

# Antioxidant activity of cashew-nut-shell liquid in black loaded natural rubber vulcanizates

R. A. Rajapakse, W. A. S. Gunasena and K. B. Wijekoon

Ceylon Institute of Scientific and Industrial Research, PO Box 787, Colombo 7, Sri Lanka

and S. Korathota

Ceylon Tyre Corporation, Kelaniya, Sri Lanka

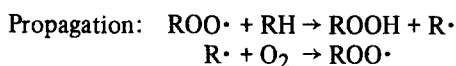
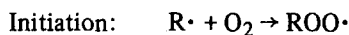
(Received 2 June 1977; revised 2 August 1977)

Cashew-nut-shell liquid (*CNSL*), which consists mainly of a mixture of two phenols each with a bulky unsaturated alkyl group at the *meta* position, has been found to protect black loaded natural rubber vulcanizates against autooxidation. Its efficiency as an antioxidant has been found to be comparable with that of the commonly used commercial antioxidants of the amine type. The high antioxidant activity of *CNSL* is qualitatively explained as being due to a combined effect of the formation of dimeric products and of a network bound antioxidant during vulcanization with sulphur.

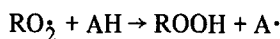
## INTRODUCTION

Oxidative degradation of organic materials is one of the most thoroughly understood reactions in organic chemistry<sup>1</sup>. The presence of unsaturation in natural and synthetic rubbers makes them particularly vulnerable to autooxidation and antioxidants are thus essential to prevent or retard the degradative processes<sup>2</sup>.

During uninhibited autooxidation of hydrocarbons, peroxy radicals, which take part in chain propagation are formed, as shown by the following sequence of reactions:



Antioxidants can function in two ways to retard autooxidation. Preventative antioxidants e.g. light absorbers, metal deactivators and peroxide decomposers, tend to reduce the rate of initiation, while the chain breaking antioxidants inhibit autooxidation by donating a H atom to a chain carrying peroxy radical<sup>1,2</sup>. Aryl amines and hindered phenols function as chain breaking antioxidants<sup>2</sup> by the following mechanism:

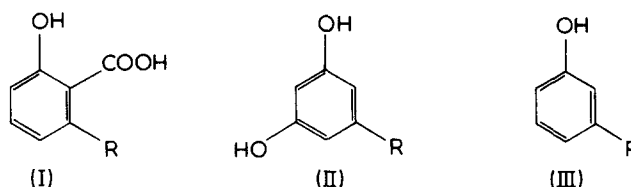


The antioxidant AH reacts with the peroxy radical forming stable products.

Of these two classes of antioxidants the chain breaking type is more widely used<sup>3</sup>. The essential technical difference between the phenolic type and the amine type of chain breaking antioxidants is the tendency of the latter to stain the rubber compound while the former is free from this tendency<sup>4</sup>. Also in black loaded compounds the amines are reported to be better antioxidants than the phenols<sup>5</sup>. Of the commercially available monophenols, the partly hindered phenols, notably those which have a normal alkyl group in one *ortho* position and a tertiary alkyl group on the other appear to give optimum antioxidant activity<sup>6</sup>. Phenols with electron releasing groups in the *meta* position are less active than those with *ortho* and *para* substituents<sup>6</sup>.

## Constituents of cashew-nut-shell liquid (*CNSL*)

*CNSL* consists of a mixture of phenols, the main components being anacardic acid and cardol. Anacardic acid (I), an aromatic hydroxy carboxylic acid with a long unsaturated alkyl side chain is present at about 80% and cardol (II) a dihydroxy alkyl phenol, at about 20%<sup>7</sup>:



R is a long C<sub>15</sub> unsaturated aliphatic chain with a degree of unsaturation lying between one and three, the first olefinic bond occurring<sup>8</sup> at C<sub>8</sub>. On heating anacardic acid undergoes easy decarboxylation to yield anacardol (III). Anacardol is also sometimes referred to as card-phenol or cardanol. Since the constituents of *CNSL* are hindered phenols, *CNSL* can be expected to have some degree of antioxidant activity.

