Inhibition of Deterioration of Rubbers by Hydroaromatics

JUNICHI KUBO

Central Technical Research Laboratory, Nippon Oil Company, Chidori-cho 8, Naka-ku, Yokohama 231, Japan

SYNOPSIS

Based on the results obtained from our previous works, which concluded that hydrogen donating hydroaromatics can be available as radical scavengers in inhibiting the deterioration of hydrocarbon products at lower oxygen partial pressure, a hydroaromatic type inhibitor which contains various hydroaromatics as its main components produced from coal tar fraction was examined by adding it to natural rubber (NR) and styrene–butadiene rubber (SBR). It was found that the inhibitor was as effective as the conventional amine-type inhibitor. From practical viewpoint, heavy hydroaromatics from petroleum (HHAP) was produced by the hydrogenation of the highly aromatic oil from the heavy fraction of petroleum to improve the physical properties of the previous inhibitor from coal tar fraction. From the deterioration tests for NR, SBR, and chloroprene (CR), the following results could be obtained: (1) HHAP showed excellent inhibiting abilities toward NR and CR, exceeding the conventional inhibitor; (2) inhibiting effect toward SBR could be recognized, but it was not so high as the conventional one; (3) physical properties such as Mooney viscosity and flex cracking were improved by the addition of HHAP. From these results, the hydrogen donation from hydroaromatics is considered to be effective in inhibiting the deterioration of rubbers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Hydroaromatics (tetralin as an example) have been considered to be easily oxidized in the conventional autoxidation studies, and their hydrogen-donating abilities have never been applied to the inhibition of the deterioration of hydrocarbon products.

On the other hand, hydroaromatics have been used as radical scavengers to reduce coke formation in coal liquefaction and heavy oil upgrading.[1-3] In view of these facts, hydroaromatics have been examined as inhibitors for the deterioration of rubbers.

The inhibiting abilities of typical hydroaromatics (tetralin and octahydrophenanthrene) toward hydrocarbon oil (lube base oil) were already studied by the thermal deterioration tests,[4-6] where the temperatures were high (350 and 395°C) and the oxygen partial pressure at the reaction sites are low, and the following results were obtained:

1. The addition of the hydroaromatics (5 wt %/ base) was obviously effective.

2. The addition of aromatics (naphthalene and phenanthrene) was not effective at all.
3. The inhibiting abilities of hydroaromatics were closely related to the hydrogen donation from the hydroaromatics.
4. The inhibiting abilities of hydroaromatics were changed by the oxygen partial pressure.

Based on these results, the synthetic hydroaromatic-type inhibitor (synthetic H/D),[7] which contains various hydroaromatics as its main components, was produced from coal tar fraction. After the hydrogen-donating ability of the synthetic H/D was confirmed, the synthetic H/D was examined as an inhibitor for NR and SBR. It was found that the synthetic H/D was as effective as a conventional amine type inhibitor; in other words, hydroaromatics are effective in inhibiting the deterioration of rubbers. Then, the physical properties (especially volatility) of the synthetic H/D were improved from practical viewpoint. Heavy hydroaromatics from petroleum (HHAP)[8,9] was produced by hydrogenating the highly aromatic heavy fraction from petroleum. HHAP has been examined by the addition to NR, SBR, and CR.

The experimental results concerning the tests of rubbers added with the synthetic H/D and HHAP are reported in this paper.

EXPERIMENTAL

First, the synthetic H/D was tested by the addition to NR and SBR. It was produced by the hydrogenation of decrystallized anthracene oil (Table I). The main properties and the main components contained in the synthetic H/D are shown in Tables II and III, respectively. The synthetic H/D contains various hydroaromatics as its main components (Table III), and it was already confirmed that the hydrogen donation from the synthetic H/D was 1.44 times of that from tetralin.

The synthetic H/D was added 2 and 5 wt % to base rubbers (NR and SBR), respectively, and the compositions of the test pieces are shown in Tables IV and V. Elongation and tensile strength after deterioration (NR: 70°C, SBR: 100°C, both in air) were measured.

