Bis(Diisopropyl)thiophosphoryl Disulfide in cis-1,4-Polyisoprene Vulcanization Reactions. I.   As a Sulfur Donor

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Synopsis

Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) is used as a sulfur donor vulcanizing system for cis-1,4-polyisoprene.   It is shown that the network structure consists of poly- and disulfidic crosslinks at early stages of cure, simplifying at optimum cure to monosulfidic crosslinks.   It is thought that pendent accelerator groups are bound to the rubber molecule at early stages of cure, but are subsequently replaced by cyclic sulfidic groups.   The good thermal and thermal oxidative aging behavior of the vulcanizate is due to the formation of zinc diisopropyldithiophosphate (ZDP) in situ.

INTRODUCTION

Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS, compound I, where R = isopropyl, $n = 2$)

is a member of the class of bis (dialkyl)thiophosphoryl sulfides, prepared by the oxidation of a dialkylphosphorodithoic acid.   The metal salts of the acid (II) are commonly referred to as metal dithiophosphates, e.g., zinc diisopropyldithiophosphate.

Since their identification in 1925,[1,2] both classes of compounds have found widespread industrial use in such applications as antioxidants,[3-7] insecticides,[8-13] ultraviolet stabilizers,[14] and accelerators. Since the claim by Romieux[15,16] that DIPDIS could be used as an accelerator, interest has been limited to natural rubber applications,[17-24] and it was not until 1969 that patents were issued for the use of DIPDIS and the corresponding tri- and tetrasulfides for use with polyisoprene and ethylene propylene termonomer elastomers.[25]

DIPDIS can also be used as a sulfur donor; and although the level of crosslinking is low, it can be increased by activation with thiourea, dimorpholyl

Synthetic polyisoprene	100
Zinc oxide	5
Stearic acid	1
DIPDIS	6

[a] Cure temperature 160°C.

disulfide, or a thiazole.   The resistance of the vulcanizate to oxidative aging is high but is lost on solvent extraction.

The purpose of the work reported here is to investigate the network structure produced when DIPDIS is used as a sulfur donor and to determine the reason for the oxidative stability of the vulcanizate.

EXPERIMENTAL

Synthesis of Bis(diisopropyl)thiophosphoryl Disulfide

Reaction of isopropanol (453 g) and phosphorous pentasulfide (333 g) at 65°C yielded diisopropylphosphorodithoic acid in situ.   The reaction mixture was cooled to 18°C and aqueous sodium hydroxide (120 g) added at such a rate to keep the temperature below 25°C.   The reaction mixture was cooled to 10°C and sodium hypochlorite added in excess.[26]   The product was recrystallized from ethanol; mp 90–91°C (90–91°C).[27,28]

ANAL. Carbon found, 33.21%, 33.54%, 33.0% (calculated, 33.73%); hydrogen found, 6.65%, 6.56%, 6.61% (calculated, 6.28%).   Infrared spectra, KBr disc, maxima (cm⁻¹) at 2991 s, 2930 m (C—H stretching), isopropyl group; 1454 m, doublet 1380–1373 s (C—H bending), C(CH₃)₂ group; 1350 w (C—H bending), 1183 m, 1145 m, 1105 m, 1020–970 s (P—O—C stretching, mainly O—C), 895 m, 809 s, (P—O—C stretching, mainly P—O), 640 s (P=S stretching), 500 s (P—S stretching), 455 m.

Preparation of Vulcanizates

All raw polymer was extracted with acetone under nitrogen for 48 hr to remove both natural and added antioxidants.   The formulation shown in Table I was prepared and vulcanized at 160°C for a range of cure times.   The vulcanized sheets, normally 4×5×0.1 in., were continuously cold extracted in the dark under nitrogen with an azeotropic boiling mixture of acetone (352 ml), chloroform (291 ml), and methanol (274 ml) for 96 hr.[29]   They were then deswollen in vacuo to constant weight and stored at −20°C.

Viscosity measurements were made on centrifuged benzene solutions of the rubber mixes and values of the limiting viscosity number of the rubber hydrocarbon component were obtained.   The initial number-average molecular weight ($\bar{M}_n$) of the rubber hydrocarbon was derived using the equation[30,31]

$$[\eta]_{\text{benzene}} = 2.29 \times 10^{-7} \, \bar{M}_n^{1.33}. \tag{1}$$

Chemical Analysis of Vulcanizates

Analyses were made on the central portion of the vulcanized sheets.   Determinations of the total sulfur and of inorganic sulfide sulfur were made by modified methods of BS903 Part B6 and Part B10.   The total sulfur was determined by combustion[32] and the sulfide sulfur by treatment of the vulcanizate with an acetic/hydrochloric acid mixture.[32,33]

The determination of crosslink type utilized the reactions of triphenylphosphine,[34] propane-2-thiol, and n-hexane thiol.[32,35]

Chemical Analysis of Solvent Extracts

The dissolved products in the azeotropic solvent mixture were analyzed after elution of the vulcanizate to identify the products of the vulcanization reaction. The boiling mixture was evaporated to dryness in vacuo in the dark and the resulting solid mixtures stored at $-20°C$. The reaction products were then separated by thin-layer chromatography (TLC) using purified, binder-free silica gel as absorbent, carbon tetrachloride as spotting solvent, and benzene as developing solvent. Before application, the TLC plates were activated at $120°C \pm 0.5°C$ for 30 min and stored in a desiccator. After development the plates were air dried and the bands located by ultraviolet irradiation and by spraying with a 0.2% ethanolic solution of 2,6-dibromo-p-benzo-4-chlorimine (Gibbs reagent) followed by gentle hot-air heating.

