Mechanistic study of the antioxidant activity of decarboxylated cashew-nut-shell-liquid in natural rubber vulcanizates

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The antioxidant activity of decarboxylated cashew-nut-shell-liquid (CNSL), which consists of a monophenol, anacardol and a diphenol, cardol, each with a bulky unsaturated alkyl group at the *meta* position, in sulphur-cured natural rubber vulcanizates has been found to be mainly due to the formation of phenolic sulphides *in situ* during vulcanization. The sulphides are formed through a substitution reaction probably at the *para* position to the phenolic group. It has also been observed that cardol, the diphenolic component, contributes more towards the antioxidant activity than the monophenol, anacardol. This has been explained as being due to the high probability of formation of the sulphides with cardol.

INTRODUCTION

In an earlier paper[1] we reported that decarboxylated cashew-nut-shell-liquid (CNSL) can protect black-loaded sulphur-cured natural rubber (NR) vulcanizates against autooxidation, when used in 2 parts per hundred (phr) rubber of raw, decarboxylated liquid and 1.5 phr of refined liquid, as effectively as 1 phr of common amine-type rubber antioxidants. Work carried out subsequently has shown that decarboxylated CNSL exhibits a high degree of antioxidant activity in NR pure gum vulcanizates and also in the presence of non-black fillers[2]. The high antioxidant activity of decarboxylated CNSL, which consists of a mixture of two phenols, anacardol (also referred to as cardanol) and cardol, each with a bulky unsaturated alkyl group at the meta position, has been qualitatively explained as being due to the formation of adducts with sulphur and a network-bound antioxidant, via the olefinic bonds in the alkyl side chain, during vulcanization with sulphur[1]. This paper reports investigations carried out to verify these postulates and to formulate a mechanism for the antioxidant activity of decarboxylated CNSL. Comparison of the antioxidant activity of decarboxylated CNSL with that of (a) decarboxylated and hydrogenated CNSL (CNSL with the side chain double bonds hydrogenated) and (b) an adduct of CNSL with sulphur monochloride, in sulphur-cured vulcanizates and a study of the antioxidant activity of decarboxylated CNSL in peroxide-cured NR vulcanizates and in a curing system without elemental sulphur, form the basis of the present investigation. Antioxidant activities of cardol and anacardol were also investigated to verify a suggestion made in our earlier study[1], that cardol contributes more towards the antioxidant activity of CNSL than anacardol.

MATERIALS AND METHODS

The following materials and methods, which were not described in the earlier study[1], were used in this study. Retention of tensile strength and elongation at break on ageing at 70° ± 1°C in an air circulating oven was used as a measure of the antioxidant activity of decarboxylated CNSL, its constituents and its derivatives.

Decarboxylated, hydrogenated CNSL (CNSL with side chain double bonds hydrogenated) and its adduct with sulphur monochloride

Decarboxylated, hydrogenated CNSL and its adduct with sulphur monochloride were prepared from distilled CNSL using procedures described by Ghatge and Gokhale[3]. The former is a reddish-brown solid melting at 50°C and the latter, the tetrahydroanacardol sulphurmonochloride adduct (THA–S_2Cl_2 adduct) can be assumed to be a phenolic sulphide[3]. Raw THA–S_2Cl_2 adduct, a brown resinous material, was used in the experiments.

Thin-layer chromatographic (t.l.c.) studies

T.l.c. studies were used extensively to separate and identify qualitatively products obtained during acetone extraction of the vulcanizates. 300 μm thick silica gel (Kiesel Gel Type 60 – Merck, Darmstadt) plates were used in these studies. A mixture of benzene–ethyl acetate (90:10 v/v) was used as the solvent and diazotized sulphanilic acid in 2% sodium bicarbonate solution was the spray reagent. Known weights of the dried acetone extracts (about 5 mg) along with samples of decarboxylated CNSL and hydrogenated CNSL, in quantities equivalent to the maximum

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amounts of these that could be present in the weights of the extracts taken for analysis assuming total extraction, were spotted on the plates. The colour intensity and the spot areas of cardol and anacardol on the t.l.c. plates after developing with diazotized sulphanilic acid were compared with those of the control samples.

Preparative t.l.c. techniques were used for separation and isolation of the products in the acetone extracts. A dilute solution of the extract to be analysed (about 100 mg) in acetone was spotted on a 500 μm silica gel plate (20 x 20 cm), covering the entire baseline. The plates were allowed to run repeatedly in the solvent mixture of benzene–ethyl acetate (90:10 v/v) till the maximum separation was obtained (3 times). The edges of the plates were then sprayed with the spray reagent to identify the areas occupied by the different components after separation on the plate, which appear as bands. These bands were then scraped off, eluted with methanol, the methanolic solution was isolated by centrifuging and the compounds were isolated by evaporating methanol.

Isolation of cardol and anacardol from decarboxylated CNSL

Using an alumina column and solvents varying from petroleum ether to benzene–ethyl acetate mixtures as eluents, it was possible to isolate anacardol and cardol from decarboxylated CNSL. On t.l.c. analysis, as described by Murthy *et al.*[4], anacardol was found to be pure but cardol was found to be contaminated with anacardic acid. Anacardic acid, which is the major constituent in raw CNSL, has been shown to have poor antioxidant activity due to the presence of a carboxylic group *ortho* to the phenolic group[1].

Infra-red studies

Infra-red (i.r.) studies were carried out with thin films (0.2 mm) of the vulcanizates before and after acetone extraction to ascertain any chemical binding of decarboxylated CNSL to the network, using a Perkin–Elmer i.r. spectrophotometer – Model 577.

