	17.50	3.32	3.33	3.30
C _N (%)	75	76	79	82	87.40	80.30	84.00	87.90	83	83	83
E = N _d /X _c	4.30	3.10	3.00	3.00	3.20	3.20	3.10	3.40	2.30	2.30	2.30

All compounds were cured at 151°C.
Symbols are identical to those in Table 1.

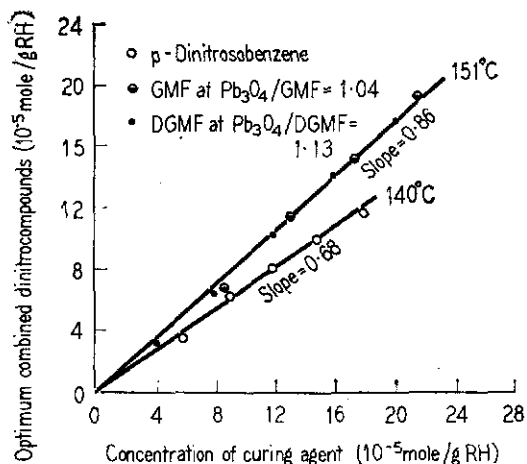


Figure 3. Concentration effect on the combined dinitrocompounds in rubber network.

In the DNB-NR system, GMF was isolated from the extracts of the vulcanisates. This was attributed to the conversion of some DNB to GMF during the crosslinking reactions. A vulcanisation mechanism is proposed in the latter section to account for

the low amount of combined DNB and the formation of GMF.

The optimum chemical crosslink density also increased linearly with the concentrations of the curing agents as shown in Tables 2, 3 and 4. But these linear relationships did not pass through the origin as shown in Figure 4. They all intercepted at crosslink density of about 0.6×10^{-5} mole per gramme RH. The nature of this deviation is not yet understood. The slopes show that 4.3 molecules of DGMF or 8.8 molecules of GMF or 12.5 molecules of DNB were involved in forming one chemical crosslink. However, this did not imply that all of the reacted quinoid molecules should be in the form of the combined dinitrocompounds.

The average number of the chemically combined dinitrocompounds per crosslink was obtained from the slope of the plot between the optimum crosslink density and

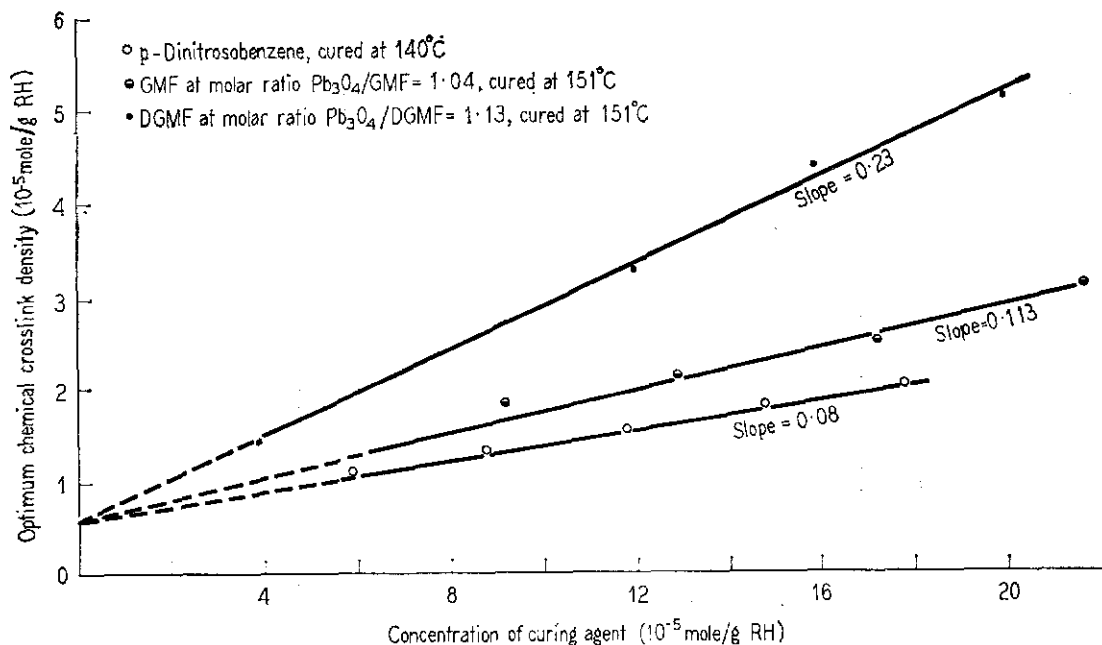


Figure 4. Concentration effect on optimum crosslink density.