Then, HHAP which was produced to improve the physical properties (especially volatility) of the synthetic H/D was tested for NR, SBR, and CR. HHAP (properties are shown in Table VII) was produced by the hydrogenation (at 350°C–400°C, 10–15 MPa, hydrogenation of aromatic carbons 55%) of highly aromatic oil (Table VIII) obtained from heavy fraction of petroleum by thermal treatment (400–500°C) and distillation. HHAP contains more than 300 components, and most of them have

Table I   Properties of Feedstock

Specific Gravity (40/4°C)	1.092
Distillation	
IBP	235°C
89.2 wt %	360°C
Elemental analysis (wt %)	
C	92.2
H	6.1
N	1.0
S	0.64
H/C (atomic ratio)	0.79
^{1}H-NMR	
Hα/H	0.819
Hα/H	0.165
Hβ/H	0.016
Hγ/H	0.000

Table II   Properties of the Synthetic Additive

Specific Gravity (15/4°C)	1.059
Flash point (coc,[a] °C)	164
Viscosity (cst)	
30°C	14.48
50°C	6.73
Pour point (°C)	−42.5
Distillation (°C)	
IBP	233
5%	257.3
50%	306.2
95%	357.3
Elemental analysis (wt %)	
C	91.2
H	8.5
N	0.3
S	< 0.01
H/C (atomic ratio)	1.11
^{1}H-NMR	
Hα/H	0.254
Hα/H	0.380
Hβ/H	0.355
Hγ/H	0.011

[a] COC = Cleveland open cup.

Table III   Main Components in the Synthetic Additive (250–400°C Fraction)

Component	Fraction (wt %)
Buthyltetralin	1.38
Diphenyl	0.77
Propyldihydronaphthalene	4.78
Acenaphthene	1.22
Tetrahydroacenaphthene	1.64
Dibenzofuran	3.16
Methyldibenzofuran	3.28
Fluorene	1.49
Methyltetrahydrofluorene	3.85
Phenanthrene and anthracene	4.39
9,10-dihydrophenanthrene	3.12
Tetrahydrophenanthrene	9.41
Octahydrophenanthrene	19.24
Octahydroanthracene	2.72
Methylphenanthrene and methylanthracene	2.01
Tetrahydrofluoranthene	1.39
Pyrene	2.44
Dihydropyrene	1.12
Hexahydropyrene	1.66

Table IV   Compositions of NR Test Pieces (wt)

Material	Sample Number 1	2	3	4
NR RSS # 3	100	100	100	100
Zinc oxide # 1	5	5	5	5
Stearic acid	1	1	1	1
HAF carbon	40	40	40	40
Vulcanization accelerator (MBTS)[a]	1	1	1	1
Vulcanization accelerator (DPG)[b]	1	1	1	0.1
Sulfur	2.5	2.5	2.5	2.5
Synthetic H/D or HHAP	0	2.0	5.0	0
Antioxidant IPPD[c,d]	0	0	0	2.0

[a] Nocceler DM produced by Ouchi Shinko Kagaku.
[b] Nocceler D produced by Ouchi Shinko Kagaku.
[c] NOCRAC 810 NA produced by Ouchi Shinko Kagaku.
[d] Comparative sample.

Table V   Compositions of SBR Test Pieces (wt)

Material	Sample Number 1	2	3	4
SBR 1502	100	100	100	100
Zinc oxide	3	3	3	3
Stearic acid	1	1	1	1
HAF carbon	40	40	40	40
Vulcanization accelerator (CBS)[a]	1	1	1	1
Sulfur	1.75	1.75	1.75	1.75
Synthetic H/D or HHAP	0	2.0	5.0	0
Antioxidant IPPD	0	0	0	2.0

[a] Nocceler CZ produced by Ouchi Shinko Kagaku.

Table VI   Compositions of CR Test Pieces (wt)

Material	Sample Number 1	2	3	4
CR WRT	100	100	100	100
Zinc oxide	5	5	5	5
MgO # 150	4	4	4	4
Stearic acid	0.5	0.5	0.5	0.5
Vulcanization accelerator (EU)[a]	0.5	0.5	0.5	0.5
FEF carbon	40	40	40	40
HHAP	0	2	5	0
Antioxidant IPPD	0	0	0	2

[a] Nocceler 22 produced by Ouchi Shinko Kagaku.

partly hydrogenated products of condensed aromatic rings (five rings in a molecule, on average). It is a mixture of heavy hydrocarbons with average molecular weight 398, odorless yellowish brown in color, and in solid/liquid state at room temperature.

