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# Journal of Elastomers and Plastics

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## Studies on Mastication Stage Binding of Antioxidants

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**ABSTRACT:** Paraphenylenediamine and diphenylamine were chemically attached to natural rubber during mastication. The rubber bound antioxidants were characterized by TLC, <sup>1</sup>H-NMR, IR and TGA. The efficiency and permanence of these bound antioxidants were compared with a conventional amine type antioxidant in filled natural rubber vulcanizates. The rubber bound antioxidants were found to be less volatile and less extractable as compared to conventional antioxidants. The vulcanizates showed improved ageing resistance as compared to vulcanizates containing conventional antioxidants. This semisolid rubber bound antioxidant can reduce the amount of plasticizer required for compounding.

### INTRODUCTION

**N**EW DEVELOPMENTS IN product design and improvements in compounding demands improved polymer stabilization. Conventional antioxidants, especially in aggressive environments can be rapidly depleted by volatility, migration, extraction and irreversible absorption on fillers [1-4]. Volatility, migration and leaching may be substantially reduced using high molecular weight polymers or polymer bound antioxidants. The physical properties of the compound that contain polymer bound antioxidants also show improved maintained properties under adverse conditions [5,6]. Numerous papers and

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reviews have appeared describing the preparation of polymer bound antioxidants [7,8]. Cain et al. reported the "ene" addition of nitroso phenols or aniline derivatives to produce polymer bound stabilizers [9]. Amine antioxidants bound to chloroprene rubber by hot melt mixing were reported by Mohamad. S. et al. [10]. Scott et al. have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position can react with natural rubber in presence of an oxidizing free radical to a yield polymer bound antioxidant [11]. Antioxidants, such as styrenated phenol, diphenylamine etc. have been bound to hydroxy terminated liquid natural rubber via modified Friedel-Craft's reaction [12]. Preparation of NR-bound diphenylamine antioxidant by photochemical reaction is also found to be effective in improving the ageing resistance of natural rubber compounds [13]. This paper describes the chemical binding of amine type antioxidants to macro alkyl radicals produced by mechano-chemical scission of natural rubber in the presence of a free radical generator. This product was subsequently used in filled natural rubber compound vulcanizates. The amine type antioxidants used were diphenylamine and paraphenylenediamine. In rubber the bound antioxidant gets attached to natural rubber during sulphur vulcanization. The antioxidant becomes nonvolatile and nonextractable. Efficiency and durability permanence of these rubber bound antioxidants were compared with conventional antioxidant in filled natural rubber compounds.

## EXPERIMENTAL

### Materials

Natural rubber (NR, ISNR-5, Mooney viscosity ML[1+4]100°C-82) was supplied by the Rubber Research Institute of India, Kottayam. Compounding ingredients, zinc oxide, stearic acid, aromatic oil, carbon black (HAF N330) used were commercial grade. Mercapto benzothiazole (MBT) and tetra methyl thiuram disulphide (TMTD) vulkanox 4020 (substituted paraphenylenediamine) were of rubber grade. They were supplied by Bayer India Ltd. Methanol, acetone and toluene were of reagent grade. Paraphenylenediamine (PD, Analar grade), was from CDH laboratories, and diphenylamine from E. Merck.

### Preparation of Natural Rubber Bound Amine Type Antioxidants

100 g of natural rubber was masticated for 25 minutes at 60°C on a two roll mill. 20 g of diphenylamine/paraphenylenediamine was added and the mastication was continued for 15 more minutes. The mastication



tion was also carried out in the presence of a free radical generator, benzoyl peroxide (0.5 phr). The unreacted antioxidants and benzoyl peroxide present in masticated NR were removed by repeated reprecipitation using toluene-methyl alcohol and dilute sodium carbonate solution. The product was dried in a vacuum oven. The rubber bound antioxidant was obtained in the form of a semi solid mass. Samples prepared by mastication with and without benzoyl peroxide were compounded natural rubber, as per formulation listed in Table 1. Efficiency of mastication in the presence of a free radical generator benzoyl peroxide, was determined by studying the retention in tensile strength after ageing the compound at 100°C for 48 h. Tensile strength retention is found to be better for vulcanizates containing the rubber bound sample prepared by mastication of natural rubber in the presence of benzoyl peroxide. Rubber bound antioxidants were prepared by mastication of natural rubber and diphenylamine/paraphenylenediamine, in presence of benzoyl peroxide.

#### Analysis of the Rubber Bound Antioxidant

Analysis of the bound antioxidant was carried out by using thin layer chromatography (TLC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy (<sup>1</sup>H-NMR) and thermogravimetric analysis (TGA).

Table 1.

	A	B	C
Natural rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
Mercaptobenzothiazole	0.6	0.6	0.6
Tetramethyl thiuram disulphide	0.2	0.2	0.2
Sulphur	02.5	2.5	2.5
Carbon black HAF (N 330)	40	40	40
Aromatic oil	1	1	5
Vulkanox 4020	—	—	1
NR-PD	10	—	—
NR-DA	—	10	—
<b>Cure characteristics</b>			
Cure time, mins	1.9'	3.5'	3.4'
Scorch time, mins	0.6	1.5	1.4

NR-PD: Paraphenylene diamine bound to natural rubber. NR-DA: Diphenylamine bound to natural rubber.



TLC was carried out using silica gel as the adsorbent. A mixed solvent of benzene and ethylacetate (4:1) was used as the developing solvent for all samples. Diazotisation using nitrous acid fumes was carried out to detect paraphenylenediamine and paraphenylenediamine bound to NR (hereafter referred as NR-PD). Ninhydrin was used to detect diphenylamine and diphenylamine bound to NR (hereafter referred to as NR-DA) and iodine for NR [14].

Molecular weight of NR-PD and NR-DA are calculated using Mark-Houwink-Sakurada equation by measuring intrinsic viscosity using an Ubbelohde viscometer and substituting the values  $K (5.02 \times 10^{-2} \text{ ml/g})$  and a (.667) of natural rubber.

IR spectra were recorded in a Perkin-Elmer Model 377 IR spectrometer.