the amount of the combined dinitrocompounds. Figure 5 shows the slopes of such plots were 3.6, 7.6 and 8.5 for the systems of Pb_3O_4 /DGMF, Pb_3O_4 /GMF and DNB respectively. This corresponded to an average of 3.6 molecules of DGMF in the form of dinitrocompounds combined in the rubber network for each chemical crosslink formation. Similarly, as many as 7.6 molecules of GMF or 8.5 molecules of DNB were combined as a result of the formation of only one crosslink. This reflected the structural complexity on these vulcanisates and it represented a wasteful amount of GMF or DNB as compared with DGMF in crosslink formation.

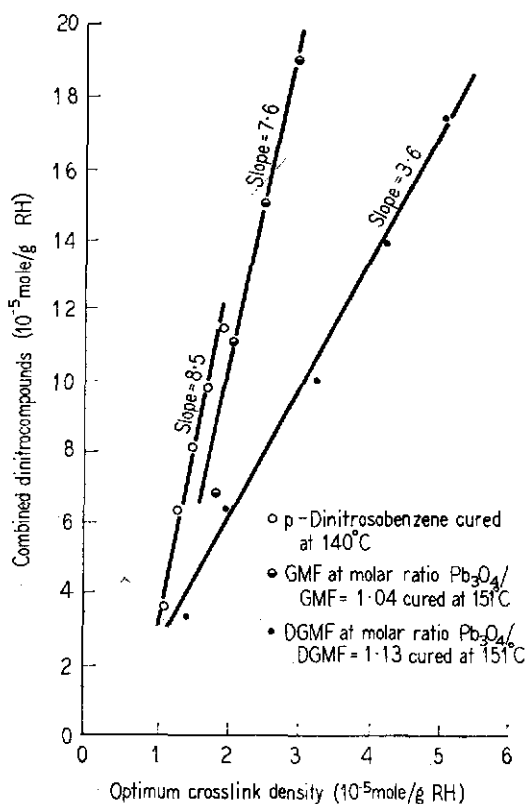


Figure 5. Relationship between optimum crosslink density and combined dinitrocompounds.

The quinoid curing agents chemically combined in the rubber network might exist as dinitro-or/and polynitro-crosslinks, intramolecular crosslinks and as the pendent groups of the dinitrocompounds. As there is still no way of differentiating them, the term 'crosslinking efficacy parameter (E)' is used to describe the average number of the combined dinitrocompounds per chemical crosslink, *i.e.* $E = N_d/X_c$. This is analogous to the nomenclature adopted in the sulfur vulcanisation systems. A low value of E represents a high crosslinking efficacy and less structural complexity.

The dependence of E on the concentration of the curing agent is depicted in Figure 6. In general, the lower the concentration of the curing agent, the lower E would be. E became nearly constant when the concentration of GMF or DNB exceeded 14×10^{-5} mole per gramme RH or 8×10^{-5} mole per gramme RH in the case of DGMF. The early onset of vulcanisation for the DNB or GMF/ Pb_3O_4 system had resulted in a higher value of E . This could be due to the uneven flow of the rubber mix and poor dispersion of the ingredients, especially at a higher concentration of curing agent. Consequently, the localised crosslinks and the pendent groups might be favourably formed under scorchy condition.

The low time-cured vulcanisates were always associated with low E which then increased parallel with cure time. As more and more of the crosslinks were formed, the vulcanising network became rigid and the rubber molecules became less likely to have the subsequent crosslinking reactions at random. The resulting vulcanisates would therefore consist of some undesirable localised crosslinks and the pendent groups. All of which contributed to the high value of E .

Other than the concentration of curing agent and cure time, E was also affected by