Formulation of the base mixes

The formulations of the base mixes used in the study are given in *Tables 1a, 1b, 1c* and *1d.*

The MBTS/S system (A mixes) enables us to compare our results with the results published by Ghatge and Gokhale on the antioxidant activity of THA–S_2Cl_2 adduct[3]. CBS/S system (B mixes) is a standard tyre retreading formulation. The peroxide-cured vulcanizates and the TMTD-cured vulcanizates are to study the role of sulphur in promoting the antioxidant activity of decarboxylated CNSL.

RESULTS AND DISCUSSION

Ageing properties of the vulcanizates

Sulphur-cured vulcanizates. The retention of the tensile strength and elongation at break of the vulcanizates on ageing at 70° ± 1°C for 7 days and 14 days, respectively, are given in *Table 2.* Many useful conclusions can be arrived at from the results included in this Table.

Firstly, decarboxylated CNSL, its constituents and its adduct with sulphur monochloride at the 1.5 phr level, protect the vulcanizates against heat ageing, the effect being comparable with 1 phr of phenyl β-naphthylamine, as we have reported earlier.

Secondly, comparison of the ageing properties of B_4, which contains 1.5 phr of cardol as the antioxidant, with those of B_5 where 1.5 phr of anacardol is the antioxidant, confirms our earlier view that cardol contributes more towards the antioxidant activity of CNSL, based on the observation that decarboxylated, raw CNSL is a better antioxidant than distilled CNSL[1]. Raw, decarboxylated CNSL contains about 14% (w/w) of cardol and distilled CNSL contains only about 4% (w/w)[1]. The superior antioxidant activity of cardol will be discussed in detail in a later paragraph. At the same time one should expect B_4 to have better ageing properties than B_1, which contains 2 phr of raw, decarboxylated CNSL. But from the results in *Table 2*, B_1 shows slightly better ageing properties than B_4. This may be explained as being due to the presence of anacardic acid in cardol as an impurity. Since anacardic acid is a poor antioxidant[1], it can reduce the antioxidant activity of cardol. Thirdly, comparing the ageing properties of B_2 with B_1 and those of A_2 with A_1 it can be concluded that the antioxidant activity of hydrogenated decarboxylated CNSL (CNSL with the side chain double bonds hydrogenated) is of the same order as that of the raw, decarboxylated CNSL. This finding places in doubt the possibility of CNSL phenols being chemically bound to the network via the olefinic bonds in the side chain during vulcanization with sulphur, which has been thought of as a plausible explanation for the high antioxidant activity of decarboxylated CNSL[1]. Yamamoto and coworkers[5] have compared the antioxidant activities of dipropyl-*p*-cresol (DPC) with that of allyl-propyl-*p*-cresol (APC) in black-loaded natural rubber vulcanizates. They have reported that although DPC shows better retention of tensile properties on ageing for short periods of time, on prolonged ageing APC shows better retention values. This has been explained by them as being due to lower volatility of APC by being grafted to the network. Similarly if the phenols in decarboxylated CNSL are to be bound to the network then they should have lower volatility in the vulcanizates than hydrogenated, decarboxylated CNSL and therefore should show superior antioxidant activity than hydrogenated CNSL on prolonged ageing

Finally, comparing the ageing properties of A_1 with A_3 and also B_1 with B_3. THA–S_2Cl_2 adduct when used at 1.5 phr level, shows similar antioxidant activity as 2 phr of raw, decarboxylated CNSL on ageing for 7 days at 70° ± 1°C. The antioxidant activity of THA–S_2Cl_2 adduct drops considerably when only 1 phr is used, as indicated by the ageing properties of B_6. In our earlier paper[1] we predicted similarities between the antioxidant activities of 2 phr raw, decarboxylated CNSL and 1.5 phr of the THA–S_2Cl_2 adduct on the basis of comparing our results with results published by Ghatge and Gokhale[3]. Their values for the antioxidant activity of THA–S_2Cl_2 adduct, using 1 phr, in Vulcafor MBTS/S-cured black-loaded natural rubber vulcanizates are comparable with our results for a similar system having 1.5 phr of raw, decarboxylated CNSL which really contains only about 1 phr of the phenols (only 75% w/w). It is also evident from the results in *Table 2* that after 14 days ageing at 70° ± 1°C the vulcanizates with 1.5 phr THA–S_2Cl_2 adduct show higher retention of tensile properties. The lower volatility of the THA–S_2Cl_2 adduct associated with its dimeric nature should explain this behaviour.

Peroxide cured vulcanizates. Table 3 contains the ageing. properties of the peroxide-cured vulcanizates expressed in terms of retention of tensile strength and elongation at break on ageing at 70° ± 1°C. All the vulcanizates show similar deterioration in tensile properties after 7 days ageing at

Table 1

(a) Composition of the sulphur-cured base mixes (A mixes) Cure time 30 minutes at 140°C. Note: 2 phr of decarboxylated raw CNSL is really 1.5 phr of anacardol and cardol[1]

	A_0	A_1	A_2	A_3	A_4
Natural rubber	100	100	100	100	100
Zinc oxide	6	6	6	6	6
Stearic acid	4	4	4	4	4
Sulphur	3.5	3.5	3.5	3.5	3.5
Dibenzthiazyl disulphide (MBTS)	0.75	0.75	0.75	0.75	0.75
Carbon black (HAF 40)	45	45	45	45	45
Decarboxylated raw CNSL	–	2	–	–	–
Hydrogenated CNSL	–	–	1.5	–	–
THA–S_2Cl_2	–	–	–	1.5	–
Phenyl-β-naphthylamine	–	–	–	–	1