## Application of *CNSL* in the rubber industry

Many uses of *CNSL* in the rubber industry are reported in the literature<sup>9-14</sup>, work relevant to our study being the publications by Ghatge and Gokhale<sup>9,11</sup> and by Banerjee and Banerjee<sup>13,14</sup>. Ghatge and Gokhale have successfully synthesized chemical derivatives of *CNSL*, which show antioxidant activity in natural rubber vulcanizates. Banerjee and Banerjee have conducted systematic work on the use of *CNSL* as a compounding ingredient for natural rubber. In their study, with gum compounds as well as in the presence of fillers, the amount of *CNSL* has always been 5 phr (parts per hundred rubber) or more. They observed improvements in the characteristics of the base mixes as well as in the mechanical properties of the vulcanizates. Their data on accelerated ageing of the vulcanizates does not indicate any improvements in the ageing characteristics when *CNSL* is used in such quantities (5-20 phr). Previous work by the authors has shown<sup>15-17</sup> that when *CNSL* is used in small

Table 1 Composition of the base mixes

	Mix 1 conven- tional	Mix 2 conven- tional	Mix 3 semi- EV	Mix 4 EV
Natural rubber	100	100	100	100
Zinc oxide	6	5	3.5	3.5
Stearic acid	4	2	2.5	2.5
Sulphur	3.5	2.5	1.2	0.33
Vulcafor MBTS	0.75	—	—	—
Vulcafor HBS	—	0.6	0.8	3
Vulcafor TMT	—	—	0.4	2
Processing oil (Dutrex R)	—	5	4	4
Carbon black (HAF)	40	40	40	40
Antioxidant Optimum cure time at 140°C	30 min	As indicated below 30 min	30 min	30 min

Antioxidants	Composition (phr)
Raw CNSL	1–2
Heated (decarboxylated) raw CNSL	1–2
Distilled CNSL	1–2
Nonox D	1
Flectol H	1

quantities (up to 2.0 phr) in natural rubber compounding, there is a considerable improvement in the ageing characteristics of the rubber vulcanizates. This paper describes work carried out by the authors in evaluating the antioxidant activity of CNSL in a series of natural rubber vulcanizates, based on conventional, semi-efficient vulcanization (semi-EV) and efficient vulcanization (EV) formulations. This work forms a part of a current research programme of Ceylon Institute of Scientific and Industrial Research to evaluate local raw materials for the rubber industry.

## EXPERIMENTAL

### Cashew-nut-shell liquid

CNSL was obtained by cold expelling of cashew-nut shells from sun-dried and decorticated nuts using a conventional screw-type expeller. This contained mainly anacardic acid and cardol. Decarboxylation of this product was affected by heating the liquid to 200°C. The distilled product used in the experiments was obtained by distilling CNSL at 225°C under a pressure of 25 mmHg. This product contained mainly anacardol and cardol.

### Commercial antioxidants and accelerators

The following commercial antioxidants and accelerators were used in this study: (1) phenyl- $\beta$ -naphthylamine (Nonox D, ICI); (2) polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (Flectol H, Monsanto Chem. Co.); (3) dibenzthiazyl disulphide (Vulcafor MBTS, ICI); (4) cyclohexyl benzthiazyl sulphenamide (Vulcafor HBS, ICI); (5) tetramethyl thiuram disulphide (Vulcafor TMT, ICI).

### Compounding, vulcanizing and testing

For mixing and vulcanization of the base mixes the procedure described in ref 18 was used. The optimum cure times of the base mixes were determined using a Shawbury–Wallace Curometer. Testing of the vulcanized mixes, cured for this period of time, was carried out according to ref 19.

### Evaluation of antioxidant activity

Three principal methods<sup>20</sup> are available to study the antioxidant activity of a substance: (a) oxygen absorption method; (b) stress relaxation studies; (c) accelerated ageing.

Accelerated ageing involves a study of the mechanical properties of rubber in air or oxygen at elevated temperatures and it predicts in a short-time test the deterioration due to autooxidation of a piece of rubber in a longer time at a lower temperature.

In our study accelerated ageing at 70°C in an air-circulating oven was adopted since this method gives the most reliable prediction of natural ageing of the vulcanizates<sup>20</sup>. Master batches of a number of natural rubber compounds based on various formulations, viz. conventional, semi-EV and EV were prepared without any added antioxidants. The antioxidants were then introduced into different stocks from the master batches, maintaining a uniform mixing time and mill temperature. The different batches were vulcanized for the optimum cure time and the changes in the tensile strength and elongation at break on ageing at 70°C  $\pm$  1°C were determined. A Hounsfield Rubber Testing machine was used to measure the tensile properties. The formulations of the base mixes are given in Table 1.

### Acetone extraction studies

Acetone extraction studies performed to check the solvent extractability of the antioxidants from the vulcanizates were carried out using a Soxhlet extraction apparatus.

## RESULTS AND DISCUSSION

### Physical properties of the base mixes and their vulcanizates

The physical properties such as minimum viscosity, Mooney scorch time and the optimum cure time of the different base mixes indicate that the effect of CNSL on physical properties is similar to that of the other antioxidants. Also the values for tensile strength, modulus at 300% elongation and the elongation at break of the vulcanizates from the base mixes cured for optimum cure time indicate that these properties are not affected by the presence of CNSL.