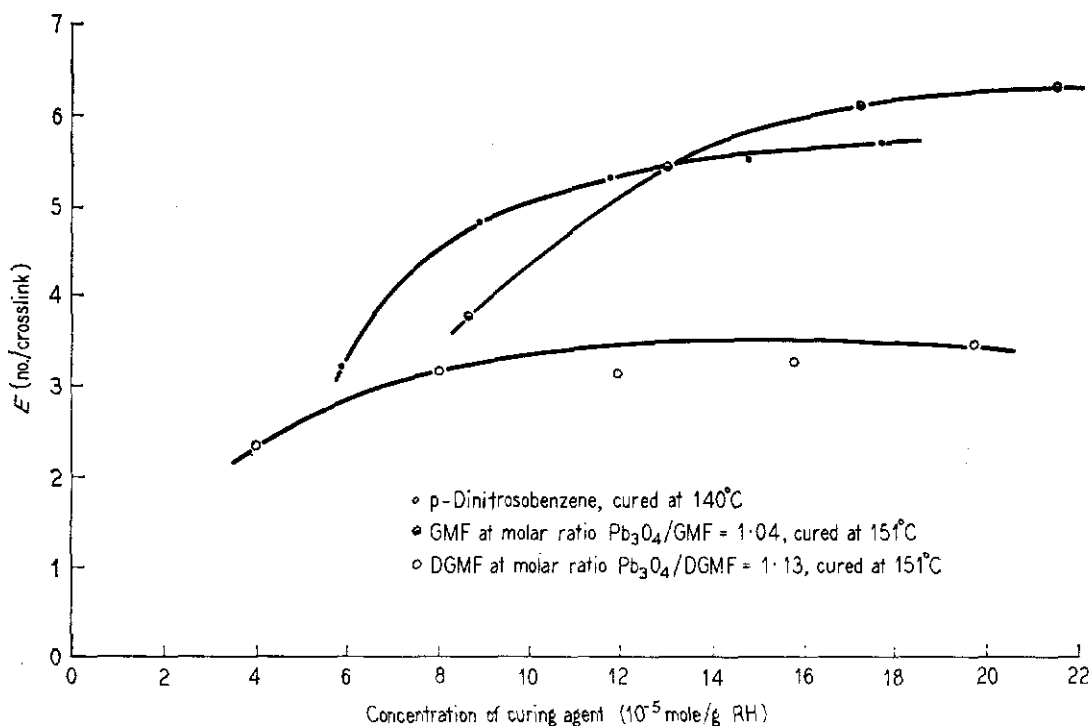


Figure 6. Concentration effect on crosslinking efficacy.

the concentration of oxidant. Low values of E were always obtained for the vulcanisates with equal or greater molar ratio of Pb_3O_4/GMF or $Pb_3O_4/DGMF$. On the other hand, Figure 7 shows that a high value of E was invariably derived from the systems with low molar ratio of Pb_3O_4/GMF or $Pb_3O_4/DGMF$. At a low oxidant concentration, the crosslinks might consist of some polydinitrocompounds in the form of azoxy units. An azoxy unit type of crosslink could only be formed through reduction of the crosslink precursor³ by some kind of reducing agents present in NR. The reduction of crosslink precursor leading to azoxy unit could be suppressed⁵ when sufficient oxidant was present.

Modulus and Tensile Strength

For the vulcanisates of both Pb_3O_4/GMF and $Pb_3O_4/DGMF$ systems, there existed a

common linear relationship between modulus and crosslink density particularly when the crosslink density is below 5×10^{-5} moles per gramme RH as shown in Figure 8. When the vulcanisates were oven-aged for eight days at $70^\circ C$, their crosslink densities were almost unchanged. But their moduli were markedly increased, especially for those with the higher crosslink densities.

When tensile strength was plotted against crosslink density as in Figure 9, a curve with a maximum strength was obtained for the vulcanisates before and after aging. The maximum strength of about 190 kg per square centimetre appeared at crosslink density of 3×10^{-5} mole per gramme RH. This corresponded to a system containing 3 p.h.r. GMF or 4.2 p.h.r. DGMF which would yield such maximum tensile strength.

