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Studies on rubber bound antioxidants

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SUMMARY:

Antioxidants were attached to hydroxy-terminated liquid natural rubber by modified Friedel-Crafts alkylation reaction using anhydrous zinc chloride as catalyst. The rubber bound antioxidants were found to be less volatile and less extractable compared to conventional antioxidants. The bound antioxidants were tried both in latex compounds and dry rubber compounds. The vulcanizates showed improved ageing resistance compared to vulcanizates based on conventional antioxidants.

ZUSAMMENFASSUNG:

Antioxidantien wurden in einer modifizierten Friedel-Crafts-Reaktion mit wasserfreiem Zinkchlorid als Katalysator an Flüssig-Naturkautschuk mit Hydroxy-Endgruppen gebunden. Die immobilisierten Antioxidantien waren weniger flüchtig und extrahierbar als konventionelle Antioxidantien. Sie wurden sowohl einem Latex als auch trockenem Kautschuk zugesetzt; die daraus hergestellten Vulkanisate zeigten eine bessere Alterungsbeständigkeit als Vulkanisate mit konventionellen Antioxidantien.

Introduction

The developments in product design and improvements in compounding have confirmed increased service life for dry rubber as well as latex products. The service requirements of the modern products require an effective antioxidant system. Many amine type and phenolic type antioxidants are commercially available. However, most of these antioxidants suffer from fairly high volatility and extractability in water or other fluids. The removal of the antioxidant from the polymer during service has been shown to have an adverse effect on the ageing and useful life of the product[1]. Water extraction of antidegradant is clearly a problem with rubber articles such as latex threads which are in regular contact with hot water or hot detergent solution[2,3]. One method of alleviating this problem is to attach the antioxidant chemically to

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a polymer. These polymer bound antioxidants are highly resistant to extraction[4]; they have less mobility and hence less migration to the surface and thus avoid blooming. Cain et al.[5] have shown that the mobility of antioxidants is not essential for heat ageing or oxidative ageing, but will become essential for protection against ozone attack or dynamic fatigue.

Kline and Miller[6] reported the incorporation of N-(4-anilinophenyl) methacrylamide in the polymer backbone (nitrile rubber) during manufacture. Polymerizable monomeric antioxidants were described by Tamura and coworkers[7, 8]. Folkers et al.[9] prepared a series of ortho and para substituted isoprenoid phenols by the straight-forward alkylation of phenol with isoprenoid alcohols. The most versatile method of polymer modification is direct introduction of an antioxidant function by the reaction of a conventional polymer with a suitable adduct. Cain and coworkers[10] reported the addition of nitrosophenols or aniline derivatives to produce polymer bound stabilizers. Minoura and coworkers[11] described an alkylation procedure for preparing bound diphenylamine, diaryl and alkyl p-phenylene diamines using hydroxy-terminated polybutadiene. This paper describes the alkylation of phenol, styrenated phenol (SP) and diphenylamine using hydroxy-terminated liquid natural rubber (HTNR) and the subsequent use of the product in natural rubber vulcanizates. The HTNR part gets attached to natural rubber during sulphur vulcanization and the antioxidants become non-volatile and non-extractable. The efficiency and permanence of these bound antioxidants are compared with conventional antioxidants in dry rubber and latex vulcanizates.

Experimental

Materials

Natural rubber (NR): ISNR 5 (Rubber Research Institute of India, Kottayam); the compounding ingredients zinc oxide, stearic acid, aromatic oil and carbon black (HAF N330) were of commercial grade, mercaptobenzothiazole (MBT), zinc diethyl dithiocarbamate (ZDC), zinc salt of mercaptobenzthiazole (ZMBT), styrenated phenol (Nonox SP) and substituted p-phenylene diamine (NA 4020) were of rubber grade supplied by Bayer India Ltd. Other reagents: phenol, diphenylamine (DA), anhydrous zinc chloride, o-xylene, methanol and toluene were analar grade supplied by E. Merck India Ltd. Fused calcium chloride was of commercial grade supplied by Polypharm Ltd.

HTNR was prepared in the laboratory according to the procedure outlined elsewhere[12]. The hydroxyl value of the sample was 44.1 and the molecular weight ($\bar{M}_w$) 1800.