(b) Composition of the sulphur cured base mixes (B mixes). Cure time 30 minutes at 140°C. Note: 2 phr of decarboxylated raw CNSL is really 1.5 phr of anacardol and cardol[1]

	B_0	B_1	B_2	B_3	B_4	B_5	B_6	B_7
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Cyclohexyl benzthiazyl (CBS) sulphenamide	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Processing oil (Dutrex R)	5	5	5	5	5	5	5	5
Carbon black (HAF 40)	45	45	45	45	45	45	45	45
Decarboxylated raw CNSL	–	2	–	–	–	–	–	–
Hydrogenated CNSL	–	–	1.5	–	–	–	–	–
THA–S_2Cl_2	–	–	–	1.5	–	–	1	–
Cardol	–	–	–	–	1.5	–	–	–
Anacardol	–	–	–	–	–	1.5	–	–
Phenyl-β-naphthylamine	–	–	–	–	–	–	–	1

(c) Composition of the peroxide-cured base mixes. Cure time 60 minutes at 150°C

	P_1	P_2	P_3	P_4	P_5
Natural rubber	100	100	100	100	100
Dicumyl peroxide	2	2	2	2	2
Pine tar	4.5	4.5	4.5	4.5	4.5
Carbon black (HAF 40)	50	50	50	50	50
Decarboxylated raw CNSL	2	–	–	–	–
Hydrogenated CNSL	–	1.5	–	–	–
Phenyl-β-naphthylamine	–	–	1	–	–
Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	–	–	–	1	–

(d) Composition of the TMTD-cured base mixes. Cure time 50 minutes at 150°C

	T_1	T_2	T_3
Natural rubber	100	100	100
Tetramethyl thiuram disulphide (TMTD)	3	3	3
Zinc oxide	5	5	5
Stearic acid	2	2	2
Phenyl-β-naphthylamine	1	–	–
Decarboxylated raw CNSL	–	2	–

70° ± 1°C. Peroxide-cured-vulcanizates are well known for their heat resistant characteristics[6]. But after 14 days the vulcanizates containing phenyl-β-naphthylamine (P_3) and polymerized 2,2,4-trimethyl-1-2 dihydroquinoline (P_4) show only a slight drop in the tensile properties while those containing raw, decarboxylated CNSL (P_1), hydrogenated decarboxylated CNSL (P_2) and no antioxidant (P_5) show considerable drops of a similar order of magnitude. From these results, it can be concluded that, while the conventional amine type of antioxidants protect the peroxide-cured NR vulcanizates against autooxidation effectively, the phenols in decarboxylated CNSL are poor antioxidants in such systems. In sulphur-cured NR vulcanizates the CNSL phenols are as effective as the amines in their antioxidant activity. Therefore, the important role played by sulphur in promoting the antioxidant activity of the decarboxylated CNSL phenols is clearly evident from the results in *Table 3*. This will be discussed in detail below along with the results.

Acetone extraction studies

The results of the acetone extraction studies have provided many useful data to explain the mechanism of antioxidant activity of decarboxylated CNSL.

Sulphur-cured vulcanizates. NR vulcanizates from the B mixes but without carbon black and processing oil and containing decarboxylated CNSL, hydrogenated decarboxylated CNSL and phenyl-β-naphthylamine were acetone extracted. The tensile properties of the vulcanizates after extraction and ageing for 7 days at 70° ± 1°C, the amount of matter extractable with acetone and the amount of sulphur in the extract as a percentage of the total elemental sulphur originally present in the vulcanizates, were determined. These results are included in *Table 4* along with the ageing properties of the unextracted vulcanizates. The period of acetone extraction was 24 h.

Results included in *Table 4* indicate that vulcanizates with raw, decarboxylated CNSL retain 61% of their original tensile strength and 81% of their elongation at break after extraction and aging, whereas with hydrogenated decarboxylated CNSL and phenyl-β-naphthylamine the retention values are much lower. This may be due to CNSL phenols becoming bound to the network to a certain extent. But the results included in *Table 2* have already indicated that the phenols in raw, decarboxylated CNSL are not likely to be bound to the network. Infra-red studies with the vulcanizates which will be described later in the text, have definitely concluded that decarboxylated CNSL does not become chemically attached to the network.

Table 2 Aging properties of the sulphur-cured vulcanizates at 70° ± 1°C

Mix	Retention of tensile strength (%)		Retention of elongation at break (%)	
	After 7 days	After 14 days	After 7 days	After 14 days
A mixes				
A_0	35	20	48	35
A_1	69	44	65	52
A_2	70	46	68	54
A_3	74	55	72	59
A_4	69	47	70	60
B mixes				
B_0	55	25	58	40
B_1	89	59	87	77
B_2	90	63	90	76
B_3	90	80	95	90
B_4	83	50	90	70
B_5	74	45	89	64
B_6	70	45	73	65
B_7	96	90	90	90

Table 3 Aging properties of the peroxide-cured vulcanizates at 70° ± 1°C

Mix	Retention of tensile strength (%)		Retention of elongation at break (%)	
	After 7 days	After 14 days	After 7 days	After 14 days
P_1	80	49	89	56
P_2	82	46	89	56
P_3	88	80	89	89
P_4	83	80	89	89
P_5	74	39	83	56