The  $^1\text{H-NMR}$  measurements were carried out using a Hitachi Perkin Elmer R-243 (60 MHz) model and the spectra were measured at  $20^\circ\text{C}$  with 10 wt% solution of the samples in  $\text{CCl}_4$  with tetramethyl silane as the internal standard.

Thermogravimetric analysis (TGA) was carried out using a Shimadzu TG-DSC standard model at a heating rate of  $10^\circ\text{C}$  per minute.

The optimum concentration of the rubber bound antioxidant for getting maximum retention in properties was determined by varying the amount of antioxidant in the mix from 3 to 15 phr.

The chemically bound antioxidants were added in NR as per formulation listed in Table 1. The amount of plasticizer can be reduced by the use of semi solid rubber bound antioxidant as shown in Table 1. The optimum cure times (time to reach 90% of the maximum torque) and scorch times (time to reach 10% of the maximum torque) of the compounds were determined on a Gottfert Elastograph model 67.85 as per ASTM D-1646 (1981).

Rubber compounds were moulded in an electrically heated laboratory hydraulic press at  $150^\circ\text{C}$  up to their optimum cure times. Dumbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick Universal Testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM D-412-80. Tear resistance of the vulcanizates were evaluated as per ASTM D 624-81 using unnicked  $90^\circ$  angled test specimens. The hardness (shore A) of the moulded sample was measured using a Zwick 3115 hardness tester in accordance with ASTM D 2240 (1981). Compression set was calculated as per ASTM D 395 (1982). Rebound resilience of the vulcanizates was evaluated using Dunlop tripsometer as per BS 903, part 22, 1950.

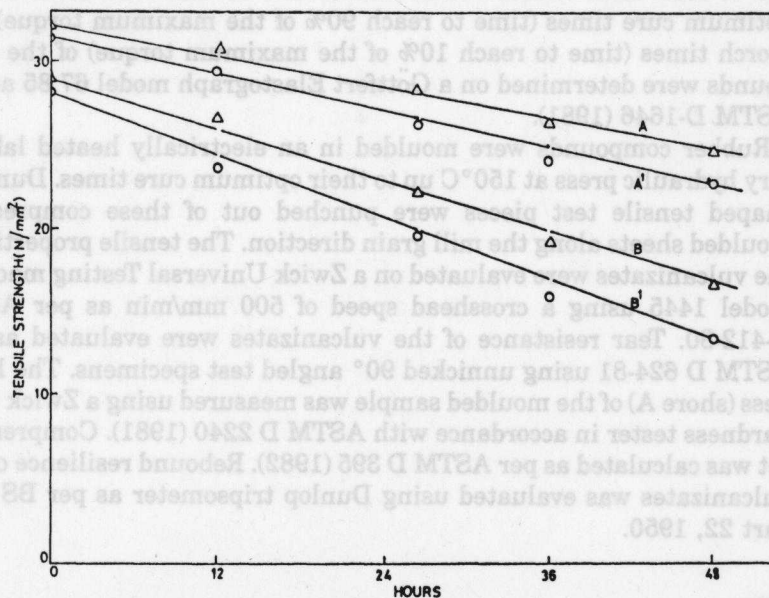
Retention in tensile properties and tear strength were evaluated after ageing the samples at 100°C for 12, 24, 36 and 48 h. Retention in compression set, heat build up, resilience and flex crack resistance were evaluated after ageing the samples at 100°C for 48 h.

The extractibility of the bound antioxidant was studied in methanol, acetone and toluene by keeping the samples in methanol, acetone (48 h, at 30°C) and in boiling toluene for 10 h. The retention in tensile properties were evaluated after ageing the extracted samples at 100°C for 48 h.

Extractibility of the bound antioxidant in dilute acid and alkali was studied by keeping the samples in HCl (pH 1.02) and in NaOH (pH 9.86) for 48 h at room temperature. The retention in tensile properties was evaluated after ageing the samples at 100°C for 12, 24, 36 and 48 h.

## RESULTS AND DISCUSSION

Figure 1 shows the variation in tensile strength versus ageing of the vulcanizates containing bound antioxidant prepared with and without



**FIGURE 1.** Variation of tensile strength of the vulcanizates before and after ageing. (a) In presence of benzoyl peroxide. A—NR-PD, B—NR-DA. (b) In absence of benzoyl peroxide. A'—NR-PD, B'—NR-DA.

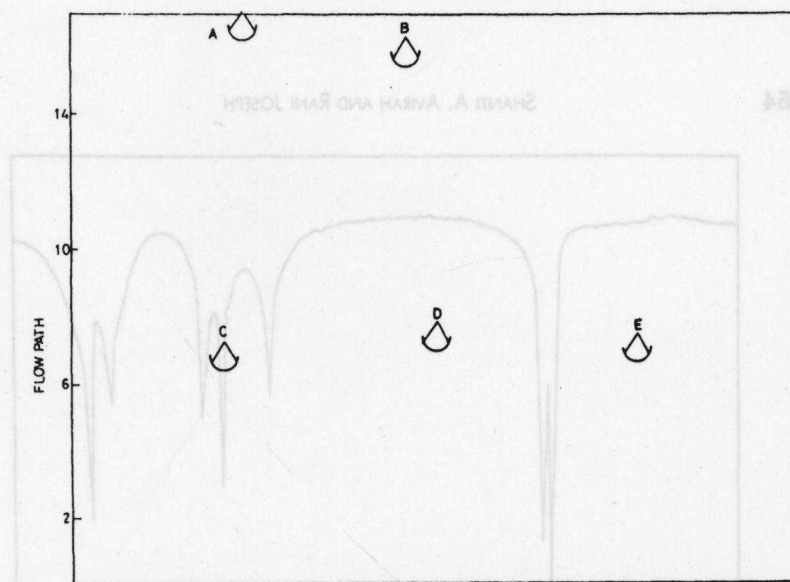


FIGURE 2. TLC of compounds. A-Diphenylamine, B-Paraphenylenediamine, C-NR-DA, D-Masticated NR, E-NR-PD.

benzoyl peroxide. Maximum ageing resistance was observed in compounds containing bound antioxidant prepared in the presence of benzoyl peroxide. Hence, benzoyl peroxide is found to be effective in increasing the rate of mechano-chemical breakdown in natural rubber.