Alkylation reaction of the antioxidants and HTNR

The antioxidants were alkylated using modified Friedel-Crafts alkylation reaction[13,14]. 150 g of HTNR (0.1 mol OH), 0.224 mol of antioxidant (phenol, SP or DA), 0.448 mol of catalyst (anhydrous zinc chloride) and 60 mol of solvent (o-xylene) were introduced into a two-necked flask fitted with a thermometer and Soxhlet extraction unit which was packed with fused $CaCl_2$. The reaction mixture was heated on a hot plate with magnetic stirring for 16 h at 145 °C. There was no appreciable degradation in the polymer during this prolonged exposure to high temperature as measured by the molecular weight measurements, probably since the atmosphere inside the set-up was not aerobic. When the reaction was complete, the reaction mixture was neutralized with sodium carbonate and washed several times with water to remove the catalyst. The content of the vessel was then poured into excess methanol with stirring to precipitate the liquid rubber. The unreacted phenol or diphenylamine was removed by repeated reprecipitation using a toluene-methanol (1:1, v/v) mixture, and the product was dried in a vacuum oven. The rubber bound antioxidant was obtained in the form of a viscous liquid.

Analysis of the rubber bound antioxidants

Analysis of the bound antioxidants was carried out using thin layer chromatography (TLC), gel permeation chromatography (GPC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy (^{1}H-NMR) and thermogravimetric analysis. The latex compounds employed for rubber bound phenolic antioxidants (phenol and SP) are shown in Tab. 1. The concentration of the bound antioxidants has been optimized. The results are not shown here. The compounds were moulded on a glass plate in the form of sheets and cured in an electrically heated laboratory oven at 125 °C for 20 min. Dumbell-shaped tensile test pieces were punched out of these sheets. 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. The ageing resistance of the vulcanizates was studied by ageing the vulcanizates for 12, 24, 36 and 48 h at 70 and 100 °C and then measuring the retention in tensile properties. The rubber bound amine antioxidant was tried in a dry rubber compound as given in Tab. 2. The optimum cure times (time to reach 90% of the maximum torque) of the compounds were determined on a Göttfert Elastograph model 67.85 as per ASTM D-1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150 °C up to their optimum cure times. Dumbell-shaped tensile test pieces were punched out of these sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated as before. The ageing resistance of the vulcanizate was studied after ageing the vulcanizate as before and compared with vulcanizates using commercial antioxidants. The extractability of the rubber bound phenolic antioxidants was studied by keeping the samples in a warm detergent solution (50 °C) for 1, 2 and 3 days and then measuring the retention in tensile properties.

Tab. 1. Latex compositions (parts by weight) for testing the bound phenolic antioxidants.

Sample	X	A	B	C
Natural rubber latex*	167	167	167	167
10% Potassium hydroxide	0.5	0.5	0.5	0.5
50% Zinc oxide	1.0	1.0	1.0	1.0
50% Zinc diethyl dithiocarbamate	1.5	1.5	1.5	1.5
50% Zinc salt of mercaptobenzothiazole	0.5	0.5	0.5	0.5
50% Sulphur	3.0	3.0	3.0	3.0
30% China clay	66	66	66	66
50% Styrenated phenol	—	2	—	—
50% HTNR-phenol	—	—	3	—
50% HTNR-SP	—	—	—	3

* 60% centrifuged latex.

Tab. 2. Rubber compositions (parts by weight) for testing the bound amine.

Sample	X	A	B
Natural rubber	100	100	100
Zinc oxide	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
Mercaptobenzothiazole	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5
Carbon black (HAF N-330)	40.0	40.0	40.0
Aromatic oil	5.0	5.0	5.0
NA 4020	—	1.0	—
HTNR-DA	—	—	3.0

TLC was carried out using silica gel as the adsorbent. A mixed solvent of benzene and ethyl acetate (4 : 1, v/v) was used as the developing solvent for all the samples while Br_2 and KI solution were used as the colour developing agents for phenolic type antioxidants, ninhydrin for the amine type and iodine for HTNR[15].

Molecular weights of the rubber bound antioxidants were measured by a gel permeation chromatograph (Waters Associates, Model 6000) employing a differential refractometer R-401.