Ashworth, Layland and Quan[7] observed that nitrile rubber vulcanizates with certain conventional amine and phenolic antioxidants which are quantitatively extractable from the vulcanizates, show retention in tensile properties on ageing after solvent extraction. They say that chemical attachment of these antioxidants to the network is not the explanation for the protection observed after extraction and have postulated that this is probably due to these antioxidants deactivating some active species present in rubber[7]. Natural rubber contains traces of metals like copper and manganese which are very powerful catalysts for auto-oxidation[8]. Therefore, the retention of tensile properties after extraction and aging may be due to a similar deactivating mechanism, deactivation with raw, decarboxylated CNSL being stronger than with the other antioxidants. The differences in the oxidative stability of the extracted rubbers may also be due to modification to the sulphur crosslink network during vulcanization. The differences in the amount of extractable sulphur from the different vulcanizates may be due to sulphur being used up differently in the networks, which again would be consistent with the above postulate. Monsanto rheometer studies with the base mixes have indicated that the cure characteristics are definitely influenced by the presence of decarboxylated CNSL[2]. For example, the onset of cure is faster and the rate of cure becomes slower with decarboxylated CNSL.

Peroxide cured vulcanizates. Acetone extraction studies of the peroxide-cured vulcanizates were carried out to verify the findings with the sulphur-cured vulcanizates. Peroxide-cured NR vulcanizates without black and pine tar were used in the study. The results of these experiments are given in *Table 5*. The percentage of antioxidant extracted has been calculated assuming that the difference between the amounts of matter extractable from vulcanizates with antioxidants and without antioxidants is equal to the amount of extractable antioxidant. This assumption will be valid provided that the antioxidants are not chemically modified during vulcanization. A similar calculation in the case of the

Table 4 Acetone extraction studies of the sulphur-cured vulcanizates along with the aging properties of the unextracted vulcanizates

Antioxidant	Retention of tensile strength after ageing at 70° ± 1°C		Retention of elongation at break after ageing at 70° ± 1°C		Matter extractable with acetone (%)	Extractable sulphur (as a % of total elemental sulphur) (%)
	After 7 days	After 14 days	After 7 days	After 14 days		
Raw, decarboxylated CNSL, acetone extracted	61	–	81	–	3.95	6.8
Hydrogenated CNSL, acetone extracted	29	–	70	–	4.32	8.9
Phenyl-β-naphthylamine, acetone extracted	27	–	70	–	4.22	10.1
No antioxidant, acetone extracted	Brittle	–	–	–	–	–
CNSL decarboxylated, unextracted	100	75	100	84	–	–
CNSL, hydrogenated, unextracted	100	78	100	84	–	–
Phenyl-β-napthylamine, unextracted	100	100	100	94	–	–
No antioxidant, unextracted	50	0	84	25	–	–

Table 5 Results of the acetone extraction studies of the peroxide-cured vulcanizates

Sample	Retention of tensile strength after aging at 70° ± 1°C		Retention of elongation at break after aging at 70° ± 1°C		Matter extracted with acetone (%)	Antioxidant extracted (%)
	After 7 days	After 14 days	After 7 days	After 14 days		
CNSL, Acetone extracted	45	–	100	–	4.92	100
Hydrogenated CNSL, acetone extracted	42	–	100	–	4.98	100
No antioxidant acetone, extracted	44	–	100	–	2.75	–
CNSL, unextracted	100	66	100	100	–	–
Hydrogenated CNSL, unextracted	100	65	100	100	–	–
No antioxident, unextracted	100	59	100	100	–	–

Table 6 Results of the acetone extraction studies of TMTD-cured vulcanizates

Sample	Retention of tensile strength after aging at 70° ± 1°C		Retention of elongation at break after aging at 70° ± 1°C		Matter extracted with acetone (%)	Antioxidant extracted (%)
	After 7 days	After 14 days	After 7 days	After 14 days		
CNSL, acetone extracted	Brittle	–	Brittle	–	12.80	100
Phenyl-β-naphthylamine, extracted	Brittle	–	Brittle	–	12.20	100
No antioxidant acetone, extracted	Brittle	–	Brittle	–	11.32	–
CNSL, unextracted	100	60	100	80	–	–
Phenyl-β-naphthylamine, unextracted	100	100	100	100	–	–
No antioxidant 100, unextracted	100	50	100	75	–	–

sulphur-cured vulcanizates is not possible due to sulphur taking part in chemical reactions with CNSL. From the results in *Table 5* it can be seen that both decarboxylated CNSL and hydrogenated CNSL are quantitatively extractable from the vulcanizates with acetone. After acetone extraction and ageing, the decarboxylated CNSL vulcanizates show tensile properties similar to vulcanizates without any antioxidants. The retention of about 40% of tensile strength and 100% of the elongation at break by all the vulcanizates after acetone extraction and ageing may be due to the good heat resistant characteristics of the peroxide cured networks[6]. The ageing properties of the unextracted CNSL vulcanizates do not differ much from those of the vulcanizates without added antioxidants. These results along with the ageing characteristics of the black-loaded peroxide-cured vulcanizates conclude that the presence of elemental sulphur is necessary for decarboxylated CNSL to be an efficient antioxidant. Also, the retention of tensile properties after solvent extraction shown by the sulphur-cured vulcanizates containing decarboxylated CNSL cannot be due to deactivation of any active species present in rubber, but due to some modification to the network during vulcanization.