The viscosity average molecular weight ( $\bar{M}_v$ ) of natural rubber, NR-PD and NR-DA were found to be 706496, 25400, 25180, respectively.

Figure 2 shows the TLC of paraphenylenediamine (PD), diphenylamine (DA), NR-PD, NR-DA and depolymerised rubber. NR showed no trace of colour change due to nitrous acid fumes/resorcinol system while NR-PD and PD did. NR-DA and DA were coloured by ninhydrin while NR was not. The  $R_f$  value of depolymerised rubber and bound antioxidants were found to be almost equal. This demonstrates that antioxidants get chemically attached to masticated natural rubber during post mastication process.

Figures 3, 4 and 5 show the IR spectra of NR, NR-PD and NR-DA. The IR spectrum of NR shows the peaks at:  $3000\text{ cm}^{-1}$  corresponding to aliphatic  $-\text{CH}$ ;  $1665\text{ cm}^{-1}$  corresponding to  $\text{C}=\text{C}$ ;  $1400\text{ cm}^{-1}$  due to  $-\text{CH}_3$ ; and  $835\text{ cm}^{-1}$  corresponding to  $-\text{C}(\text{CH}_3)=\text{CH}-$ . The IR spectrum of NR-PD shows additional peaks at  $3500\text{ cm}^{-1}$  (N-H stretching, primary),  $3310\text{ cm}^{-1}$  (N-H stretching, secondary),  $1590\text{ cm}^{-1}$  (N-H bending),



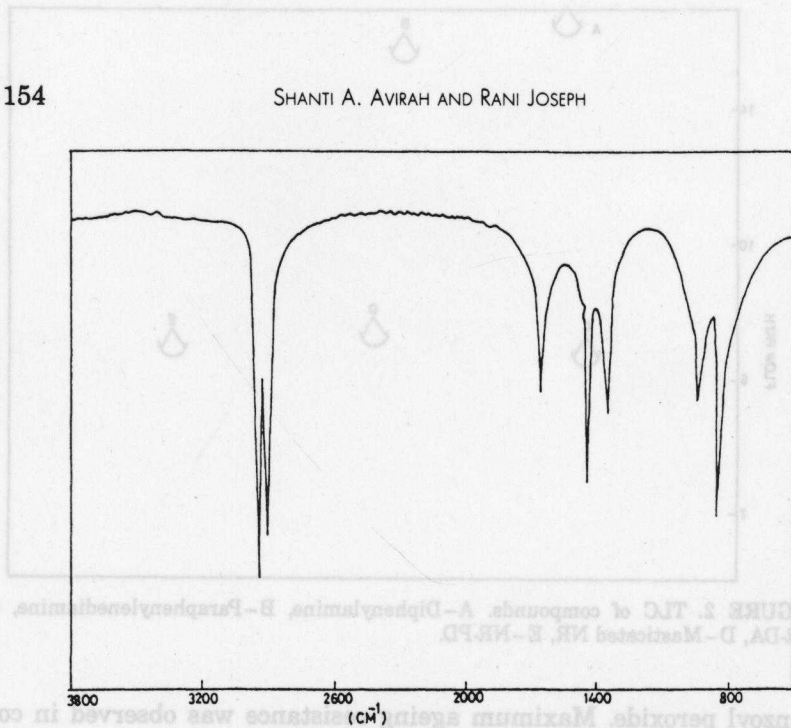


FIGURE 3. IR spectrum of NR.

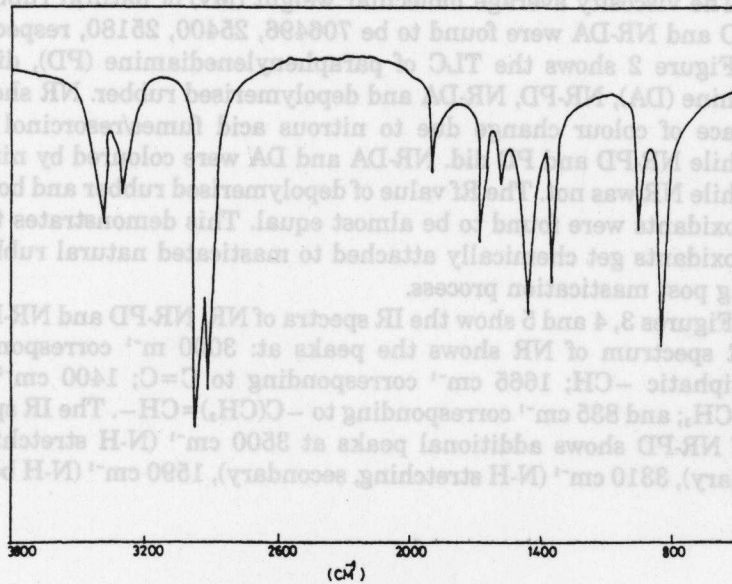


FIGURE 4. IR spectrum of NR-PD.

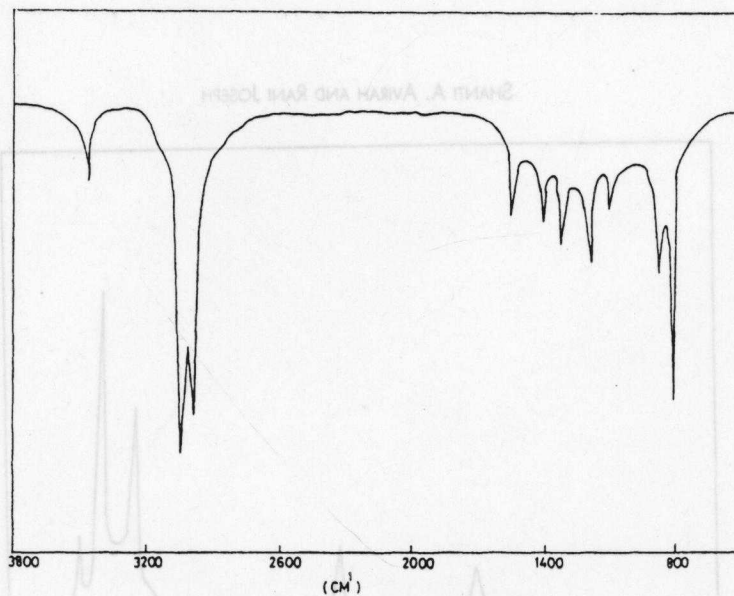


FIGURE 5. IR spectrum of NR-DA.