For quantitative TLC, a micrometer syringe (Aglar) was used to measure the quantity of solution applied to the absorbent. The plate was developed in the normal manner, and the bands were located and removed from the plate. From an equivalent blank area of the plate, and area of absorbent was removed having the same weight as the band. Both samples were eluted using absolute ethanol (0.5 ml), agitated overnight, filtered, and centrifuged. The solutions were made up to 5 ml and, using the blank sample in the reference beam, the ultraviolet absorption spectrum was plotted. Using preconstructed graphs of pure DIPDIS and ZDP concentrations as a function of ultraviolet absorption maxima at 208 mμ and 203 mμ, respectively, it was possible to establish the concentration of either material in the unknown mixtures.

The mass spectra of the various unknown bands in the thin-layer chromatogram were determined using a method similar to the ultraviolet absorption method. After elution of the sample bands, the sample was evaporated in vacuo in the dark and the dried extract analyzed using a high-resolution double-focussing mass spectrometer (AEI MS9) with a probe temperature of 220°C. The fragmentation spectra were analyzed using standard procedures.

Physical Characterization of the Vulcanizates and Determination of the Degree of Chemical Crosslinking

Dry Extension. Stress–strain measurements were made at 22°C on extracted vulcanized sheets using an instrument designed by Greensmith and O'Dwyer.[36] The Mooney-Rivlin equation,[37,38]

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

where F is the applied force required to maintain a sample of unstrained cross-sectional area A_0 at an extension λ, was then used to obtain values of C_1 and C_2 from plots of $F(2A_0[\lambda - \lambda^{-2}])^{-1}$ versus λ^{-1} in the regions of low and moderate extension.

Swollen Compression. The compression stress–strain characteristics of vulcanizates swollen in benzene were determined by the microcompression technique developed by Smith[39] using a Wallace reticulometer. Samples of edge dimension 0.4 cm were cut with a scapel from adjacent areas of the sheet, 0.2 cm thick. The samples were then weighed, the linear dimensions measured with a vernier microscope, and then swollen in benzene. They were then weighed,

tested by the Smith[39] method, and deswollen in vacuo. The resultant values of stress F and strain Δh were determined; C_1 was calculated from the relationship given by eq. (3)[40]:

$$C_1 = \frac{F \nu_r^{1/3}}{2A_0} \left[\frac{3h_s \Delta h^2 - 3h_s^2 \Delta h - \Delta h^3}{h_s^3 - 2h_s^2 \Delta h + h_s \Delta h^2} \right]^{-1} \qquad (3)$$

where h_s is the unstrained swollen height.

Chemical Degree of Crosslinking. It was necessary to standardize the determination of C_1,[41] as the values obtained will vary with the conditions of measurement and sample pretreatment. The measured C_1 was corrected to 25°C by the equation

$$C_{1,\mathrm{ERV}} = C_1(\text{measured at } t°C) \ 298/(273 + t) \qquad (4)$$

where $C_{1,\mathrm{ERV}}$ is the C_1 term for the extracted rubber vulcanizate at 25°C. $C_{1,\mathrm{ERV}}$ was corrected for the stiffening effect of nonreinforcing fillers[42] and is described as $C_{1,\mathrm{ERM}}$, the C_1 term for the extracted rubber matrix:

$$C_{1,\mathrm{ERM}} = C_{1,\mathrm{ERV}} (1 + 2.5 \, V_f + 14.1 \, V_f^2)^{-1} \qquad (5)$$

where V_f is the total volume fraction of fillers in the rubber vulcanizate. The chemical degrees of crosslinking were calculated using the relationship determined by Mullins[43,44] and Moore and Watson[45]:

$$C_{1,\mathrm{ERM}} = (\rho RT[2M_{c,\mathrm{chem}}]^{-1} + 0.78 \times 10^6)(1 - 2.3M_{c,\mathrm{chem}}\bar{M}_n^{-1}) \qquad (6)$$

where ρ is the density of the rubber hydrocarbon, M_n is the number-average molecular weight of the raw polymer, R is the gas constant, T is the absolute temperature, and $M_{c,\mathrm{chem}}$ is the number-average molecular weight of the extracted rubber matrix chain segments between adjacent chemical cross links.