### Ageing characteristics of the vulcanizates

The values for retention of tensile strength and elongation at break of the different vulcanizates on ageing at 70°C  $\pm$  1°C are given in Table 2. The decrease in the retention of tensile strength and the elongation at break with time on ageing at 70°C  $\pm$  1°C for the vulcanizates from base mix 1 is graphically represented in Figures 1 and 2. The time dependence of the retention of tensile strength and elongation at break of the other vulcanizates on ageing shows a similar behaviour, but depends on the curing system.

The ageing characteristics of the vulcanizates as indicated in Table 2 and illustrated in Figures 1 and 2 clearly show that 2 phr of heated (decarboxylated) CNSL has similar antioxidant activity as 1 phr of amine antioxidants which are commonly used in the rubber industry. CNSL without the heat treatment has low antioxidant activity. This is to be expected because of the deactivation of the phenolic group in anacardic acid, which constitutes about 80% of CNSL, by the carboxyl group at the *ortho* position.

The vulcanizates of base mix 2, according to Table 2, are best protected against autooxidation by Flectol H, the protective action of Nonox D being slightly lower and that of CNSL being still lower. The accelerator in this base mix, namely

**Table 2** Retention of tensile strength and elongation at break of the vulcanizates on ageing at  $70^{\circ} \pm 1^{\circ}\text{C}$ 

Antioxidant	Retention of tensile strength		Retention of elongation at break	
	After 7 days	After 14 days	After 7 days	After 14 days
<b>Base Mix 1:</b>				
Nonox D	69	47	70	60
Flectol H	63	41	60	50
CNSL (raw 2 phr)	40	25	56	40
CNSL (heated 2 phr)	69	42	63	51
Nil	33	17	48	33
<b>Base Mix 2:</b>				
Nonox D	96	90	90	90
Flectol H	100	100	90	90
CNSL (heated 2 phr)	84	64	82	72
Nil	55	25	58	40
<b>Base Mix 3:</b>				
Nonox D	84	78	92	90
Flectol H	90	83	92	90
CNSL (heated 2 phr)	82	70	88	83
Nil	67	50	78	75
<b>Base Mix 4:</b>				
Nonox D	92	89	100	100
Flectol H	92	89	100	100
CNSL (heated 2 phr)	92	87	100	96
Nil	83	80	90	90

Vulcafor HBS, contains an amine and has been shown to have some antioxidant activity<sup>21</sup>. Superior antioxidant activity of Flectol H and Nonox D as compared to CNSL may be due to their better synergistic effect with Vulcafor HBS. The phenomenon of synergism is discussed in detail in a later paragraph. The formulation of the base mix 2 is a standard tyre tread compound formulation. According to ref 22, the change in the tensile strength of a vulcanized tyre tread compound on ageing at  $70^{\circ}\text{C}$  for 7 days can be  $\pm 20\%$ . Thus the compound formulation with CNSL as the antioxidant satisfies the British Standard Specification for tyre tread compounds with regard to the ageing test since it shows a retention of tensile strength of 84%.

#### Comparison of the antioxidant activity of CNSL in doses between 1 phr and 2 phr

The effect of using smaller quantities of CNSL (<2 phr) on the ageing characteristics of the vulcanizates is indicated in Table 3.

The effect of increasing the amount of CNSL from 1 to 2 phr is clearly indicated by the results in Table 3. It can be seen that for CNSL to act as an antioxidant which is as effective as 1 phr of the commonly used amine type of antioxidants, a higher dose ( $\sim 2$  phr) has to be used.

#### Effect of refining of CNSL on its antioxidant activity

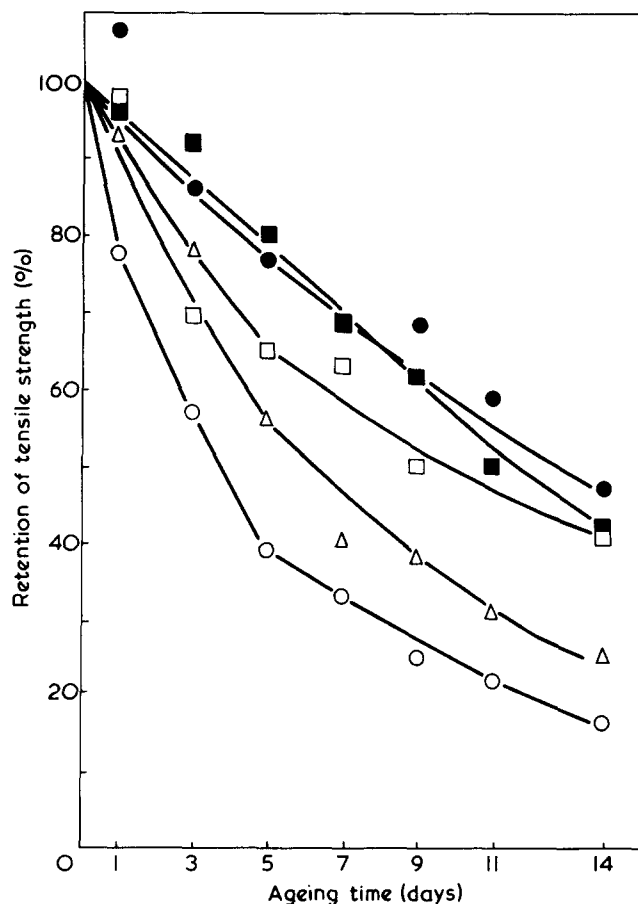
In the investigations reported so far raw CNSL has been used. Since raw CNSL is reported to contain mineral constituents, such as Fe of unknown composition<sup>12</sup>, it is worthwhile investigating whether the removal of these will improve its antioxidant activity. Table 4 contains the ageing charac-