IR spectra were taken on a Beckman spectrometer at 20 °C in a NaCl plate cell.

The NMR measurements were carried out using a Hitachi Perkin Elmer R-243 (60 MHz) model and the spectra were measured at 20 °C with 10 wt.-% solutions of the samples in CCl_4 with tetramethylsilane as the internal standard.

Thermogravimetric analysis (TGA) was carried out using a DuPont TG-DSC standard model in nitrogen atmosphere at a heating rate of 10 °C/min.

Results and discussion

Fig. 1 shows the TLC of phenol, styrenated phenol (SP), diphenylamine (DA), HTNR, phenol bound to HTNR (HTNR-phenol), styrenated phenol bound to HTNR (HTNR-SP) and diphenylamine bound to HTNR (HTNR-DA). HTNR was not coloured by Br_2 and KI or ninhydrin, but the HTNR-SP and HTNR-phenol were coloured by Br_2 and KI solution and HTNR-DA was coloured by ninhydrin. The R_f values of the HTNR-SP, HTNR-phenol and HTNR-DA are found to be different from those of SP, phenol and DA. The R_f values of the rubber bound antioxidants were found to be almost equal to the R_f value of HTNR. This confirms the alkylation of SP, phenol and DA by HTNR.

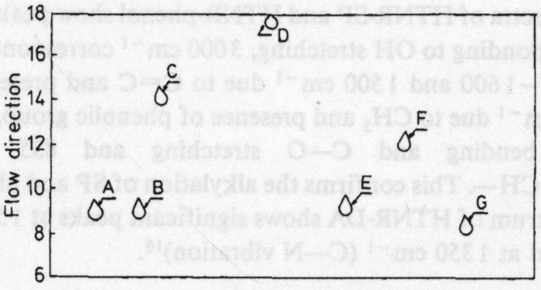

Fig. 1. TLC of compounds (A) HTNR, (B) HTNR-DA, (C) DA, (D) Phenol, (E) HTNR-phenol, (F) SP, (G) HTNR-SP.

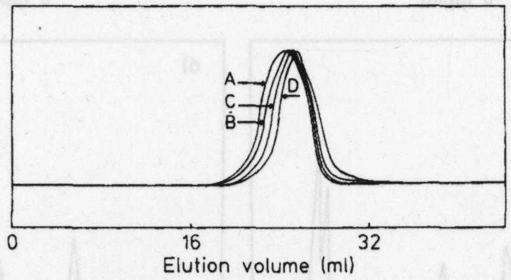

Fig. 2. GPC traces of (A) HTNR-SP, (B) HTNR-DA, (C) HTNR-phenol, (D) HTNR.

Fig. 2 shows the traces of the gel permeation chromatograms of the rubber bound antioxidants. The molecular weights of the rubber bound antioxidants HTNR-phenol ($\bar{M}_w$ = 1990), HTNR-SP ($\bar{M}_w$ = 2000) and HTNR-DA ($\bar{M}_w$ = 1996) obtained from GPC are very close to that of HTNR ($\bar{M}_w$ = 1800). This indicates that alkylation at one of the positions of the phenol and SP and one of the para positions of diphenylamine was successful.

The IR spectra of HTNR-SP and HTNR-phenol show peaks at 3600 – 3400 cm^{-1} corresponding to OH stretching, 3000 cm^{-1} corresponding to aliphatic C—H, 1665 – 1600 and 1500 cm^{-1} due to C=C and presence of aromatic ring, 1400 cm^{-1} due to CH_3 and presence of phenolic group, 1050 cm^{-1} due to O—H bending and C—O stretching and 835 cm^{-1} due to —C(CH_3)=CH—. This confirms the alkylation of SP and phenol by HTNR. The IR spectrum of HTNR-DA shows significant peaks at 1550 cm^{-1} (N—H bending) and at 1350 cm^{-1} (C—N vibration)[16].