Efficiency of Vulcanization

Using the derived values of $M_{c,\mathrm{chem}}$, total sulphur S_T, and inorganic sulfide sulphur S^{2-}, the efficiency of vulcanization parameter E was determined by

$$E = \frac{(S_T - S^{2-})}{3200[2M_{c,\mathrm{chem}}]^{-1}}. \qquad (7)$$

Similarly, the F value, relating to the concentration of zinc sulfide produced per chemical crosslinked generated, was determined by

$$F = \frac{[S^{2-}]}{[2M_{c,\mathrm{chem}}]^{-1}}. \qquad (8)$$

RESULTS AND DISCUSSION

Bis(diisopropyl)thiophosphoryl disulfide, DIPDIS, was compounded with both natural rubber and synthetic cis-1,4-polyisoprene at differing concentrations. At 140°C, DIPDIS was ineffective as a sulfur donor; and at 160°C although a cure was obtained, the cure time was prolonged. Monsanto rheographs of the sulfur donor system, Table I, exhibited secondary vulcanization, i.e., a first modulus plateau followed by further crosslinking to a second modulus plateau (Fig. 1). The time required to reach the second modulus plateau was dependent on DIPDIS, zinc oxide, and stearic acid concentrations (Figs. 1 and 2). The
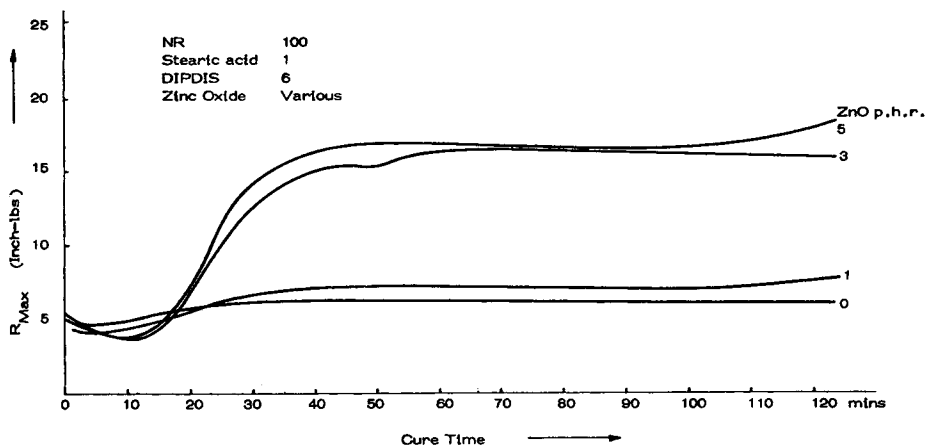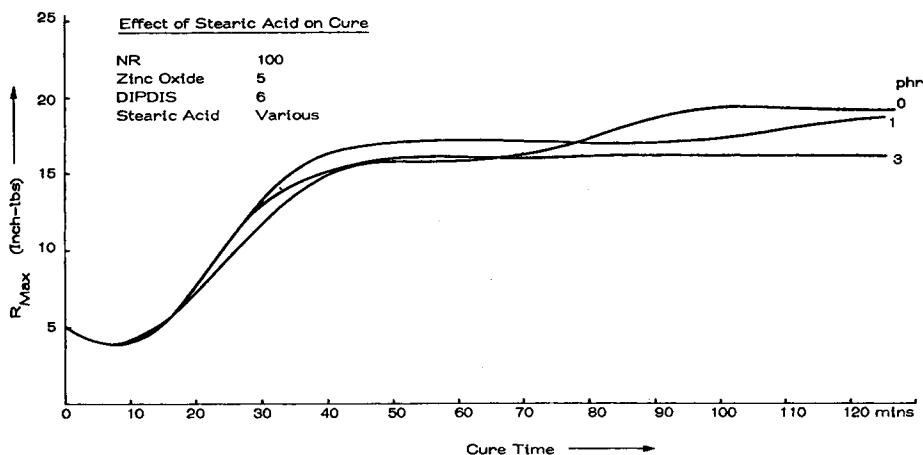
Fig. 1. Effect of zinc oxide on cure.

Fig. 2. Effect of stearic acid on cure.

overall vulcanization reaction was affected by zinc oxide concentration but independant of stearic acid concentration.

Network Analysis

The results are given in Table II, III, and IV. During the early stages of cure, 30 min at 160°C, the degree of crosslinking at which measurements were made was low. Measurement of elastic parameters at such low degrees of crosslinking is subject to high experimental error, especially swollen compression measurements where the sample is near collapse. For low levels of cure, therefore, $C_{1,ERM}$ values obtained from extension stress–strain measurements were used. At higher degrees of crosslinking, the results from swollen compression and dry extension methods were similar (Fig. 3).

The treatment of the vulcanizates with chemical probes was assumed to proceed in a similar manner as conventional vulcanizates.[46,47] The efficiencies of vulcanization E and E' were calculated using the chemical degree of crosslinking derived from dry extension measurements and the sulfur combined in the network.