Prior to the addition of HHAP into rubbers, the

Table VII   Properties of Heavy Hydroaromatics from Petroleum (HHAP)

Density (15°C, g/cm³)	1.028
Viscosity (100°C, cst)	25.36
Carbon residue (wt %)	1.15
Pour point (°C)	27.5
Flash point (°C)	234
Elemental analysis (%)	
C	89.7
H	10.1
S	0.08
N	—
H/C (atomic ratio)	1.35
Average molecular weight	398
Refractive index	1.5978
Distillation (°C)	
IBP/5%	348/374
10/30	385/420
50/70	447/478
90/EP	525/584
Composition	
Saturates	21.3
Aromatics	78.7
¹H-NMR of aromatics	
Hα/H	0.16
Hα/H	0.30
Hβ/H	0.37
Hγ/H	0.17
fa (partition of aromatic carbons)	0.38

inhibiting ability of HHAP was examined by the thermal deterioration test (350°C, 72 h) already reported.[4-6] The addition of 5 wt % of HHAP to lube base oil (SAE-50) was tested with the condition that the gas phase was completely replaced with nitrogen

Table VIII   Properties of Highly Aromatic Oil before Hydrogenation

Density (15°C, g/cm³)	1.10
Viscosity (100°C, cst)	150
Elemental analysis	
C	91.1
H	7.9
S	0.6
H/C (atomic ratio)	1.04
Average molecular weight	374

and the liquid phase was purged by nitrogen for 20 min prior to the heating.

HHAP was added 2 and 5 wt % to base rubbers (NR, SBR, and CR), respectively, and the compositions of the test pieces are shown in Tables IV–VI.

Aging tests (deterioration tests) and Mooney viscosity tests for NR, SBR, and CR, cycle tests, flex cracking tests, and contamination tests for NR and SBR by the addition of HHAP were conducted. Testing conditions are summarized in Table IX. A conventional inhibitor (IPPD, phenylisopropyl-p-phenylenediamine) was examined at the same time for the comparison.

RESULTS

Inhibition of Deterioration of Rubbers by Synthetic H/D[10]

From the results of the tests for NR at 70°C (Figs. 1 and 2), it can be seen that the effects on preservation of elongation and tensile strength by the addition of the synthetic H/D are obvious. Compared with the results of the addition of IPPD, the addition of the synthetic H/D is as effective as that of IPPD.

Table IX   Conditions of the Tests

Tests for Unvulcanized Rubbers	
Mooney viscosity test	
Method	JIS K6300
Conditions	ML_{1+4} (100°C)