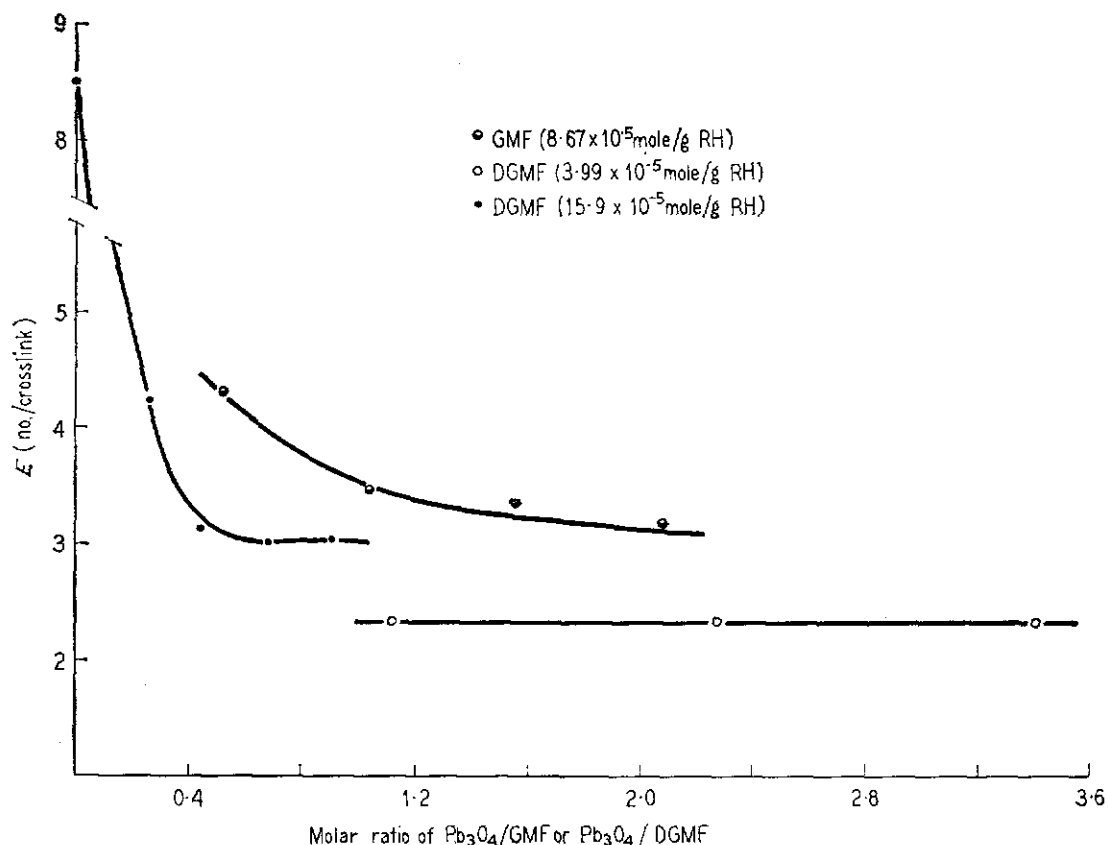


Figure 7. Effect of molar ratio of Pb_3O_4 /GMF or Pb_3O_4 /DGMF on crosslinking efficacy.

For the conventional sulfur-cured NR gum vulcanisates, tensile strength of about 300 kg per square centimetre can easily be obtained. Whereas the maximum tensile strength of an EV-gum vulcanisate will be only about 200 kg per square centimetre. This figure is comparable to that of the quinoid vulcanisate. In view of their chemical structures, both the quinoid and monosulfidic crosslinks are less flexible. These rigid types of crosslink could be associated with their low tensile strength¹⁴.

Aging

In spite of no added antioxidant, the aging property of the quinoid vulcanisates at 70°C was acceptable as shown in Figures 8

and 9. However, their tensile strength deteriorated badly at 100°C as summarised in Table 5. Even so, it was unexpected to find that their aged moduli at 300% elongation were slightly increased. When the vulcanisates were aged in a vacuum oven at 100°C, a substantial increase in moduli were again observed but their crosslink densities remained unchanged whereas the tensile strength were reduced considerably.

The results proved that the quinoid crosslinks were thermally stable. It seemed that some kind of structural modification also occurred. This modification affected only the slope of the Mooney-Rivlin plot, i.e. C_2 value but not the intercept C_1 . It is

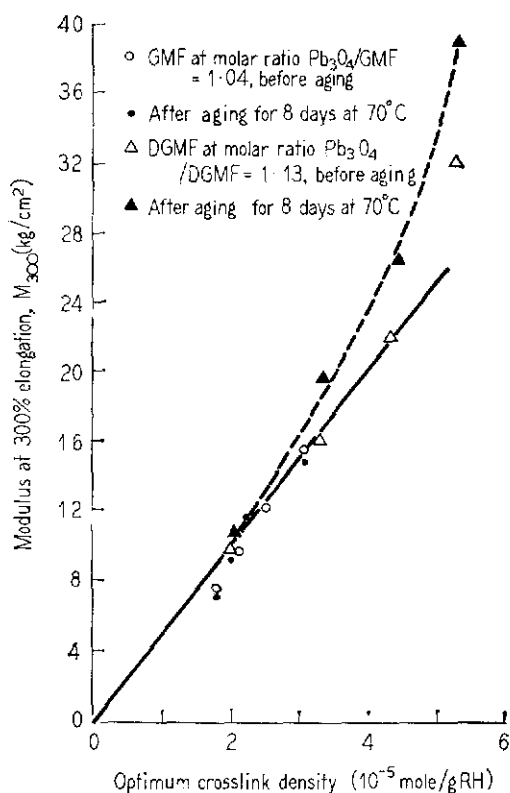


Figure 8. Effect of crosslink density on modulus before and after aging.