TMTD cured vulcanizates. To confirm the results obtained with the peroxide-cured vulcanizates that elemental sulphur is necessary for decarboxylated CNSL to be an effective antioxidant, similar studies were also carried out with TMTD-cured vulcanizates. The vulcanizates are based on the formulation given in *Table 1.* Values of retention of tensile properties of acetone extracted and unextracted samples on ageing at 70° ± 1°C are given in *Table 6.* The amount of extractable antioxidant was calculated on the same basis as for peroxide-cured vulcanizates. The results included in *Table 6* confirm the findings with the peroxide-cured vulcanizates, that for decarboxylated CNSL to act as an effective antioxidant, the presence of elemental sulphur in the vulcanizing system is essential and also that the retention of tensile properties after acetone extraction and ageing is due to some modifications to the sulphur crosslink network during vulcanization and not due to any deactivation mechanism. In TMTD-cured vulcanizates mainly monosulphidic and disulphidic crosslinks are possible whereas with conventional curing systems (high dosage of elemental sulphur), for example in vulcanizates from A and B mixes, various types of sulphur crosslinks including polysulphidic crosslinks are possible[9]. Since polysulphidic crosslinks are sensitive to heat and tend to undergo changes during heat ageing[9], modifications to the sulphur crosslink network are most likely to occur only with curing systems containing a high dosage of elemental sulphur.

T.l.c. studies of acetone extracts

Qualitative t.l.c. analysis. Figure 1 represents the results of a t.l.c. analysis of the acetone extracts from sulphur-cured vulcanizates (base mix B), along with the t.l.c. patterns of decarboxylated CNSL and hydrogenated CNSL, in quantities equivalent to the maximum possible quantity which could be present in the acetone extracts (assuming total extraction). Spots of decarboxylated CNSL in quantities equal to 1/2 (spot 5) and 1/10 (spot 6) the maximum possible amount in the extract do also appear on the plate for purpose of comparison.

In the t.l.c. patterns for CNSL the lower spot is due to cardol and the upper spot is due to anacardol[4]. Comparing t.l.c. patterns 4 (decarboxylated CNSL) and 3 (hydrogenated CNSL) it can be concluded that the R_F values of cardol and anacardol (20.5 and 65.7, respectively) remain unaffected on hydrogenation. Comparing the t.l.c. pattern of the acetone extract from the vulcanizate containing decarboxylated CNSL (pattern 1), with that of decarboxylated CNSL (pattern 4), it can be seen that the spot areas of anacardol in both are comparable in magnitude, whereas that of cardol is less in pattern 1. The same observation was made with the colour intensities of the corresponding spots. The quantity of decarboxylated CNSL used in spotting 4 is equivalent to the maximum amount of decarboxylated CNSL (assuming

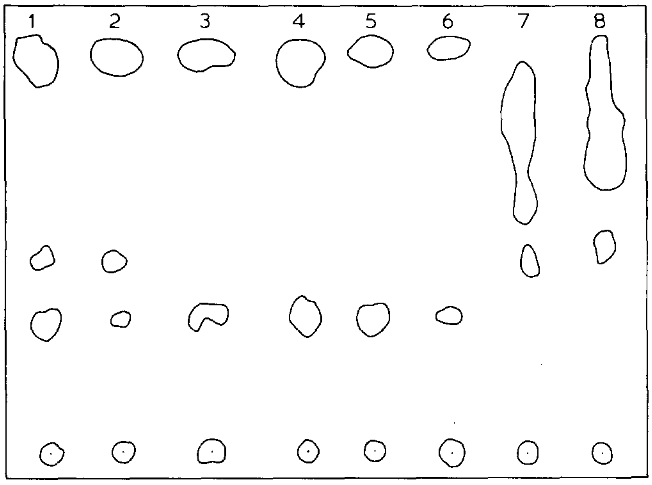

Figure 1 T.l.c. patterns of (1) the acetone extract of sulphur cured decarboxylated CNSL vulcanizates; (2) acetone extract of sulphur-cured hydrogenated CNSL vulcanizates; (3) hydrogenated CNSL; (4) decarboxylated CNSL; (5) decarboxylated CNSL, 50% w/w as in (4); (6) decarboxylated CNSL, 10% w/w as in (4); (7) THA–S_2Cl_2 adduct; (8) CNSL heated with 10% sulphur, at 140°C for 30 min. R_F values: cardol = 20.5; anacardol = 65.7; suspected thiobisphenol of CNSL = 32. Solvent mixture, benzene and ethyl acetate (90:10 v/v)

total extraction) that can be present in the quantity of the extract used in spotting 1. This indicates that while most of the anacardol is extractable from the vulcanizate, only a fraction of the cardol originally present in decarboxylated CNSL is now present in the extract. The colour intensity and the spot area of cardol in pattern 1 were found to be comparable with those of cardol in pattern 5 indicating qualitatively, that only about 50% (w/w) of the original cardol is present in the acetone extract. The use of the spot areas (and spot intensities) as a qualitative measure of the amounts of cardol and anacardol is justified by the fact that a gradual decrease in the concentration of decarboxylated CNSL leads to a proportionate decrease in the areas (and intensities) of the spots corresponding to cardol and anacardol as indicated in t.l.c. patterns 4, 5 and 6. Similarly, comparing the spot areas of hydrogenated cardol and hydrogenated anacardol in the t.l.c. pattern of the corresponding acetone extract (pattern 2) with those in the pattern for hydrogenated CNSL (pattern 3) it may be inferred qualitatively that, while most of hydrogenated anacardol is extractable, only a fraction of the original hydrogenated cardol is present in the extract. A close examination of the t.l.c. patterns 1 and 2 indicate that between the cardol spot and the anacardol spot, a new spot appears (R_F value 32), not present in the patterns for decarboxylated CNSL and hydrogenated CNSL. This spot could be due to a new compound formed from decarboxylated CNSL and hydrogenated CNSL during vulcanization with sulphur, as t.l.c. analysis of the acetone extract from vulcanizates without decarboxylated CNSL under similar conditions do not show any spots, and also the acetone extracts of the peroxide-cured vulcanizates and TMTD-cured vulcanizates both containing decarboxylated CNSL, have t.l.c. patterns identical to that of decarboxylated CNSL.