teristics of refined (distilled) CNSL containing vulcanizates along with the ageing characteristics of vulcanizates with raw CNSL.

The results included in Table 4 can be interpreted as follows. Firstly the metallic constituents in CNSL do not affect the ageing characteristics of the rubber vulcanizates, probably because they are not present in an active form to serve as oxidation catalysts.

Using thin layer chromatography (t.l.c.), adopting techniques described by Murthy *et al.*<sup>23</sup>, it was established that in raw heated CNSL the phenolic constituents are mainly anacardol (86%) and cardol (14%). The composition of anacardol and cardol in the distilled product was found to be 96 and 4%, respectively. The better antioxidant activity of raw CNSL, as indicated by the retention of tensile strength after 7 days ageing, may be explained on the basis of the higher content of cardol in it. To verify this view, studies on the antioxidant activities of pure anacardol and pure cardol, separated from CNSL using chromatographic techniques are in progress.

Finally the results in Table 4 indicate 1.5 phr of purified CNSL to be the optimum antioxidant concentration. The total content of phenols mainly as anacardol and cardol in raw heated CNSL (obtained by heating CNSL from cold expelling of the decorticated nuts to  $200^{\circ}\text{C}$ ) has been found (using a chromatographic separation) to be about 75% of the total weight. Thus for example, 2 phr of raw heated CNSL is actually 1.5 phr of anacardol and cardol.



**Figure 1** Retention of tensile strength of the vulcanizates from base mix 1, on ageing at  $70^{\circ} \pm 1^{\circ}\text{C}$ . ○, No antioxidant; △, CNSL (raw); □, Flectol H; ■, CNSL (decarboxylated); ●, Nonox D

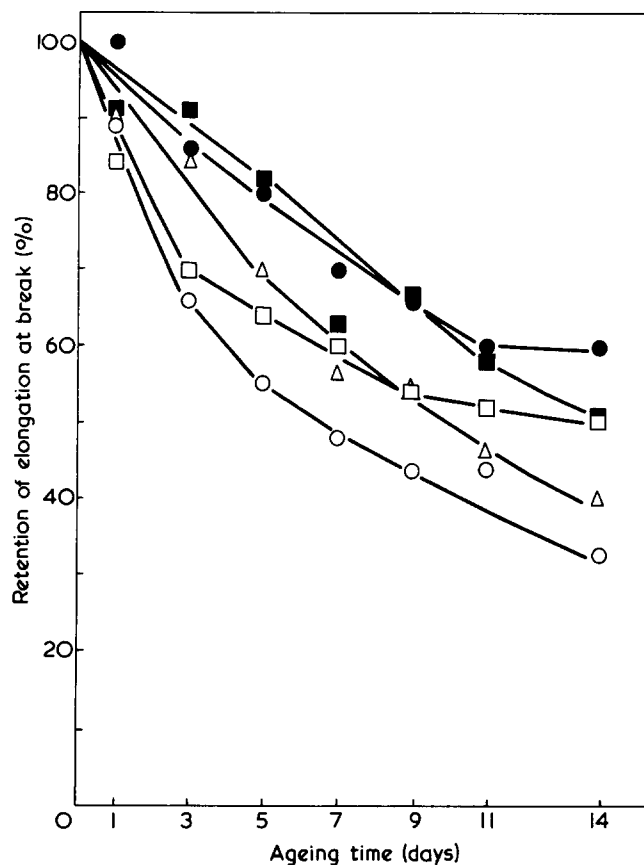


Figure 2 Retention of elongation at break of the vulcanizates from base mix 1, on ageing at  $70^{\circ} \pm 1^{\circ}\text{C}$ . ○, No antioxidant; △, CNSL (raw); □, Flectol H; ■, CNSL (decarboxylated); ●, Nonox D