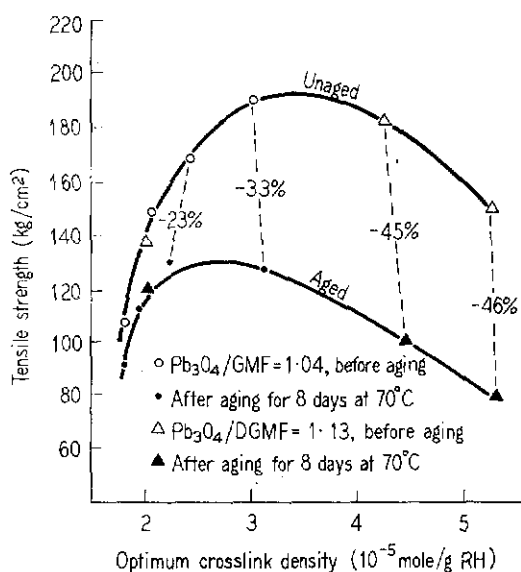


Figure 9. Effect of crosslink density on tensile strength before and after aging.

speculated that this stiffening effect might be due to the cyclisation of the pendent groups during heat treatment. Consequently, modulus was increased and tensile strength was inevitably reduced because of

TABLE 5. AGING OF THE Pb_3O_4 -DGMF-NR VULCANISATES

Sample	Condition	Crosslink density (mole/g RH, 10^{-5})	M_{300} (kg/cm ²)	Tensile strength (kg/cm ²)	Elongation (%)
DGMF (8×10^{-5} mole/g RH) at $Pb_3O_4/DGMF = 1.04$	Unaged	2.02	9.8	138	795
	Oven aged at 70°C (8 days)	2.04	10.8	121	750
	Oven aged at 100°C (8 days)	1.52	10.1	17	370
	Vacuum-aged at 100°C (8 days)	2.07	15.2	110	630
DGMF (15.9×10^{-5} mole/g RH) at $Pb_3O_4/DGMF = 1.04$	Unaged	4.34	22.2	183	590
	Oven aged at 70°C (8 days)	4.46	26.5	101	500
	Oven aged at 100°C (8 days)	3.09	23.4	23.8	305
	Vacuum-aged at 100°C (8 days)	4.41	30.7	101	495

the hindrance of strain-induced crystallisation due to cyclisation. If cyclisation did occur, it would reduce the unsaturation of main chains and consequently it would also enhance thermal stability generally.

MECHANISM FOR QUINOID VULCANISATION OF NATURAL RUBBER

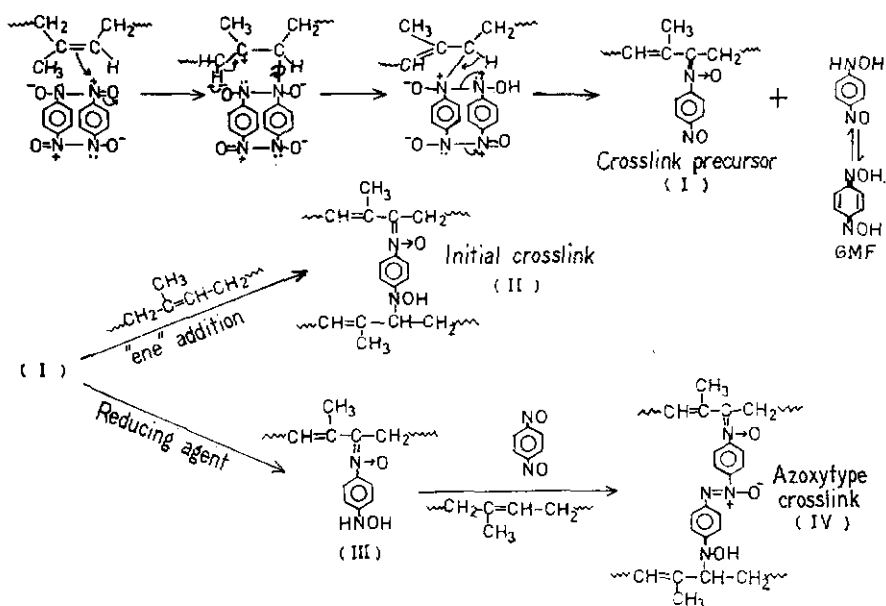
It is known³ that DNB can exist as a dimer in hydrocarbon. When bulk DNB was added to NR, it is believed that this dimeric DNB reacted with the isoprene units. By analogy with Baldwin and his co-workers¹⁵, who studied quinoid vulcanisation on EPDM, we suggest *Reaction Scheme 1* for the crosslinking reactions of NR by DNB.