The t.l.c. pattern for the THA–S_2Cl_2 adduct (the crude product), indicates that it is a mixture of several components and that during its formation cardol appears to have reacted quantitatively. The lower spot in the t.l.c. pattern of the adduct has a R_F value of 32, which is identical with that of the new spot in the t.l.c. pattern of the acetone extract of the sulphur-cured vulcanizates (patterns 1 and 2, *Figure 1*). Since the THA–S_2Cl_2 adduct is a mixture of bisphenols of decarboxylated CNSL[3,10]: the compound giving the new spot on t.l.c. analysis of the acetone extracts of sulphur cured vulcanizates with decarboxylated CNSL and hydrogenated CNSL may also be a thio-bisphenol of decarboxylated CNSL Since the spot area (and colour intensity) of cardol in patterns 1 and 2 in *Figure 1* have decreased compared with its spot area (and intensity) in patterns 3 and 4 and also since cardol is completely absent in crude THA–S_2Cl_2 adducts it can be inferred that cardol, whether hydrogenated or not, contributes more towards the formation of this product. The upper oval-shaped spot on the t.l.c. pattern of the adduct has an R_F value similar to that of anacardol. This spot should be due to unreacted anacardol and new reaction products. Therefore, it is also possible that the spot corresponding to anacardol on t.l.c. patterns of the acetone extracts is due to anacardol and other products, which are possibly formed from anacardol during vulcanization. T.l.c. pattern 8 in *Figure 1* is that of decarboxylated CNSL heated with about 10% w/w of sulphur at 140°C for 30 min. It is different from the pattern for decarboxylated CNSL and it closely resembles the pattern of the THA–S_2Cl_2 adduct. This similarity may be used as supporting evidence for the formation of the bisphenols of decarboxylated CNSL during vulcanization.

Isolation and attempts to characterize the new compound formed from decarboxylated CNSL during vulcanization with sulphur.

The compound was isolated using preparative t.l.c. techniques described earlier in the text. Infra-red spectra of the product confirmed the presence of the phenolic hydroxyl group. A qualitative analysis of the compound for the elements present, using standard techniques in qualitative organic analysis (sodium fusion extract) showed the presence of sulphur. Cardol isolated from the same t.l.c. plate showed definite absence of sulphur in it, this confirming that sulphur detected in the new compound is present as an element in the compound and not due to any sulphur in the extract moving on t.l.c. The compound is a dark brown resinous product, soluble in common organic solvents. Attempts to purify the compound for complete characterization were not successful. The presence of the phenolic hydroxyl group and sulphur in the compound together with similarities between its R_F values and the R_F value of the lower spot in the t.l.c. pattern of the THA–S_2Cl_2 adduct may be taken as sufficient evidence to assume that it is a thiobisphenol of decarboxylated CNSL.

Infrared studies

Infrared (i.r.) studies with vulcanizates before and after solvent extraction confirmed that decarboxylated CNSL does not become bound to the network. I.r. analysis of CNSL showed a broad peak at 3350 cm^{-1}, characteristic of the phenolic hydroxyl group. But in the i.r. spectra of rubber vulcanizates containing decarboxylated CNSL this peak does not appear, as illustrated in *Figure 2*. Vulcanized rubber always gives a broad peak at 3285 cm^{-1} in i.r. probably due to hydroxyl groups formed during mastication, as indicated in *Figures 2* and *3* and also reported in other investigations[11]. In the i.r. spectra of vulcanizates containing CNSL this peak and the peak for the phenolic hydroxyl group appear together, as seen from *Figure 2*. But in the i.r. spectra of vulcanizates containing a standard phenolic antioxidant diter-

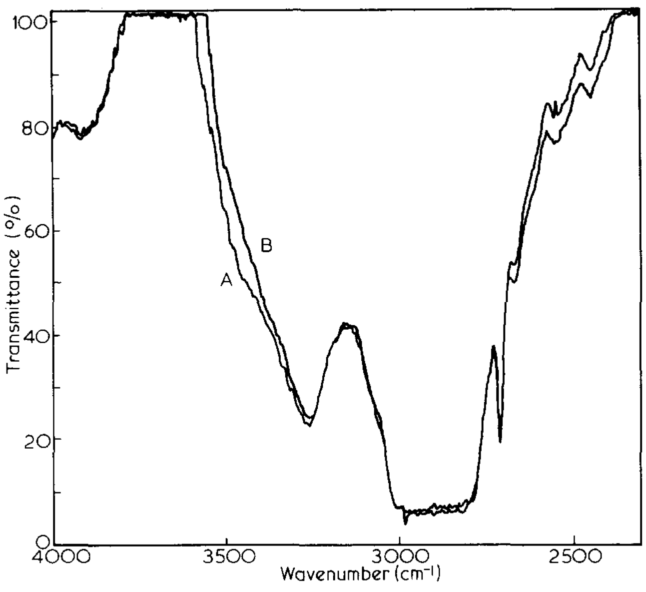

Figure 2 I.r. spectrum of rubber vulcanizate with decarboxylated CNSL (2 phr), up to 2500 cm^{-1}: A, before acetone extraction; B, after acetone extraction