TABLE II

Characterization of Vulcanizate Networks Derived from
DIPDIS/Polyisoprene Sulfur Donor System

Cure time, min at 160°C	$[S_c]$ $(\times 10^4)$[a]	$[S^{2-}]$ $(\times 10^4)$[b]	$(2M^{ERM}_{c,chem})^{-1}$ $(\times 10^4)$[c] (extension)	E[d]	F[e]
30	1.07	0.086	0.1389	7.7	0.62
40	0.69	0.316	0.1837	3.7	1.72
50	0.937	0.403	0.1951	4.8	2.06
60	0.641	0.403	0.2136	3.0	1.89
65	0.453	0.388	0.1701	2.7	2.28
85	0.755	0.566	0.1677	4.5	3.37
120	0.791	0.850	0.1628	4.9	5.2
30[f]	0.777	0.189	0.1642	4.7	1.15
40[f]	1.123	0.24	0.2000	5.6	1.20

[a] Gram-atom of sulfur per gram of rubber hydrocarbon in network.
[b] Gram-ion of sulfide per gram of rubber hydrocarbon in network.
[c] Gram-mole chemical crosslinks per gram of rubber hydrocarbon in network.
[d] Number of sulfur atoms combined in the network per chemical crosslink present.
[e] Number of sulfide ions formed in the network per chemical crosslink present.
[f] Revulcanized for 40 min after extraction.

TABLE III

Characterization of Vulcanized Networks Derived from DIPDIS/Polyisoprene Sulfur
Donor Systems After Treatment with Triphenyl Phosphine

Cure time, min at 160°C	$[S_c]$ $(\times 10^4)$[a]	$(2M^{ERM}_{c,chem})^{-1}$ $(\times 10^4)$[b]	$E' - 1$	$E - (E' - 1)$
30	0.743	0.1389	4.4	3.3
40	0.309	0.1837	0.7	3.0
50	0.679	0.1951	2.5	2.3
65	0.335	0.1701	1.0	1.7
85	0.585	0.1677	2.5	2.0
120	0.651	0.1628	3.0	1.9
30[c]	0.368	0.1642	1.2	3.5
60[c]	0.223	0.20	0	5.5

[a] Gram-atom of sulfur per gram of rubber hydrocarbon in network.
[b] Gram-mole of chemical crosslinks per gram of rubber hydrocarbon in network.
[c] Revulcanized for 40 min at 160°C after extraction.

Analysis of the vulcanizate revealed that a simple network is generated. By reference to the change in E values, as the vulcanization proceeds it becomes apparent that a complex network is initially formed (30 min at 160°C) but simplifies as the reaction proceeds. The presence of a high concentration of pendent accelerator groups bound to the rubber molecule is indicated by the increase in crosslink density that occurs when the extracted 30-min-cured vulcanizate is recured for 40 min at 160°C. By analogy with other vulcanization systems,[48,49] it is probable that the pendent groups will be of the type $R(S)_n$-$SP(S)(OisoPr)_2$, where R is cis-1,4-polyisoprene. The F value of unity indicates efficient use of sulfur for crosslinking purposes. This is typical of other sulfur-donor vulcanizates where an active sulfurating species of high crosslinking efficiency is initially formed.

TABLE IV
Crosslink Type Determination of Vulcanizates Derived from
DIPDIS/Polyisoprene Sulfur Donor System

Cure time, min at 160°C	Degree of crosslinking, $(2M^{\mathrm{ERM}}_{c,\mathrm{chem}})^{-1}(\times 10^4)$[a]			Crosslink type, %		
	Untreated	Propan-2-thiol	n-Hexan-thiol	$-S_x-$	$-S_2-$	$-S_1-$
30	0.1349	0.1339	0.1312	0.7	2.0	97.3
40	0.1901	0.1779	0.1457	6.4	16.9	76.7
50	0.2029	0.1872	0.1429	7.7	21.8	70.5
65	0.1572	0.1694	0.1208	0.0	23.2	76.8
85	0.1583	0.1501	0.1303	5.1	12.5	82.4
120	0.1511	0.1563	0.1244	0.1	17.7	82.3
30[b]	0.1710	0.1664	0.1393	2.7	15.9	81.4

[a] Gram-mole chemical crosslinks per gram rubber hydrocarbon in the network determined from swollen compression measurements.