Table 3 Ageing characteristics of vulcanizates from base mix 1 containing 1, 1.5 and 2 phr of CNSL (at  $70^{\circ} \pm 1^{\circ}\text{C}$ )

Amount of CNSL	Retention of tensile strength		Retention of elongation at break	
	After 7 days (%)	After 14 days (%)	After 7 days (%)	After 14 days (%)
0	33	17	48	33
1	42	25	50	43
1.5	49	32	54	47
2	69	42	63	51

#### Ageing characteristics at $100^{\circ} \pm 1^{\circ}\text{C}$

Ageing characteristics of some of the vulcanizates were also determined at  $100^{\circ} \pm 1^{\circ}\text{C}$  to obtain more evidence in support of the studies at  $70^{\circ} \pm 1^{\circ}\text{C}$ .

The results obtained with the vulcanizates from base mix 1 are tabulated in Table 5.

The results of the ageing tests at  $100^{\circ} \pm 1^{\circ}\text{C}$  included in Table 5 are much lower than at  $70^{\circ}\text{C} \pm 1^{\circ}\text{C}$  and the activity of CNSL is comparable only with that of Nonox D. Phenols and aromatic amines are reported to be less efficient inhibitors at elevated temperatures ( $>100^{\circ}\text{C}$ ) than would be predicted from their behaviour at moderate temperature. This is because of their removal from the system by evaporation, because of direct reaction with oxygen to give free radicals and because of the homolytic decomposition of the products they form (peroxides) during the termination of chain carry-

ing peroxy radicals<sup>24</sup>. Flectol H shows better antioxidant activity than Nonox D and CNSL on ageing at  $100^{\circ} \pm 1^{\circ}\text{C}$  probably due to its lower volatility at high temperatures associated with its polymeric nature.

#### Synergistic studies

When a combination of antioxidants is used better protection is obtained in the rubber molecule, the phenomena being referred to as synergism. The use of combinations of antioxidants is common in rubber technology, but the selection of these combinations is frequently empirical<sup>3</sup>. The synergistic effect of a number of combinations of raw heated CNSL and Nonox D was studied and the results of this study are given in Table 6. Figure 3 illustrates the retention of tensile strength as a function of time of the vulcanizates containing the synergistic mixtures, as compared with 1 phr Nonox D and 2 phr raw heated CNSL.

These results confirm the synergistic effect of these CNSL and Nonox D mixtures and indicate that best protection in rubber is obtained with the mixture consisting of 1.5 phr CNSL and 0.5 phr Nonox D.

#### Acetone extraction studies

The results of the experiments described so far indicate that raw decarboxylated CNSL shows antioxidant activity comparable with commonly used amine antioxidants, in black loaded rubber vulcanizates. Since CNSL phenols have only one bulky substituent and that also in the *meta* position, a possible activation of the phenolic groups by this substituent cannot account for the strong antioxidant activity of CNSL. It is well established that antioxidants which are chemically bound to the network show antioxidant activity much supe-

Table 4 Antioxidant activities of refined and raw CNSL in vulcanizates from base mix 1, aged at  $70^{\circ} \pm 1^{\circ}\text{C}$

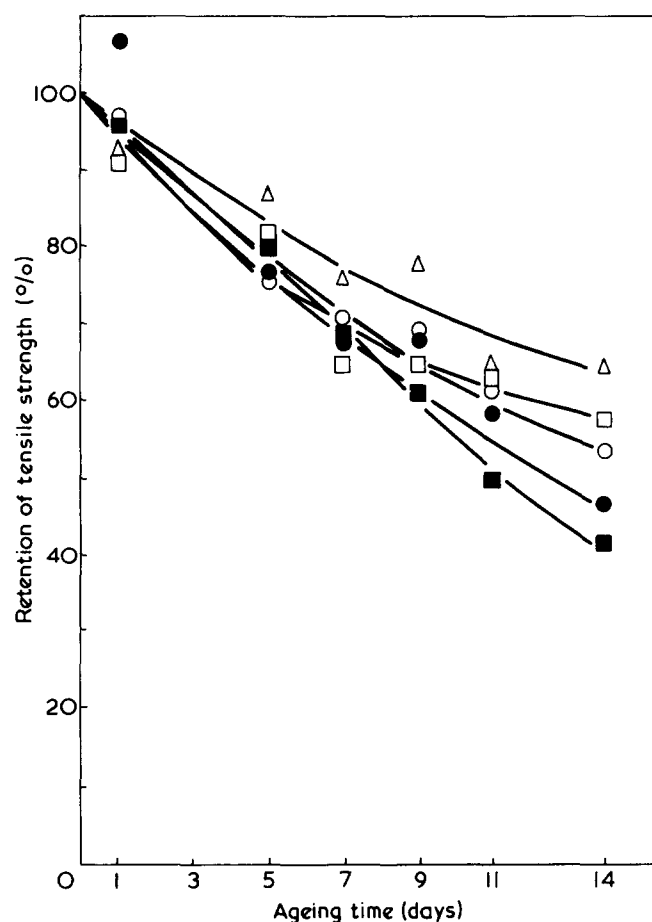
Type of CNSL	Retention of tensile strength		Retention of elongation at break	
	7 days (%)	14 days (%)	7 days (%)	14 days (%)
CNSL (raw, heated) 2 phr	69	42	63	51
CNSL (raw, heated) 1.5 phr	49	32	54	47
CNSL (distilled) 2 phr	64	43	56	49
CNSL (distilled) 1.5 phr	64	42	56	47