tiary butyl *para*-cresol, the two peaks appear separately, as illustrated in *Figure 3*. Therefore, the peak at 1580 cm^{-1}, characteristic of the benzene ring, and a peak at 690 cm^{-1}, characteristic of an unsaturated C–H bond were used to identify the presence of decarboxylated CNSL in the vulcanizates. Both these peaks are absent in the i.r. spectra of vulcanizates (from base mix B) without decarboxylated CNSL. Also i.r. spectra of both decarboxylated CNSL and decarboxylated hydrogenated CNSL display these two bands prominently. Because decarboxylated CNSL imparts a dark colour to the vulcanizates, even at small dosages, the transparency of the films used in i.r. studies was not good. The spectra obtained were therefore not very sharp. *Figure 4* contains the i.r. spectra of vulcanizates from base mix B containing decarboxylated CNSL (2 phr), before and after acetone extraction. It is clearly seen that the peaks at 1580 cm^{-1} in the spectra of unextracted samples disappear completely on acetone extraction. Similar results were obtained with vulcanizates containing 1–5 phr of decarboxylated CNSL. Therefore these results confirm that decarboxylated CNSL does not become bound to the network during vulcanization.

CONCLUSIONS

This study has provided experimental evidence to verify the postulates we have suggested in our earlier study[1] to explain the high antioxidant activity of decarboxylated CNSL in sulphur-cured natural rubber vulcanizates. It has provided sufficient evidence for the formation of thiobisphenols of decarboxylated CNSL *in situ* during vulcanization and also has disproved conclusively that decarboxylated CNSL becomes bound to the network. The retention of tensile properties on ageing after being subjected to acetone extraction has been shown to be due to some modification to the sulphur crosslink network. The results included in *Table 2* and the t.l.c. studies have indicated that cardol contributes more towards the antioxidant activity of decarboxylated CNSL and also towards the formation of the thiobisphenols. Phenols react readily with sulphur monochloride giving mixtures of mono and polysulphides, substitution occurring most readily at the *para* position and if the *para* position is occupied it can occur at the *ortho* position[11]. Decarboxylated CNSL phenols have both the *para* and the *ortho* positions free and it may be possible that decarboxylated CNSL reacts with sulphur under conditions of vulcanization to give such products. *Figure 5* indicates the structures of three thiobisphenols that are possibly formed during vulcanization. If substitution occurs only at the *para* position, anacardol can react only at one position, whereas cardol, which has two phenolic groups *meta* to each other can react at two different positions *para* to each of the phenolic groups. This explains how cardol contributes more towards the formation of the bisphenols and therefore more towards the antioxidant activity of decarboxylated CNSL. Organic sulphides and disulphides are known to be powerful antioxidants through a peroxide decomposer mechanism[12–15]. According to Scott, at high temperatures a relatively simple organic sulphide, which belongs to the class of preventative antioxidants, is over 100 times more effective than the most effective phenolic structure known[14].

The conversion of decarboxylated CNSL into the thiobisphenols takes place only to a limited extent. The t.l.c. studies have shown that it is possible that about 50% of cardol can become converted into a thiobisphenol, while nothing definite can be said at this stage about anacardol. This means that the yield of the thiobisphenols may only be around 10% of the total phenolic content. The fact that the THA–S_2Cl_2 adduct protects the vulcanizates better than decarboxylated CNSL, especially on prolonged ageing (*Table 2*), clearly proves that the thiobisphenol content in decarboxylated CNSL is much less than in the adduct.

Therefore the high antioxidant activity of decarboxylated CNSL, which consists of a mixture of *meta* substituted phenols, is mainly due to the formation of sulphur components *in situ* during vulcanization. It has not been possible to characterize these sulphur compounds compltely due to difficulties in purifying them, but they have been proved to be phenolic compounds containing sulphur. T.l.c. analysis indicates that these sulphur compounds are most probably thio-

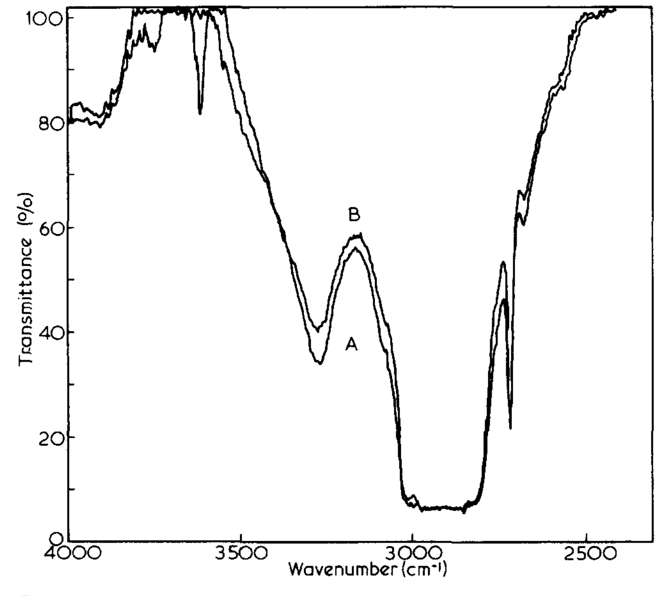

Figure 3 I.r. spectrum of rubber vulcanizate with ditertiary butyl-*para*-cresol (1 phr): A, before acetone extraction; B, after acetone extraction