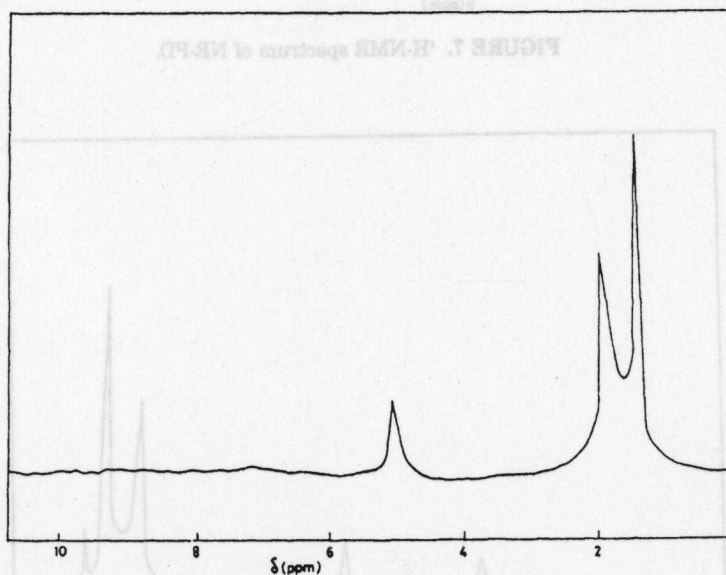
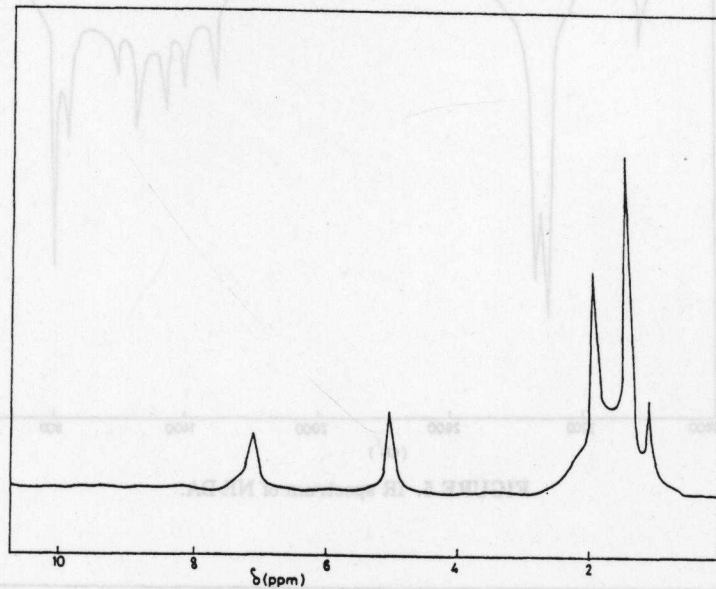
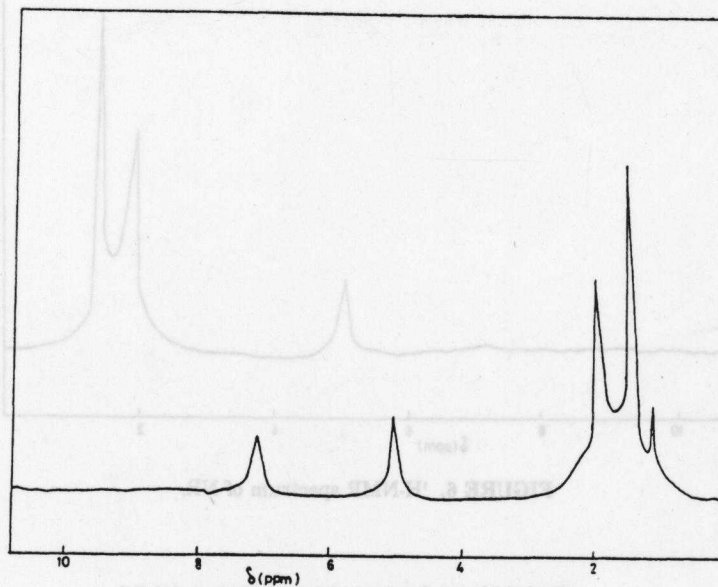


FIGURE 6. <sup>1</sup>H-NMR spectrum of NR.

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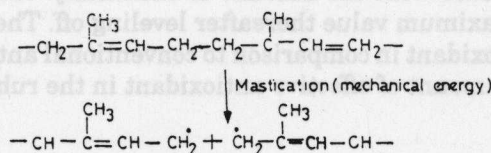
FIGURE 7. <sup>1</sup>H-NMR spectrum of NR-PD.FIGURE 8. <sup>1</sup>H-NMR spectrum of NR-DA.



1350 (C-N vibration) and 1500  $\text{cm}^{-1}$  corresponding to the aromatic ring in paraphenylenediamine. IR spectrum of NR-DA shows peaks at 1500  $\text{cm}^{-1}$  aromatic ring 1350  $\text{cm}^{-1}$  (C-N vibration) and 3400  $\text{cm}^{-1}$  (N-H stretching). This confirms the chemical bonding of antioxidants to NR [15].