[b] Revulcanized for 40 min at 160°C after extraction.
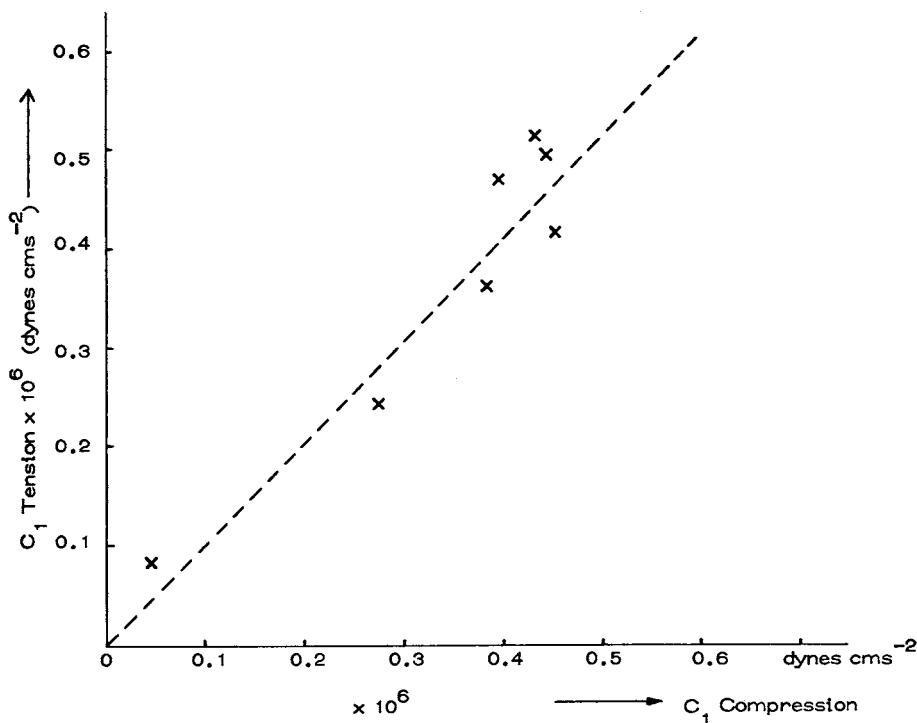
Fig. 3. Comparison of the elastic parameter C_1 from dry extension and swollen compression measurements.

Crosslink type determination is in general agreement with the average cross-link length determined from vulcanization efficiency data, indicating the revulcanized network is mainly mono- and disulfidic.

As the cure proceeds, the overall network complexity decreases until, at optimum cure (60–65 min at 160°C), the E value is 2.7–3.0. The efficiency of the sulfur used for crosslinking, the F value, decreases as cure proceeds until, at the

TABLE V
Concentration of Zinc Diisopropylthiophosphate (ZDP)
as a Function of Vulcanization Time

Cure time at 160°C, min	Wt. loss on extraction of raw vulcanizate, wt-%	Concn. of ZDP found in the residue, wt-%
30	4.9	71
40	5.8	70
50	4.7	83
60	5.8	100
65	5.4	95
85	4.6	88
120	5.5	78

optimum, two moles of zinc sulfide are formed for each chemical crosslink intro-
duced. The increased yield of zinc sulfide may result from the thermal destruc-
tion of the small concentration of initially formed polysulfidic crosslinks.

Crosslink length determinations indicate low concentrations of polysulfidic
crosslinks (7%) with di- (22%) and monosulfides (72%) that reduce at the opti-
mum cure time to di- (23%) and monosulfides (77%). This is supported by the
$E - (E' - 1)$ values that fall from 3.35 at the initial stage of cure to 1.7 at the
optimum cure. The concentration of sulfurated main-chain modifications de-
creases with an increase in cure time. There is probably an increase in the cyclic
sulfide concentration at the expense of the pendent accelerator groups. This is
indicated by the reheating of the extracted optimum cured vulcanizate (60 min)
for a further 40 min at 160°C. No further crosslinking occurred and the degree
of chemical crosslinking fell slightly. Network complexity increased slightly,
E value increased from 3.0 to 5.6, with a decrease in the sulfurated modification
concentration. The crosslink length increased from mono- and disulfidic to poly-
sulfidic (Tables II and III).

Although the degree of crosslinking shows no increase at long cure times, (70
min), dynamic modulus measurements indicate that a modulus rise occurs, i.e., a
secondary vulcanization. The initial "secondary crosslinks" introduced are
expected to be polysulfidic. These would undergo exchange and shortening
reactions, and the extruded sulfur would react to produce an increase in the
main-chain cyclic sulfide groups. This secondary reaction when superimposed
on a simple network would explain the rise in E and F values for the vulcanization
times longer than 70 min (Table II).