According to this reaction scheme, a crosslink precursor (I) was formed simultaneously with a p-nitrosophenyl hydroxylamine. The latter rearranged rapidly to give quinone dioxime (GMF) which had been isolated from the extracts of these vulcanisates. As the crosslink precursor (I)

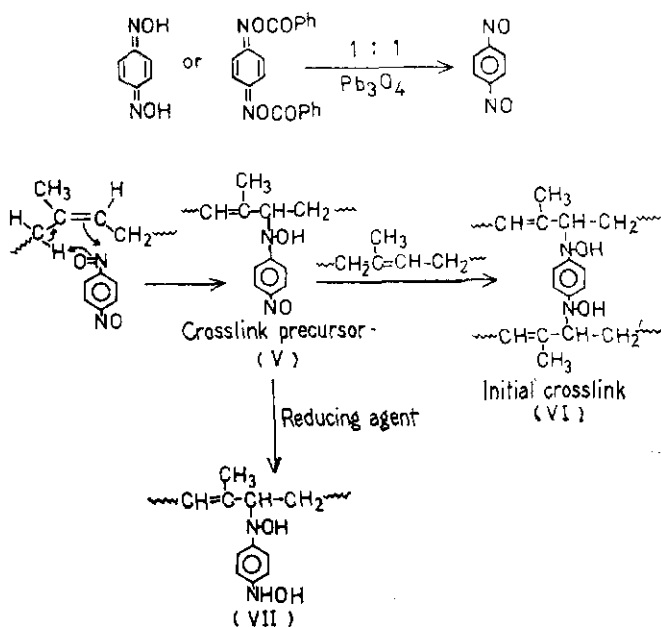
still possessed an active nitroso group, it could either react with another isoprene unit or be reduced to a secondary hydroxylamine. In view of the availability of the abundant reactive sites of isoprene units, crosslinking reaction via 'ene' addition to form initial crosslink (II) might have prevailed, especially in the early state of cure.

Reduction of the nitroso group of the crosslink precursor (I) to a secondary hydroxylamine (-NHOH) was also possible by some kind of reducing agent present in NR. Successive reactions of this secondary hydroxylamine with DNB and rubber molecule led to the formation of crosslink containing an azoxy unit (IV). The hydroxylamine group in the newly formed crosslink (II) or (IV) could be further transformed¹⁶ into either an anil, or an amine or a nitrone type of quinoid crosslink.

In the case of GMF or DGMF oxidised by red lead, the instantaneous concentration of the formed DNB was governed by two



Reaction Scheme 1. Crosslinking reactions of NR by DNB.



Reaction Scheme 2. Crosslinking reactions of NR by oxidised GMF or DGMF.

factors: the rate of DNB formation by oxidation and the rate of DmB disappearance by reaction with isoprene unit. As DNB was very reactive towards the isoprene unit, the newly formed DNB would unlikely accumulate to form a dimer.

The Reaction Scheme 2 shows that the crosslink precursor (V) was produced via 'ene' addition of the rubber molecule by monomeric DNB which was formed through oxidation of GMF or DGMF by red lead. The subsequent 'ene' addition of the nitroso group of (V) resulted in the initial crosslink (VI). As mentioned earlier, this newly formed crosslink could be further transformed to a more stable type of quinoid crosslink. Although the formation of azoxy type crosslink such as in the Reaction Scheme I was also possible, it might be at a minimum or if not, totally inhibited in the presence of oxidant⁵.

The maximum percentage of the combined curing agents in NR and butyl vulcanisates

were very similar for the corresponding DNB, GMF and DGMF, both oxidised by red lead. In contrast to butyl rubber, the isoprene units in NR were in close proximity. This might favour not only the formation of the vicinal or/and intramolecular crosslinks, but also the pendent groups such as (III), (V) and (VII). It is therefore not surprising to find that the quinoid-NR vulcanisates had much higher value of *E* than that of butyl, though the major crosslinking reactions for both are considered to be similar.

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