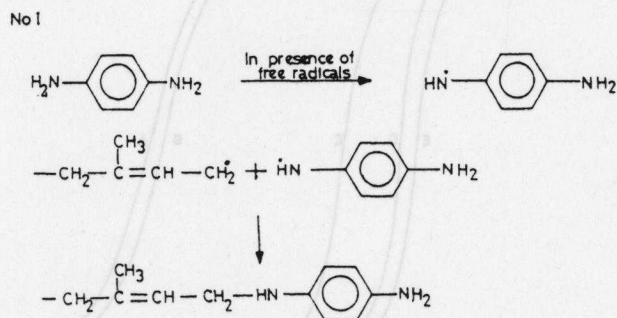
Figure 6 shows the  $^1\text{H-NMR}$  spectrum of NR. There are peaks at  $\delta = 5.1$  ( $-\text{C}=\text{C}-$ ),  $\delta = 1-2$  ( $\text{CH}_2$ ) and  $\delta = 1.65$  ppm ( $-\text{CH}_3$ ). Figures 7 and 8 show  $^1\text{H-NMR}$  spectra of NR-PD and NR-DA which show additional peak at which  $\delta = 1.19$  and  $\delta = 7.1$  ppm corresponding to amino group and aromatic ring present in bound antioxidants. This again confirms the chemical bonding of antioxidants to NR.

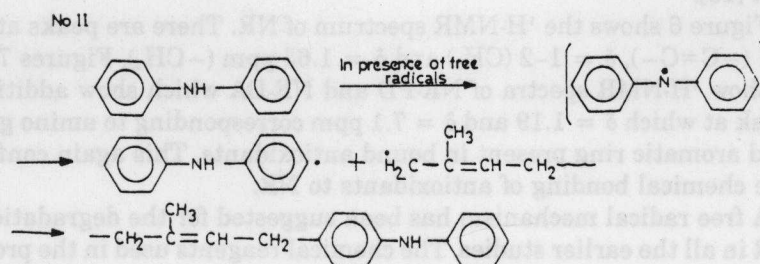
A free radical mechanism has been suggested for the degradation of NR in all the earlier studies. The chemical reagents used in the process are free radical generators such as thiols, peroxides etc. [16-21]. The presence of a  $-\text{CH}_3$  group attached to ethylenic carbon atom in polyisoprene tends to reduce the  $-\text{CH}-$  dissociation energy by hyperconjugation [22]. Free radicals produced by the free radical generators interact with the labile C-H bond abstracting the proton and leaving behind the macroradicals [23]. Based on the complex transformations of aro-



matic amine during ageing in the presence of free radicals and from the mechanism of mastication of NR, the following mechanism can be suggested for the attachment of paraphenylenediamine (No. I) Diphenylamine (No. II) on to depolymerised NR [24,25,26].

Figure 9 shows the thermograms of PD, DA, NR-PD and NR-DA. The





low molecular weight antioxidants volatilize easily while rubber bound antioxidants are less volatile.

Figure 10 shows the variation in tensile strength after ageing with concentration of the antioxidant. The tensile strength retention is found to increase with the amount of chemically bound antioxidant, reaching a maximum value thereafter leveling off. The higher amount of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the rubber bound product.

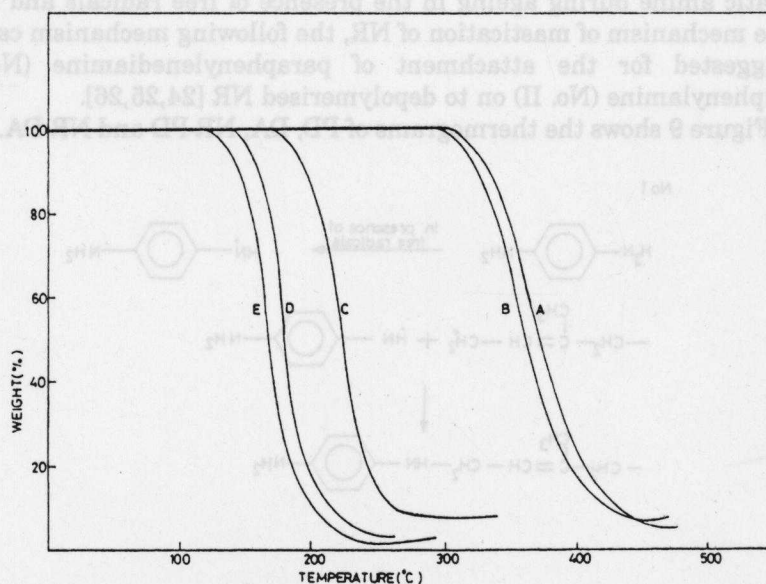


FIGURE 9. TGA of compounds. A-NR-PD, B-NR-DA, C-Vulkanox 4020, D-diphenylamine, E-Paraphenylenediamine.

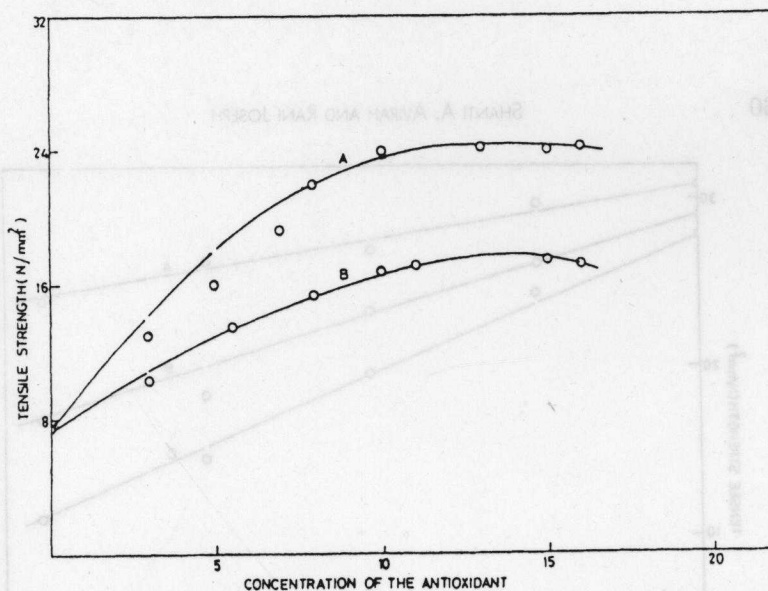


FIGURE 10. Variation of tensile strength of the vulcanizates after ageing with concentration of the antioxidant. A—NR-PD, B—NR-DA.

Figure 11 shows the tensile strength of the vulcanizates of the compounds, shown in Table 1, before and after ageing. All the vulcanizates show fairly good resistance to ageing at 100°C for 24 h but the compounds containing NR-PD and NR-DA alone shows good ageing resistance when ageing time is increased to 48 h. This shows the superiority of bound antioxidants over conventional antioxidants.