Vulcanization Products

Using the techniques described earlier, the major product of the vulcanization
reaction was found to be zinc diisopropyldithiophosphate, ZDP (Table V).
This was confirmed by mass spectrometry. No DIPDIS was found at early
stages of cure, 30 min, but a high proportion of ZDP was found. With increas-
ing vulcanization time, the ZDP concentration increased until at the optimum
degree of crosslinking, 60 min, 100% of the extracted material was ZDP. A
further increase in vulcanization time decreased the ZDP concentration, and at
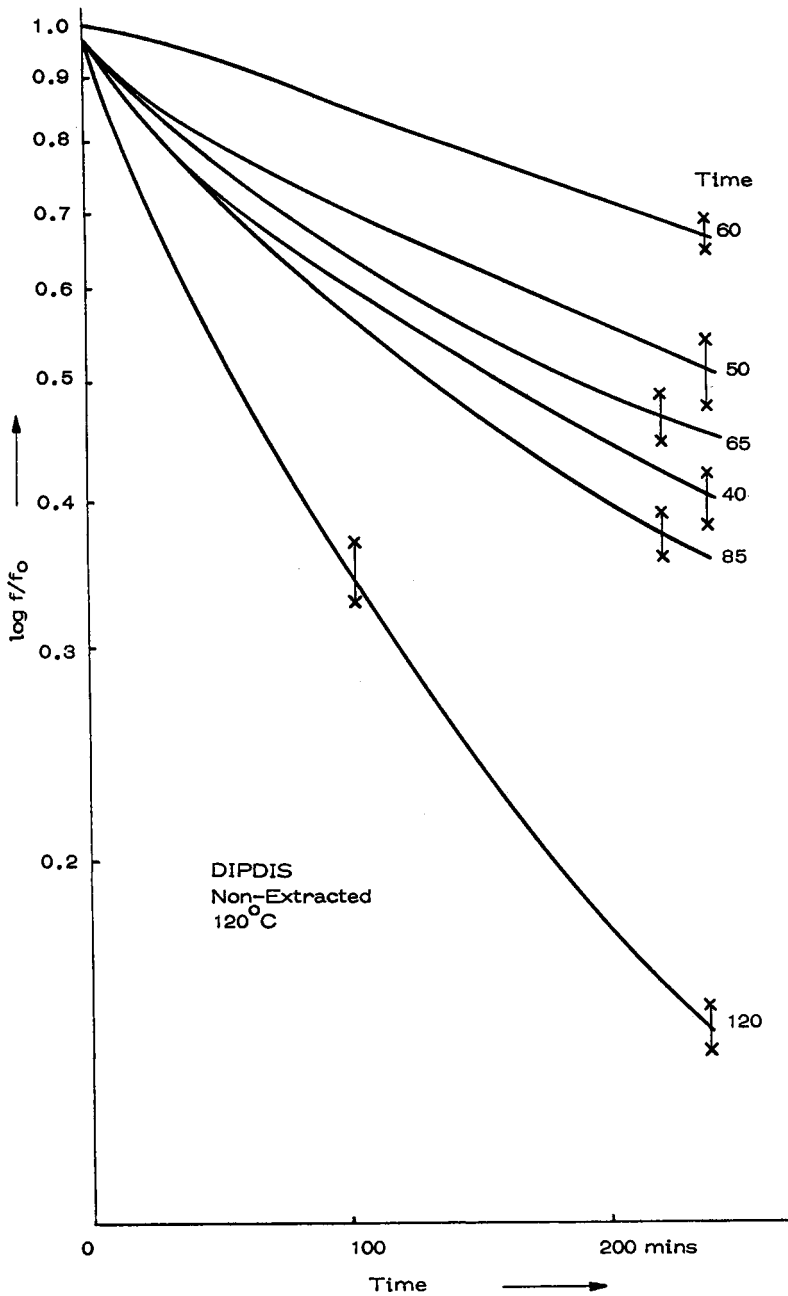85 min a small concentration of DIPDIS was detected.

Fig. 4. Thermal oxidative continuous stress relaxation.

Thermal Oxidative Aging Behavior

The thermal oxidative aging behavior of the DIPDIS sulfur donor vulcanizate before extraction was markedly dependent on the cure time (Fig. 4). The aging properties improved with cure time until after optimum cure when the aging properties deteriorated rapidly. At optimum modulus, the aging behavior was
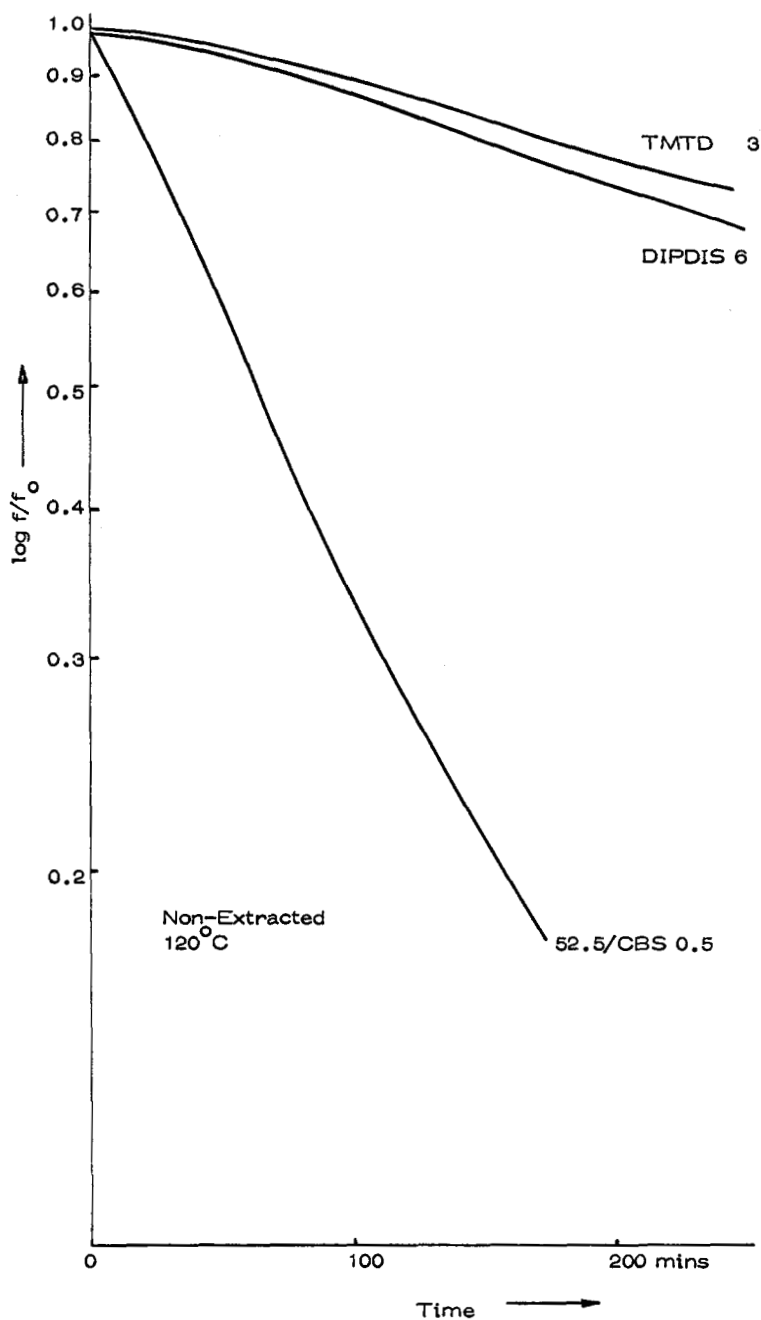
Fig. 5. Thermal oxidative continuous stress relaxation.