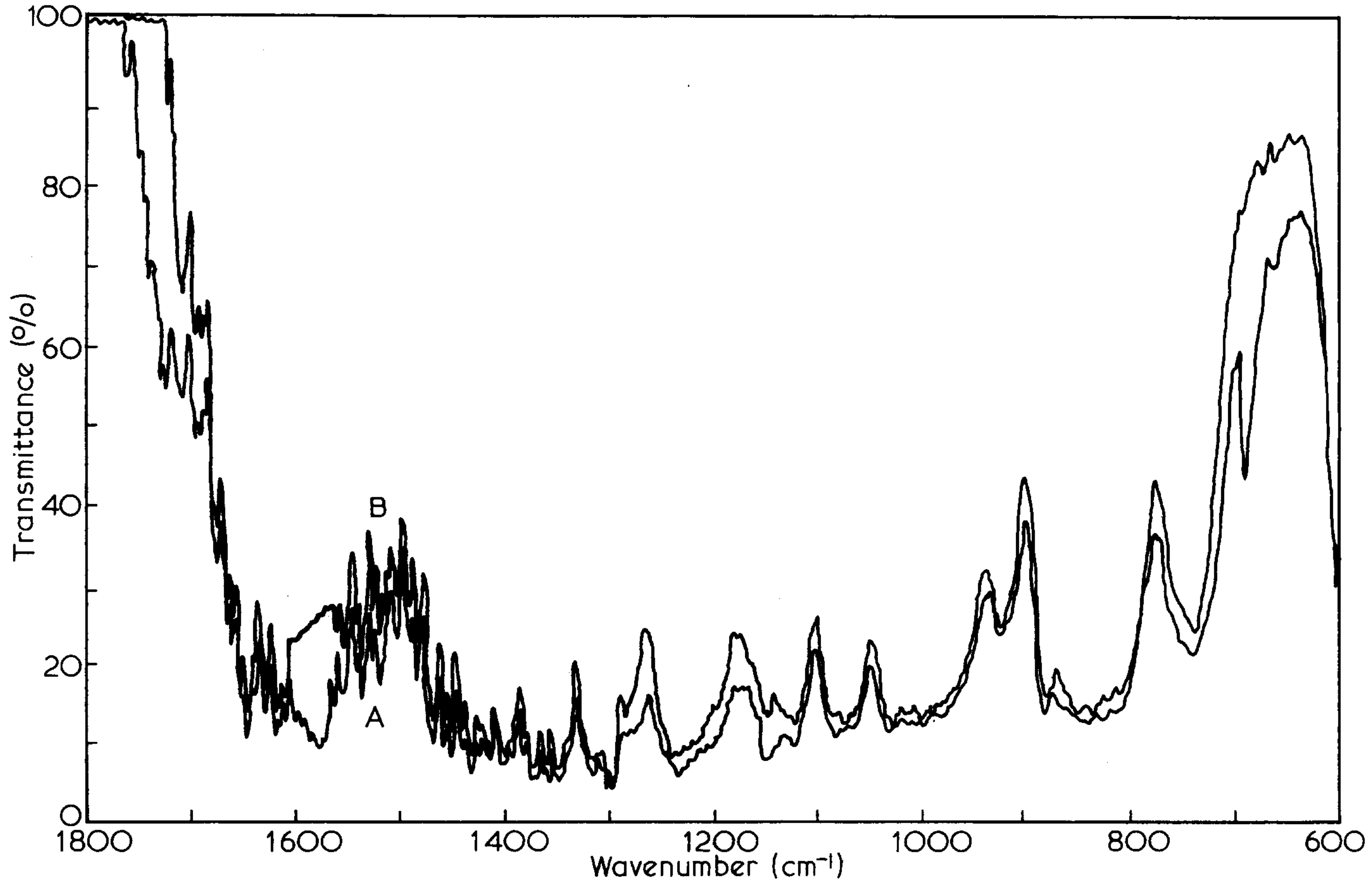

Figure 4 I.r. spectrum of rubber vulcanizate with decarboxylated CNSL (2 phr), from 1800 cm^{-1}: A, unextracted; B, extracted

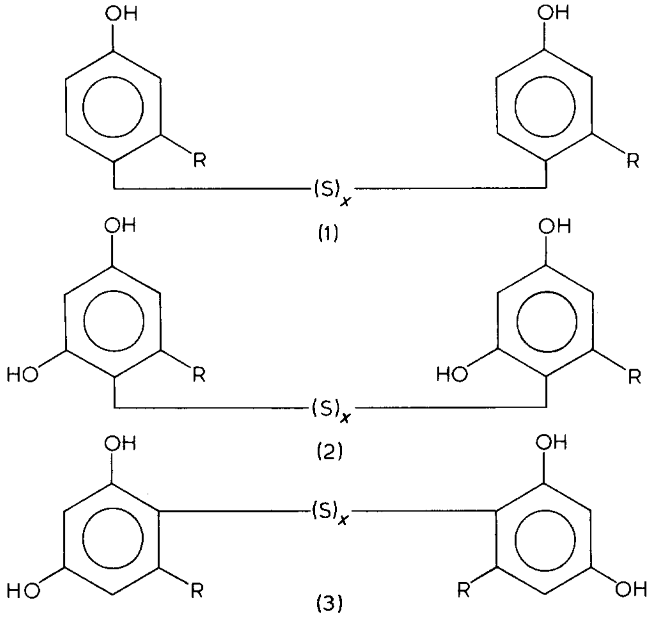

Figure 5 Possible structures of the thiobisphenols of decarboxylated CNSL, assuming only substitution (1) from anacardol; (2) and (3) from cardol

bisphenols. Further studies are in progress to ascertain whether the antioxidant behaviour of decarboxylated CNSL is due to a peroxide decomposer mechanism because of the formation of sulphur compounds or due to an increase in its chain breaking activity as a result of substitution.

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