Table 5 Ageing characteristics at  $100^{\circ} \pm 1^{\circ}\text{C}$  of vulcanizates from base mix 1

Antioxidant	Retention of tensile strength	
	After 4 days (%)	After 7 days (%)
Nil	13	13
Nonox D	26	16
Flectol H	40	34
CNSL (Heated)	23	14

**Table 6** Synergistic effect of CNSL and Nonox D, on ageing at  $70^{\circ} \pm 1^{\circ}\text{C}$ 

Synergistic mixture		Retention of tensile strength		Retention of elongation at break	
CNSL (raw, heated) (phr)	Nonox D (phr)	7 days (%)	14 days (%)	7 days (%)	14 days (%)
2	0	69	42	63	51
0	1	69	47	70	60
1	0.5	71	54	63	45
1.5	0.5	76	65	63	58
2	0.25	65	58	60	49


**Figure 3** Retention of tensile strength of the vulcanizates from base mix 1 containing synergistic mixtures of CNSL and Nonox D, on ageing at  $70^{\circ} \pm 1^{\circ}\text{C}$ . ■, CNSL (2 phr); ●, Nonox D (1 phr); ○, CNSL (1 phr), Nonox D (0.5 phr); □, CNSL (2 phr), Nonox D (0.25 phr); △, CNSL (1.5 phr), Nonox D (0.5 phr)

rior to that of the same antioxidants which are not bound to the network<sup>3</sup>. Therefore formation of a bound antioxidant of CNSL phenols with rubber was suspected and to verify this, acetone extraction studies on the vulcanizates were performed. Vulcanized rubber samples based on the formulation, rubber (pale crepe, acetone extracted) = 100, zinc oxide = 5, stearic acid = 2, sulphur = 2.5, Vulcafor HBS = 0.6, CNSL (raw, heated) = 2, were acetone extracted. The acetone extract was analysed for extractable sulphur (extractable elemental sulphur together with sulphur from extracted accelerator etc.) content according to ref 25 and the ageing characteristics of the extracted vulcanizates were studied. *Table 7*

contains the ageing characteristics of the rubber vulcanizates both acetone extracted and unextracted, sulphur content in the acetone extract expressed as a percentage of the total elemental sulphur in the vulcanizates, along with the results for the control (without antioxidants).

Rubber used to prepare the mix, the acetone extraction studies on the vulcanizates of which are given in *Table 7*, could be assumed to be free of natural antioxidants (acetone extracted). The fact that the vulcanizates without any added antioxidant show a certain degree of retention of tensile strength and elongation at break on ageing at  $70^{\circ}\text{C}$  for 7 days may be attributed to the antioxidant activity of the accelerator, Vulcafor HBS. The antioxidant activity of Vulcafor HBS has already been discussed in an earlier paragraph. After acetone extraction, the vulcanizates without any added antioxidants show a 100% loss in tensile strength on ageing, indicating a total extraction of the accelerator component which acted as an antioxidant. Vulcanizates with CNSL show an appreciable retention of tensile strength and elongation at break on ageing after being acetone extracted suggesting the possibility of a certain fraction of CNSL phenols becoming chemically attached to the rubber molecules. The quantity of matter extracted with acetone is less in the case of vulcanizates with CNSL than from the vulcanizates without any added antioxidant. Also the extractable sulphur is less from the CNSL vulcanizates than from unprotected vulcanizates. Considering all these factors it can be qualitatively postulated that a fraction of CNSL gets bound to rubber via sulphur linkages.