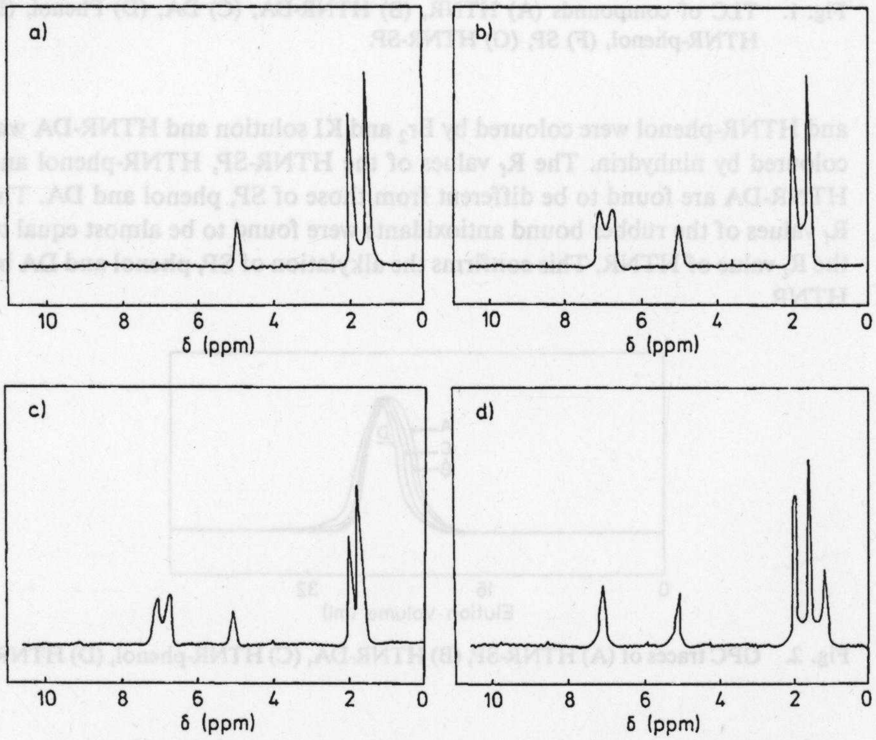

Fig. 3. ¹H-NMR spectra of (a) HTNR, (b) HTNR-SP, (c) HTNR-phenol, (d) HTNR-DA.

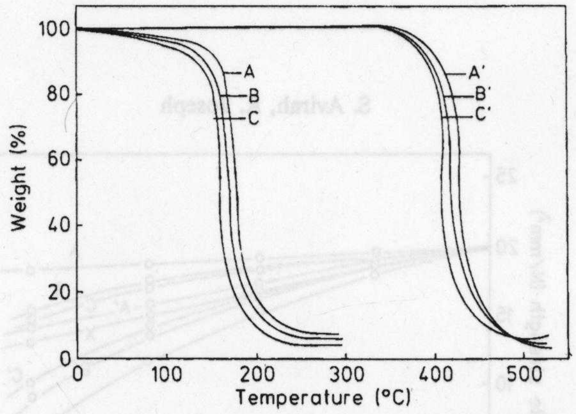

Fig. 4. Thermograms of the antioxidants; (A) SP, (B) DA, (C) phenol, (A') HTNR-SP, (B') HTNR-DA, (C') HTNR-phenol.

Fig. 3a shows the ^{1}H-NMR spectrum of HTNR. There are three peaks at $\delta = 5.1$ ($>C{=}\underset{\mathrm{H}}{C}<$), $\delta = 1.2$ (—CH_2—) and $\delta = 1.65$ ppm (—CH_3); the signal due to allylic hydroxy protons in the ^{1}H-NMR spectrum is masked by the multiplet at $\delta = 5.1$ ppm of the $>C{=}\underset{\mathrm{H}}{C}<$. Fig. 3b and 3c show the ^{1}H-NMR spectrum of HTNR-SP and HTNR-phenol, respectively, which show additional peaks at $\delta = 6.8$ and $\delta = 7.1$ ppm corresponding to the aromatic —OH group in polymer association and aromatic ring, respectively. Fig. 3d is the ^{1}H-NMR spectrum of HTNR-DA, which shows additional peaks at $\delta = 1.2$ and $\delta = 7.1$ ppm corresponding to amino group and aromatic ring present in diphenylamine.