Figure 12 shows the change in elongation at break of the vulcanizates before and after ageing. The compounds containing bound antioxidants show better retention in elongation at break after ageing; which confirms the superiority of the bound product.

Figure 13 shows the change in tear strength of the vulcanizates before and after ageing, this again shows that bound antioxidants can improve the ageing resistance of NR compounds.

Figure 14 shows the variation in modulus of the vulcanizates before and after ageing. The increase in modulus after 48 h ageing may be partially due to co-crosslinking of the chemically bound antioxidant with rubber and partially due to the breakdown of polysulphide linkage to disulphidic and monosulphidic linkage.

Figure 15 shows the variation of hardness of the vulcanizates before and after ageing. Hardness values of the vulcanizates containing



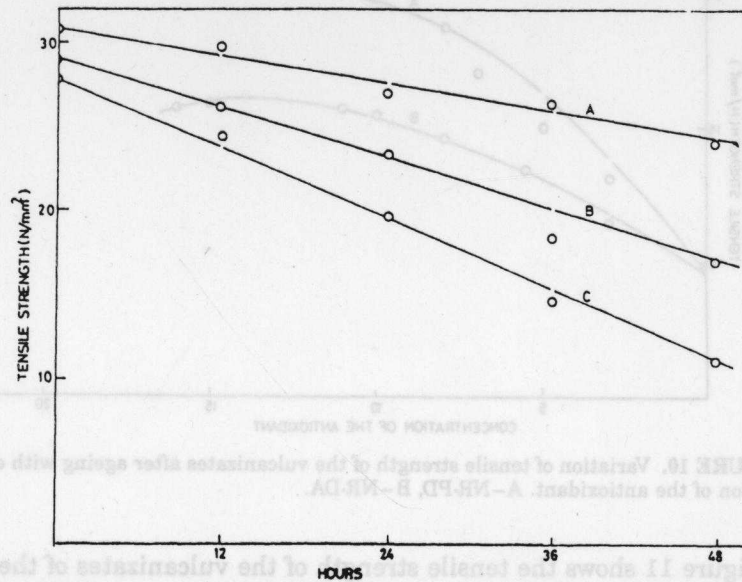


FIGURE 11. Variation of tensile strength of the vulcanizates before and after ageing. A-NR-PD, B-NR-DA, C-Vulkanox 4020.

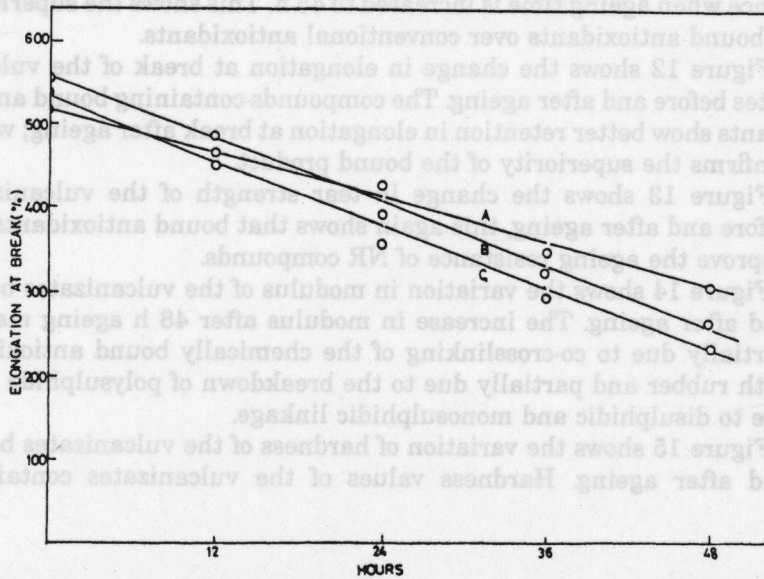


FIGURE 12. Variation of elongation at break of the vulcanizates before and after ageing. A-NR-PD, B-NR-DA, C-Vulkanox 4020.

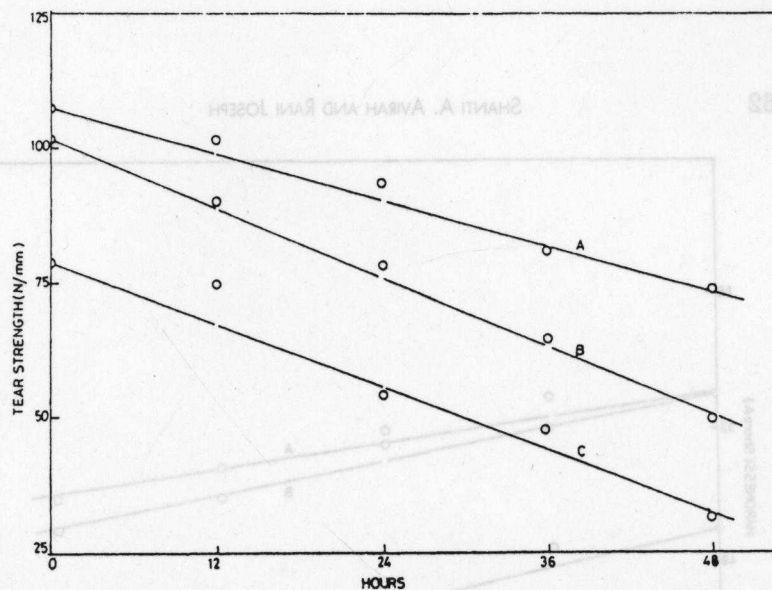


FIGURE 13. Variation of tear strength of the vulcanizates before and after ageing. A-NR-PD, B-NR-DA, C-Vulkanox 4020.