comparable to a TMTD sulfur donor cure and superior to a S/CBS vulcanizate (Fig. 5).

Cold extraction of the vulcanizate with the methanol–acetone–chloroform azeotropic mixture reduced the resistance to thermal oxidative aging (Fig. 6), the relaxation rate increasing with increasing cure time. Unlike the autocatalytic nature of extracted TMTD vulcanizates, extracted DIPDIS vulcanizates
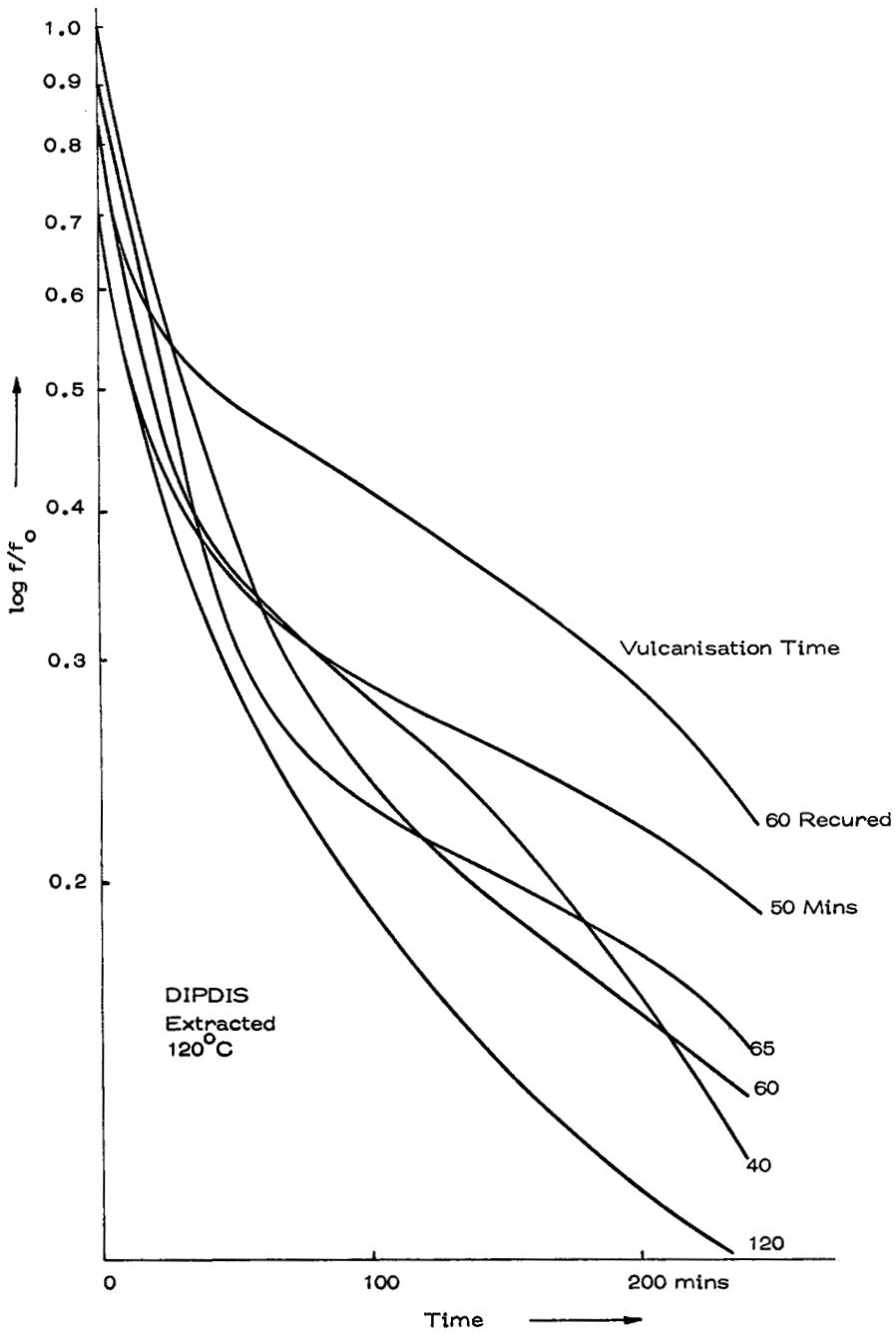
Fig. 6. Thermal oxidative continuous stress relaxation.