Fig. 4 shows the thermograms of the HTNR-SP, HTNR-phenol, HTNR-DA, SP, phenol and diphenylamine. The low molecular weight conventional anti-ageing compound volatilizes easily while the HTNR bound antioxidants are much less volatile.

Fig. 5a shows the tensile strength of the vulcanizates of the compounds shown in Tab. 1 before and after ageing. All the vulcanizates show fairly good resistance to ageing at 70 °C, but only bound antioxidants show good ageing resistance when the ageing temperature is increased to 100 °C, which shows the superiority of HTNR bound antioxidants over conventional antioxidants. Fig. 5b shows the change in elongation at break of the above vulcanizates

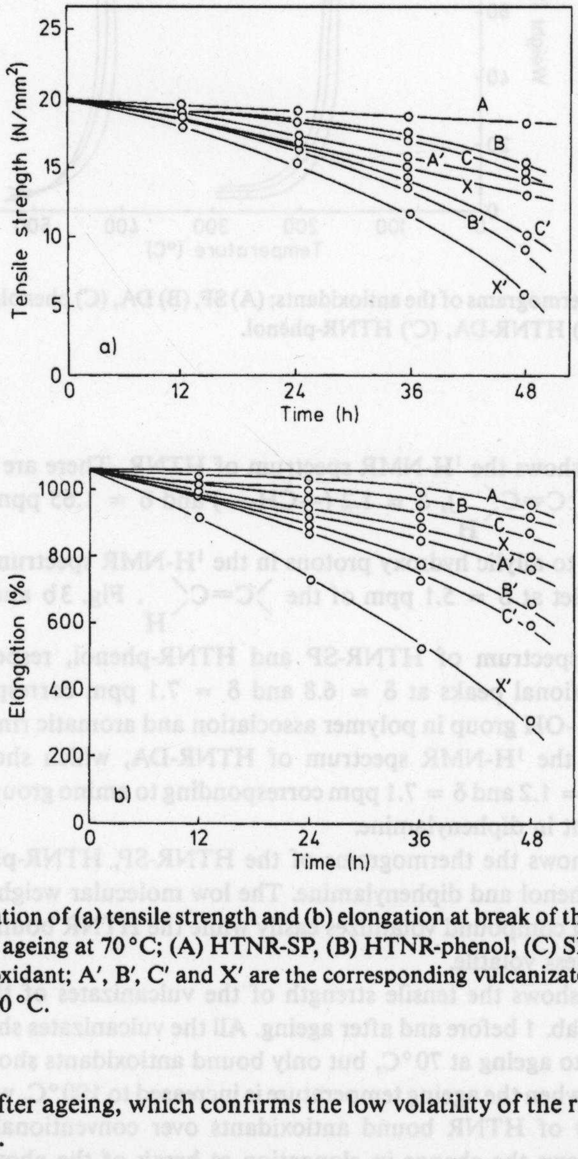

Fig. 5. Variation of (a) tensile strength and (b) elongation at break of the vulcanizates after ageing at 70 °C; (A) HTNR-SP, (B) HTNR-phenol, (C) SP, (X) without antioxidant; A′, B′, C′ and X′ are the corresponding vulcanizates after ageing at 100 °C.

before and after ageing, which confirms the low volatility of the rubber bound antioxidants.

Fig. 6a shows the variation in tensile strength of the vulanizates of the compounds shown in Tab. 2 before and after ageing. This also confirms the low volatility of the rubber bound antioxidants. Fig. 6b shows the variation in elongation at break of the above vulcanizates before and after ageing, which further confirms the superiority of rubber bound antioxidants.