| Tests for Vulcanized Rubbers	
(1) Properties	
Hardness	"A" type hardness tester
Specimen	Dumbbell # 3
Tester	Loadcell, capacity 50 kgf
Tensile speed	500 mm/min
(2) Aging tests	
Tester	Gear type tester
Conditions	70°C × 24, 47, 72, 168 h (NR)
	100°C × 24, 48, 72, 168 h (SBR)
	120°C × 72, 96, 168 h (CR)
(3) Cycle tests	
Tester	Gear type tester (for aging)
Oil	Isooctane (for dipping)
(4) Flex cracking test	
Tester	De Mattia type (with notch)
	Number of bending from 2 to
Judgment	12 mm of crack
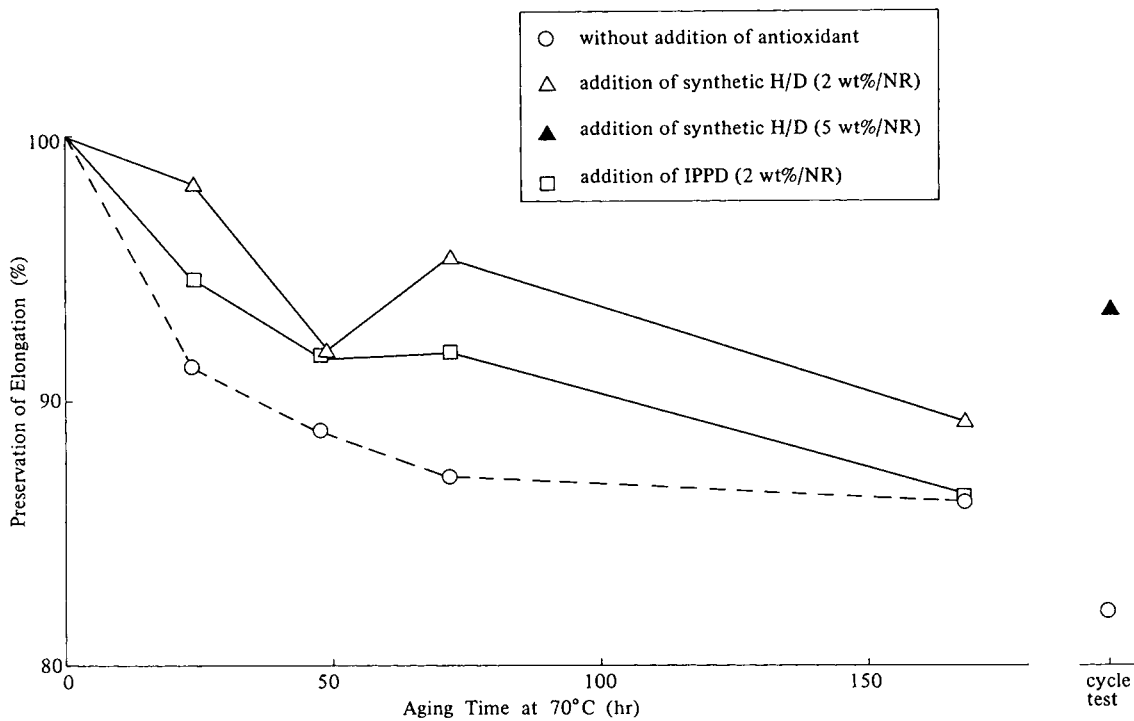
Figure 1   Effects of the addition of synthetic H/D on preservation of elongation (NR).
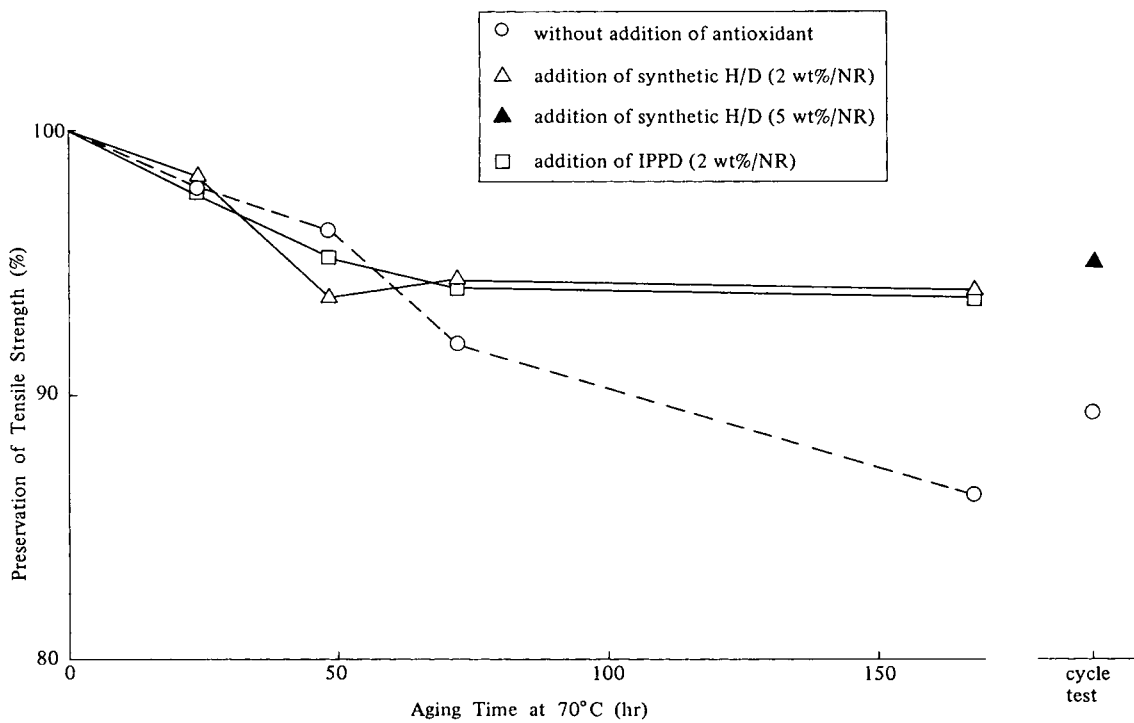