## CONCLUSION

The results of our experiments indicate that raw, decarboxylated CNSL can be used as an effective antioxidant in black loaded rubber vulcanizates. To obtain the same effect as with 1 phr of widely used general purpose amine antioxidants, 2 phr of CNSL has to be used. Earlier work of Banerjee and Banerjee<sup>14</sup> has shown in natural rubber vulcanizates loaded with 50 phr of SRF black and having high doses of CNSL (between 10 and 30 phr), CNSL does not show any improvement in the ageing characteristics. With 10 phr of CNSL the vulcanizates even have poorer ageing

**Table 7** Results of the acetone extraction studies of the vulcanizates

Sample	Retention of tensile strength after 7 days ageing at $70^{\circ} \pm 1^{\circ}\text{C}$ (%)	Retention of elongation at break after 7 days ageing at $70^{\circ} \pm 1^{\circ}\text{C}$ (%)	Matter extractable with acetone (%)	Extractable sulphur (as a % of the total elemental sulphur) (%)
With CNSL acetone extracted	45	80	7.3	5.1
No antioxidant, acetone extracted	0	33	10.1	5.6
With CNSL unextracted	100	100	—	—
No antioxidant, unextracted	45	93	—	—

characteristics than the control (without any antioxidants). These findings could be explained on the basis that at doses higher than the optimum concentration, antioxidants can also serve as prooxidants<sup>3</sup>. In our studies the optimum concentration of *CNSL* as an antioxidant has been found to be 1.5–2 phr. The results of our experiments are interesting for the following reasons:

(1) *CNSL* consisting of hindered phenols can protect black loaded natural rubber vulcanizates against oxidative degradation, the protective effect being comparable with that of commercial amine antioxidants, whereas according to existing literature<sup>5</sup> amine antioxidants are superior to phenolic antioxidants in black loaded rubber vulcanizates.

(2) The phenols present in *CNSL* are *meta* substituted whereas the commonly used phenolic type of antioxidants are *ortho* and *para* substituted with alkyl groups<sup>6</sup>.

Alkyl groups at *ortho* and *para* positions activate the phenolic group and facilitate the donation of a hydrogen atom of the OH-group to a polymer chain carrying peroxy radical, thereby arresting the autooxidation processes. Any possible activation of the phenolic group(s) in *CNSL* by the bulky alkyl group at the *meta* position cannot account for its strong antioxidant activity. The noteworthy behaviour of *CNSL* as an effective antioxidant may be explained as being due to:

(a) Formation of a network bound antioxidant by *CNSL* phenols becoming chemically attached to the vulcanizates through sulphur linkages, thus enhancing its antioxidant activity. This is possible through chemical combination of *CNSL* phenols via the double bonds in the side chain, with rubber in the presence of sulphur. The acetone extraction studies, the results of which are given in *Table 7*, strongly favour the fact that at least a part of *CNSL* is chemically bound to rubber via sulphur bonds.

(b) Chemical combination of the *CNSL* phenols with rubber via the CHO groups, which are possibly formed during mastication of rubber. Banerjee and Banerjee<sup>13</sup> have already suggested this as a possible explanation for the superior performance of *CNSL* as a rubber compounding ingredient. The formation of network bound antioxidant will also be the result of such a combination. To verify this, acetone extracted pale crepe was masticated with 2 phr *CNSL* for about 30 min on an open mill, maintaining a mill temperature of about 100°C at the latter stages and this rubber was subjected to acetone extraction. It was established that the *CNSL* phenols were quantitatively extractable from the rubber mix, indicating that under the above experimental conditions they do not get chemically attached to rubber.

(c) Formation of high molecular products (high molecular weight antioxidant) of *CNSL* phenols via sulphur linkages:— The participation of the double bonds in the C<sub>15</sub> side chain to form polymeric products of *CNSL* with sulphur could well be anticipated. The fact that *CNSL* forms a rubbery mass when heated with sulphur can be taken in support of this view.

Ghatge and Gokhale<sup>11</sup> have compared the antioxidant activity of the reaction product of hydrogenated anacardol (THA) and sulphur monochloride (S<sub>2</sub>Cl<sub>2</sub>), with Nonox D and Santowhite-MK (Mosanto Chem. Co., a reaction product of 6-tert-butyl-*m*-cresol with S<sub>2</sub>Cl<sub>2</sub>, consisting mainly of a dimerized product of the phenol through a sulphide bond at the *para* position) in black loaded natural rubber vulcanizates (2.5 phr sulphur, 1 phr Vulcafor MBTS and 50 phr black). Their results for the retention of tensile strength of the vulcanizates on ageing at 70 ± 1°C indicate that the antioxidant activity of THA–S<sub>2</sub>Cl<sub>2</sub> reaction product (46% retention after 7 days and 35% retention after 14 days) is