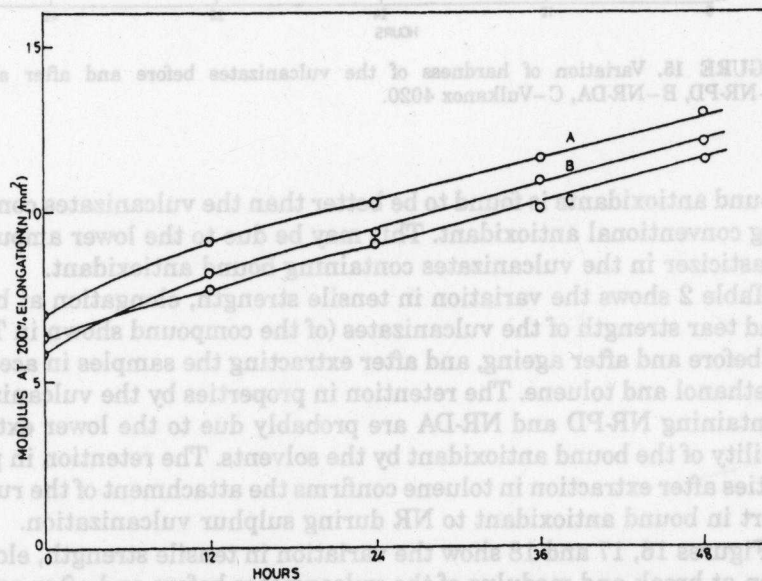


FIGURE 14. Variation of modulus of the vulcanizates before and after ageing. A-NR-PD, B-NR-DA, C-Vulkanox 4020.

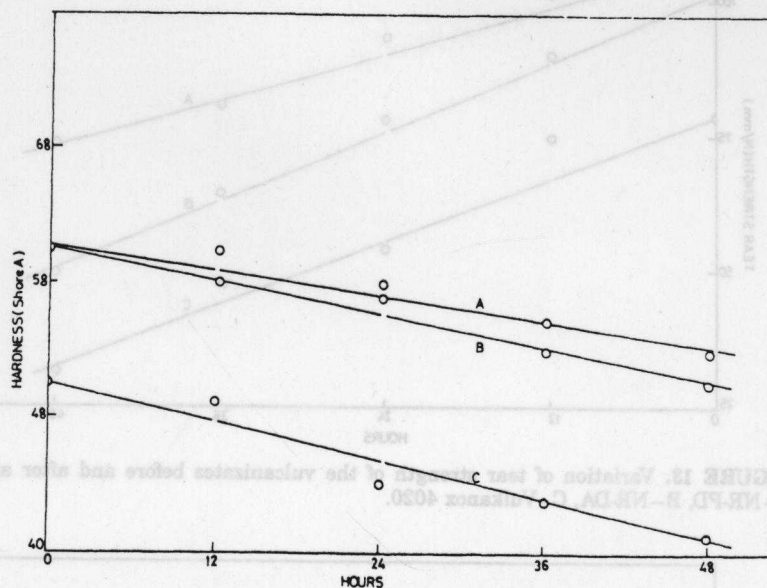


FIGURE 15. Variation of hardness of the vulcanizates before and after ageing. A-NR-PD, B-NR-DA, C-Vulkanox 4020.

bound antioxidants is found to be better than the vulcanizates containing conventional antioxidant. This may be due to the lower amount of plasticizer in the vulcanizates containing bound antioxidant.

Table 2 shows the variation in tensile strength, elongation at break and tear strength of the vulcanizates (of the compound shown in Table 1) before and after ageing, and after extracting the samples in acetone, methanol and toluene. The retention in properties by the vulcanizates containing NR-PD and NR-DA are probably due to the lower extractability of the bound antioxidant by the solvents. The retention in properties after extraction in toluene confirms the attachment of the rubber part in bound antioxidant to NR during sulphur vulcanization.

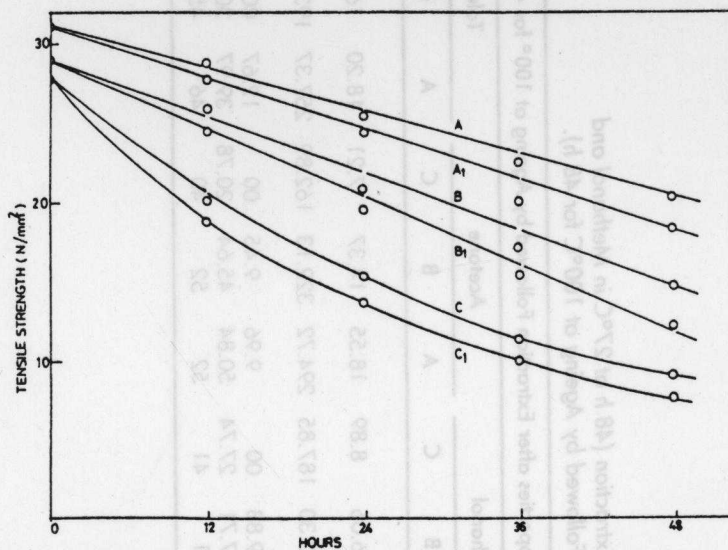
Figures 16, 17 and 18 show the variation in tensile strength, elongation at break and modulus of the vulcanizates before and after ageing and after extraction in dilute HCl and dilute NaOH. The retention in properties shown by compounds containing bound antioxidant may be due to its resistance to leaching in acidic and alkaline medium.

Table 3 shows the properties resilience, heat build up, flex crack resistance, and compression set of the vulcanizates of the compound shown in Table 1 before and after ageing. The retention in these proper-

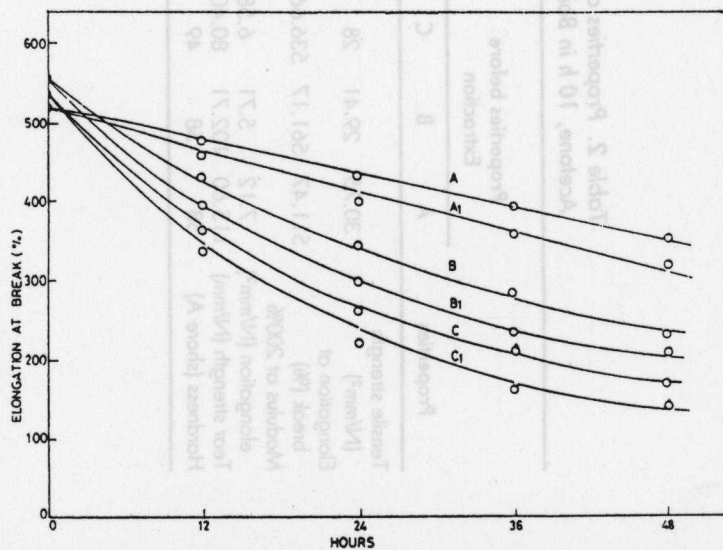


Table 2. Properties after Solvent Extraction (48 h at 27°C in Methanol and Acetone, 10 h in Boiling Toluene Followed by Ageing at 100°C for 48 h).