exhibited autoinhibitive behavior followed at later stages of aging by an auto-catalytic relaxation curve. This variance between the extracted TMTD and DIPDIS vulcanizates may be the result of DIPDIS accelerator residues being combined in the network so as to be unextractable. The autoinhibition shown by the relaxation curves is in agreement with the idea of sulfoxide formation
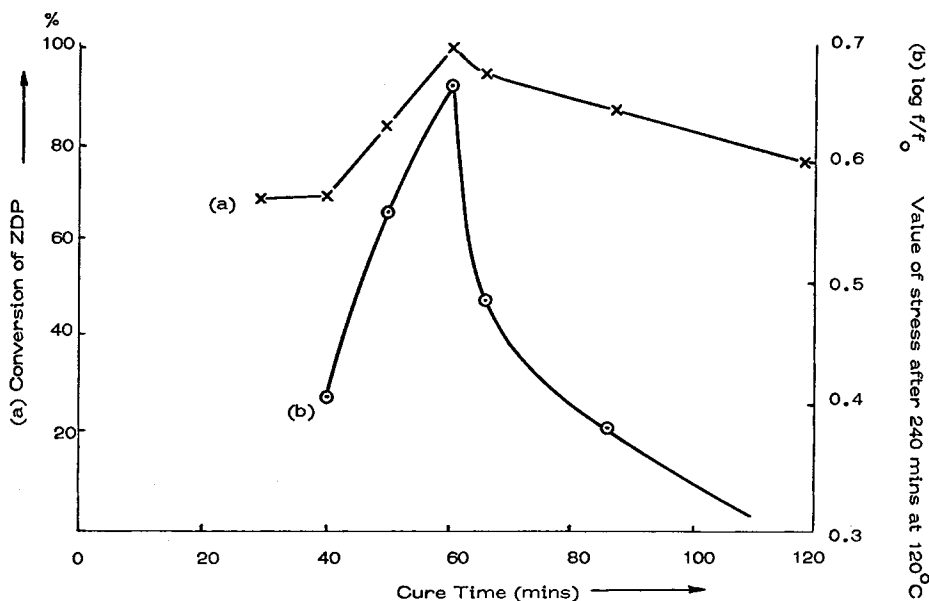
Fig. 7. Relationship between ZDP formation and thermal oxidative aging.

from a crosslink during the initial oxidation. The generated sulfoxide may then generate an active antioxidant species thought to be either SO_2[50] or a thiosulfinate.[51] After the active species has been consumed, the oxidation would become autocatalytic.

The difference between the unextracted and extracted aging behavior is explained by the formation of the antidegradant ZDP in situ. If the relaxation log f/f_0 values at 240 min and the concentrations of ZDP are plotted as a function of cure time, the curves follow similar trends (Fig. 7). Hence, the ZDP concentration is the dominant factor of the unextracted thermal-oxidative aging behavior. The 60-min vulcanizate with 100% concentration of ZDP exhibited an initial pro-oxidant effect followed by an autoretarding effect (Fig. 4). This is in agreement with other workers[52,53] who have shown that dithiophosphates act as typical peroxide decomposers which would be initially ineffective and then autoretard subsequently producing an antioxidant.

CONCLUSIONS

DIPDIS has been evaluated as a sulfur donor for cis-1,4-ployisoprene and found to be inactive at 140°C. At 160°C, a predominantly monosulfidic network is generated, the major product of the vulcanization reaction being ZDP, analogous to the reaction of TMTD as a sulfur donor. The thermal-oxidative aging behavior of the DIPDIS vulcanizate is superior to a conventional S/CBS cure, but inferior to a TMTD sulfur donor vulcanizate. The aging behavior is shown to be due to the formation of ZDP in situ and is consistent with it being a hydroperoxide decomposer. Evidence has been gained for an active antioxidant produced from a sulfur crosslink in the absence of added or generated antioxidant.

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