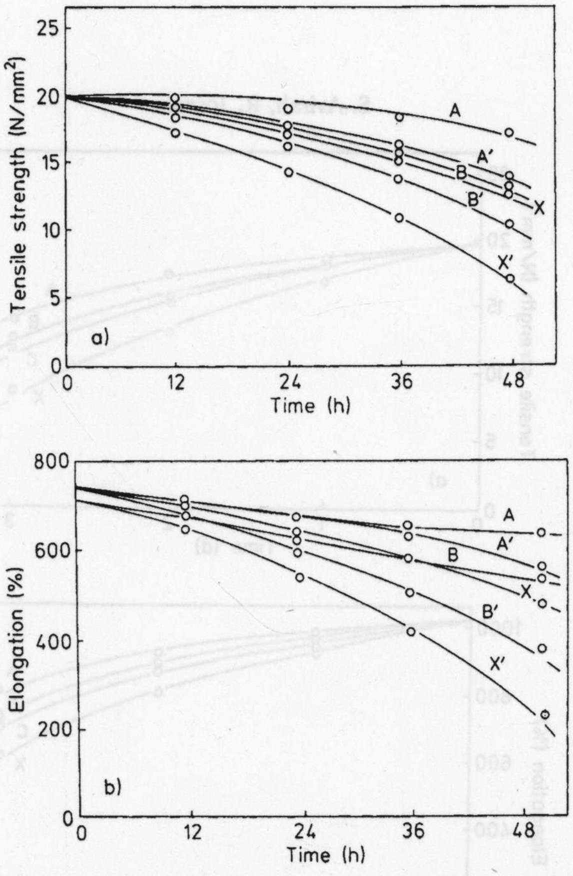

Fig. 6. Variation of (a) tensile strength and (b) elongation at break of the vulcanizates after ageing at 70 °C; (A) HTNR-DA, (B) NA 4020, (X) without antioxidant; A′, B′ and X′ are the corresponding vulcanizates after ageing at 100 °C.

Fig. 7 a and 7 b show the variation in tensile strength and elongation at break of the vulcanizates of the compounds shown in Tab. 1 after extracting the samples in warm detergent solution for 1, 2 and 3 days, respectively. The retention of the properties by the vulcanizates containing bound antioxidants is probably due to its resistance to extraction by warm detergent solution.

These results show that rubber stabilized with bound antioxidants could be used in critical applications.

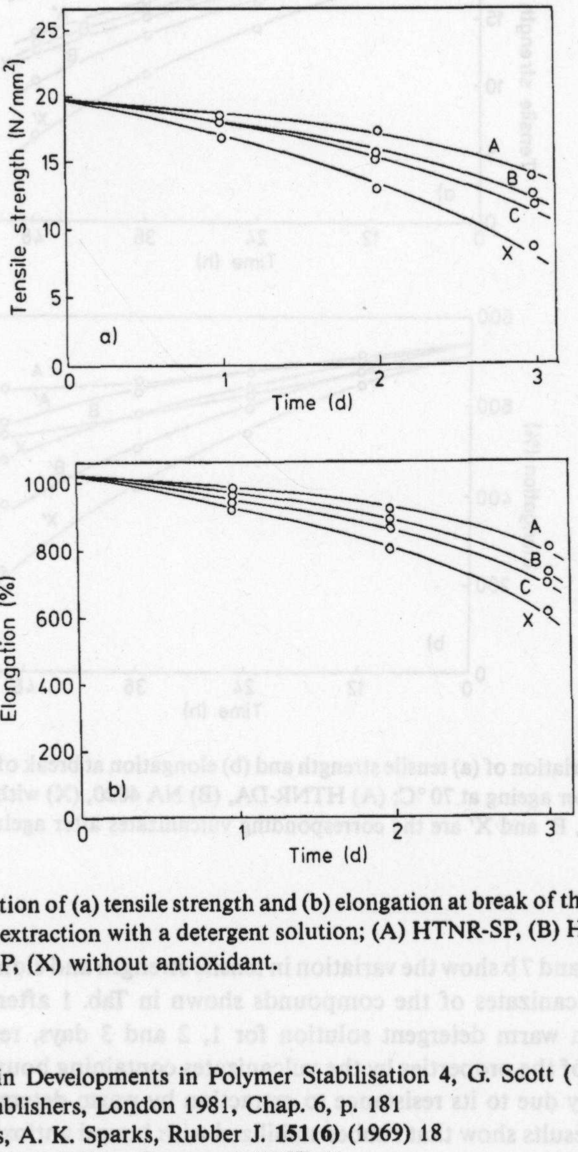

Fig. 7. Variation of (a) tensile strength and (b) elongation at break of the vulcanizates after extraction with a detergent solution; (A) HTNR-SP, (B) HTNR-phenol, (C) SP, (X) without antioxidant.

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