Properties	Properties after Extraction Followed by Ageing at 100° for 48 h											
	Properties before Extraction			Methanol			Acetone			Toluene		
	A	B	C	A	B	C	A	B	C	A	B	C
Tensile strength (N/mm <sup>2</sup> )	30.75	29.41	28	20.48	16.06	8.89	18.55	14.37	7.21	18.20	16	7.04
Elongation at break (%)	511.47	561.17	536.66	306.96	312.30	187.85	294.72	322.13	162.89	257.37	193.42	188.52
Modulus at 200% elongation (N/mm <sup>2</sup> )	7.12	5.71	6.58	10.93	9.88	00	9.96	9.45	00	12.67	00	00
Tear strength (N/mm)	115.60	102.71	80.40	52.85	47.71	27.74	50.84	45.64	20.78	39.97	30.80	20.97
Hardness (shore A)	58	58	49	52	51	41	52	52	40	46	45	30



**FIGURE 16.** Variation in tensile strength of the vulcanizates before and after ageing after extraction. (a) In dilute NaOH, A-NR-PD, B-NR-DA, C-Vulkanox 4020. (b) In dilute HCl, A<sub>1</sub>-NR-PD, B<sub>1</sub>-NR-DA, C<sub>1</sub>-Vulkanox 4020.



**FIGURE 17.** Variation of elongation at break of the vulcanizates before and after ageing after extraction. (a) In dilute NaOH, A-NR-PD, B-NR-DA, C-Vulkanox 4020. (b) In dilute HCl, A<sub>1</sub>-NR-PD, B<sub>1</sub>-NR-DA, C<sub>1</sub>-Vulkanox 4020.

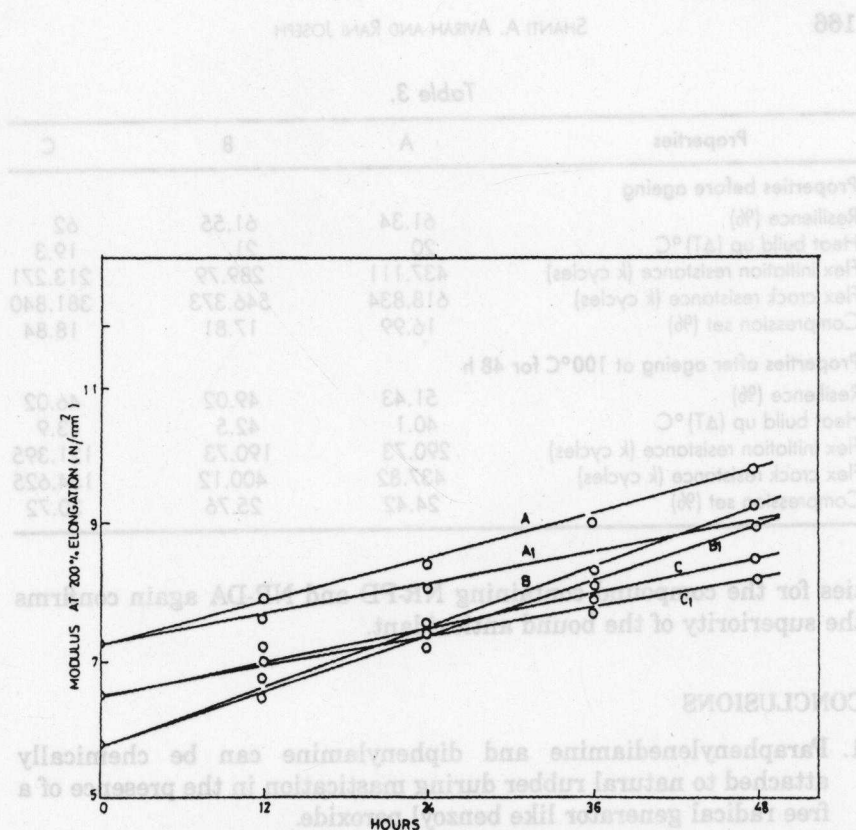


FIGURE 18. Variation in modulus of the vulcanizates before and after ageing after extraction. (a) In dilute NaOH, A-NR-PD, B-NR-DA, C-Vulcanox 4020. (b) In dilute HCl, A<sub>1</sub>-NR-PD, B<sub>1</sub>-NR-DA, C<sub>1</sub>-Vulcanox 4020.

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Table 3.

Properties	A	B	C
<b>Properties before ageing</b>			
Resilience (%)	61.34	61.55	62
Heat build up ( $\Delta T$ ) °C	20	21	19.3
Flex initiation resistance (k cycles)	437.111	289.79	213.271
Flex crack resistance (k cycles)	618.834	546.373	381.840
Compression set (%)	16.99	17.81	18.84
<b>Properties after ageing at 100°C for 48 h</b>			
Resilience (%)	51.43	49.02	46.02
Heat build up ( $\Delta T$ ) °C	40.1	42.5	43.9
Flex initiation resistance (k cycles)	290.73	190.73	121.395
Flex crack resistance (k cycles)	437.82	400.12	154.625
Compression set (%)	24.42	25.76	30.72

ties for the compound containing NR-PD and NR-DA again confirms the superiority of the bound antioxidant.

### CONCLUSIONS

1. Paraphenylenediamine and diphenylamine can be chemically attached to natural rubber during mastication in the presence of a free radical generator like benzoyl peroxide.
2. The rubber bound antioxidants have superior resistance to volatility and extractibility compared to conventional antioxidants.
3. The rubber bound antioxidants could improve the ageing resistance of the rubber vulcanizates.
4. The rubber bound antioxidant can reduce the amount of plasticizer required for compounding.

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