much lower than that of Nonox D (66% and 45%) and Santowhite-MK (90% and 80%), using 1 phr of the antioxidant in each case. The lower antioxidant activity of the THA–S<sub>2</sub>Cl<sub>2</sub> reaction product as compared with Santowhite-MK has been explained by them as due to the presence of the tert-butyl group in one *ortho* position in Santowhite-MK. In our experiments we have obtained for the retention of tensile strength on ageing at 70 ± 1°C for 7 and 14 days, respectively, for a conventional vulcanizing system (base mix 1), 69 and 47% with 1 phr Nonox D, 69 and 42% with 2 phr *CNSL*, and 49 and 32% with 1.5 phr *CNSL* (*Tables 2 and 3*). Thus the retention of the tensile properties with 1 phr of the THA–S<sub>2</sub>Cl<sub>2</sub> adduct is comparable with the retention values with 1.5 phr of raw heated *CNSL*, which really contains only about 1 phr of the phenolic mixture (only 75%). This indicates that 1.5 phr of the adduct may have the same antioxidant activity as 1 phr of Nonox D and 2 phr of raw heated *CNSL*. THA–S<sub>2</sub>Cl<sub>2</sub> adduct can be expected to be a dimer of THA with a structural formula similar to Santowhite-MK. Therefore on the basis of these results the possibility of dimerization of *CNSL* phenols during the process of vulcanization cannot be excluded.

Thus it is most likely that the high antioxidant efficiency of *CNSL* is due to the combined effect of the formation of dimeric products with sulphur and the formation of network bound antioxidant via sulphide bonds. Then its lower antioxidant activity at 100°C (*Table 5*) should probably be due to its direct reaction with oxygen to give free radicals and due to the homolytic decomposition of the products it forms during the termination of chain carrying peroxy radicals and not due to any volatility effect.

Further work is in progress to verify the two postulates, namely the dimerization of the *CNSL* phenols and the formation of network bound antioxidants and also to formulate a mechanism of the binding of the phenols to the rubber. The results will be published in a subsequent paper.

## ACKNOWLEDGEMENTS

The authors wish to thank Mr M. S. Wijeratne, Deputy Director, Ceylon Institute of Scientific and Industrial Research, for going through the manuscript and making valuable suggestions and Mrs Iranganie Bandara for secretarial assistance.

## REFERENCES

- 1 Scott, G. 'Atmospheric Oxidation and Antioxidants', Elsevier, Amsterdam, 1965
- 2 Shelton, J. R. *Rubber Chem. Technol.* 1974, 47, 949
- 3 Dunn, J. R. *Rubber Chem. Technol.* 1974, 47, 960
- 4 Buist, J. M. 'Ageing and Weathering of Rubber', Heffer, Cambridge, 1956, p 120
- 5 Shelton, J. R. and Cox, W. L. *Rubber Chem. Technol.* 1954, 27, 686
- 6 Scott, G. 'Atmospheric Oxidation and Antioxidants', Elsevier, Amsterdam, 1965, pp. 124, 452
- 7 Tyman, J. H. P. and Morris, L. J. *J. Chromatogr.* 1967, 27, 287
- 8 Tyman, J. H. P. and Jacobs, N. J. *J. Chromatogr.* 1971, 54, 83
- 9 Ghatge, N. D. and Gokhale, R. G. *Indian J. Technol.* 1971, 9, 391
- 10 Ghatge, N. D. and Gokhale, R. G. *Rubber India* 1972, 24, 13, 36
- 11 Ghatge, N. D. and Gokhale, R. G. *Rubber Age* 1969, 101, 52
- 12 'Cashew Nut Shell Liquid Patents', Cashew Export Promotion Council, Ernakulam – 6, India, 1964, Vols 1 and 2
- 13 Banerjee, S. K. and Banerjee, S. *Indian J. Technol.* 1971, 9, 424

- 14 Banerjee, S. K., Sujit and Banerjee, S. *Indian J. Technol.* 1971, 9, 467
- 15 Korathota, S. *MSc. Thesis* University of Sri Lanka (1976)
- 16 Rajapakse, R. A. *Proc. Sri Lanka Association Adv. Sci. Annu. Sessions* 1976, p 82
- 17 Sri Lanka Pat. Application No. 7623, 12th May 1977
- 18 BS 1674: 1976
- 19 BS 903: Part A2: 1971
- 20 Ambelang, J. C., Kline, R. H., Lorenz, O. M., Parks, C. R. and Wadelin Coe *Rubber Chem. Technol.* 1963, 36, 1510
- 21 Shelton, J. R. and Cox, W. L. *Rubber Chem. Technol.* 1953, 26, 632
- 22 BS AU 144a: 1970, specification for Retreaded Car and Commercial Vehicle Tyres
- 23 Murthy, B. G. K., Sivasamban, M. A. and Aggarawal, J. S. *J. Chromatogr* 1968, 32, 520
- 24 Howard, J. A. *Rubber Chem. Technol.* 1974, 47, 986
- 25 BS 903: Part B7: 1958