Figure 2   Effects of the addition of synthetic H/D on preservation of tensile strength (NR).
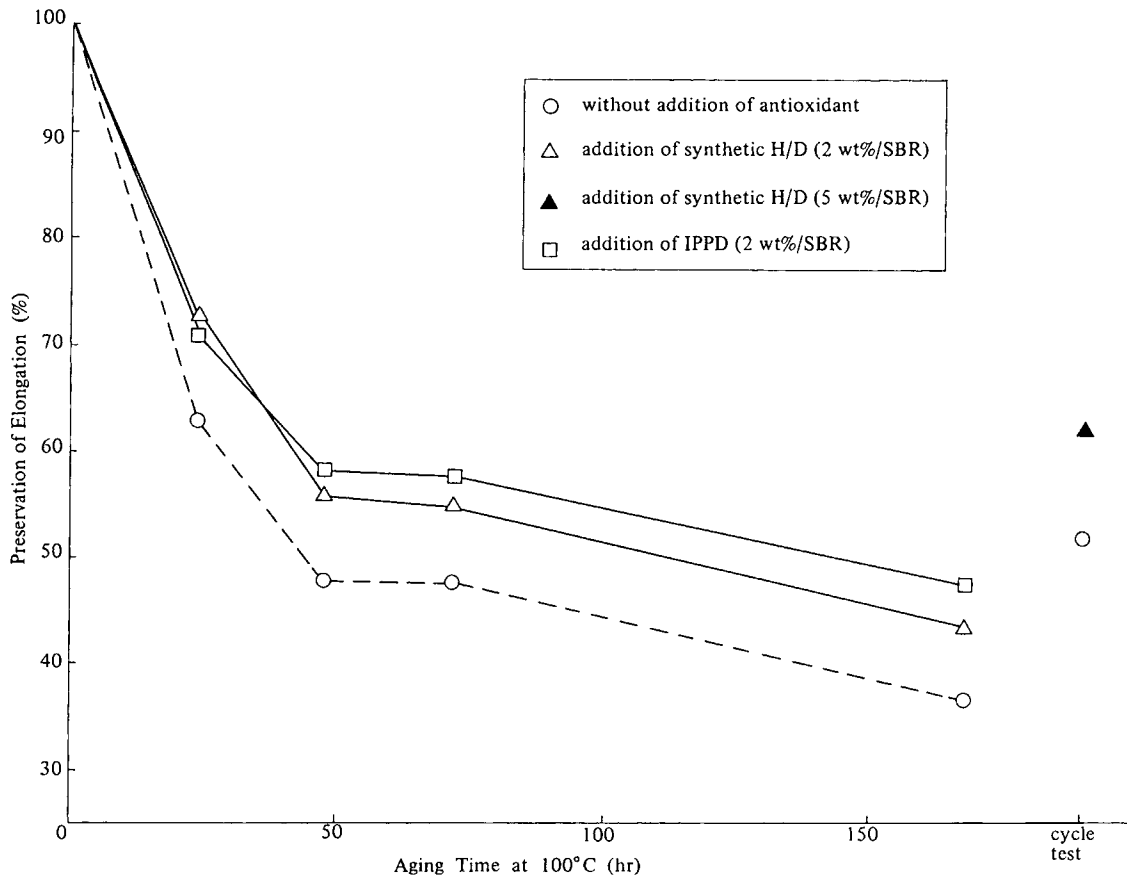
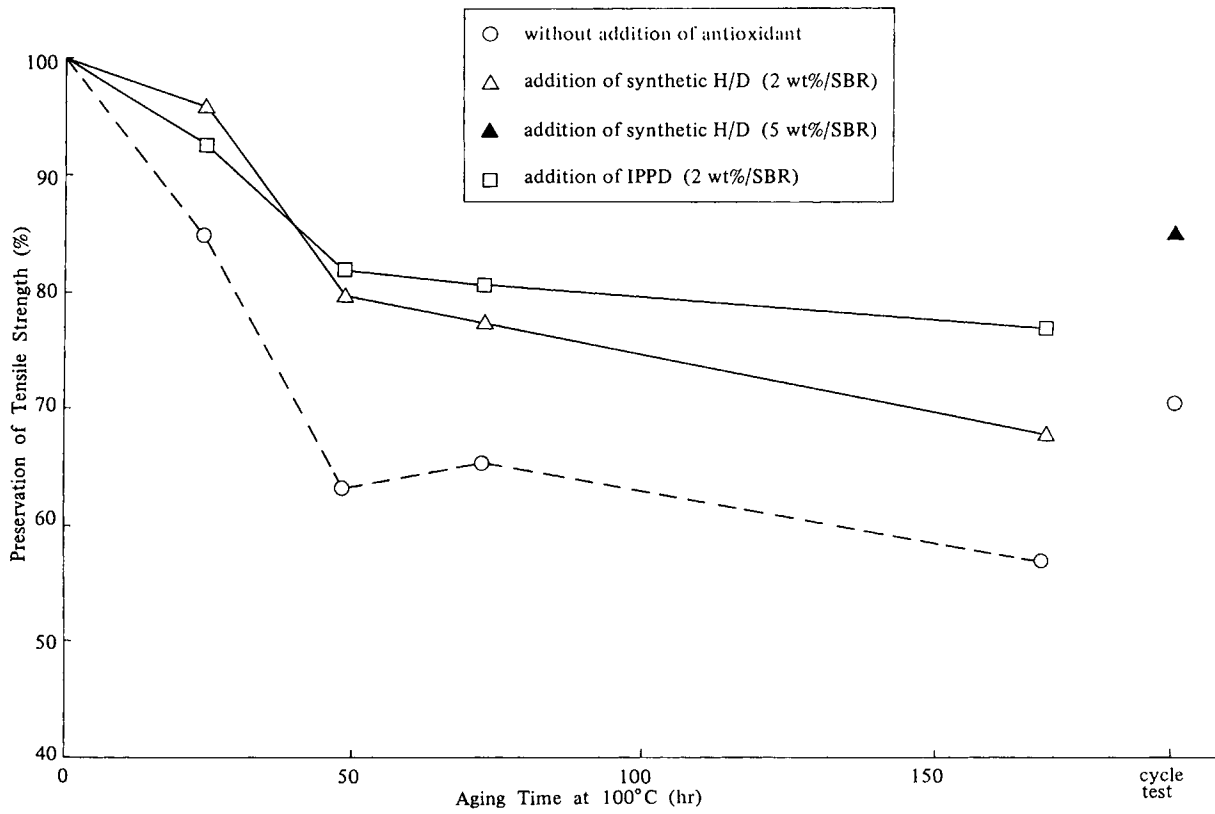**Figure 3** Effects of the addition of synthetic H/D on preservation of elongation (SBR).

Figure 4 Effects of the addition of synthetic H/D on preservation of tensile strength (SBR).

From the results of the tests for SBR at 100°C by the addition of the synthetic H/D and IPPD (Figs. 3 and 4), the effects of the addition of the synthetic H/D can be recognized; however, they are not so effective as the addition of IPPD, and the effects of the synthetic H/D for SBR are not so high as for NR.

The synthetic H/D has various hydroaromatics as its main components (Table III), and the inhib-

iting ability of the synthetic H/D can be attributed to the hydrogen donation from hydroaromatics.

Inhibition of Thermal Deterioration by HHAP

From the photo (Fig. 5) showing the samples before and after the tests, it can be observed that HHAP has an excellent inhibiting ability toward the thermal deterioration of lube base oil.

Sample
after the test
$\left(\begin{array}{l}\text{HHAP 5.0 wt\%}\\ \text{addition}\end{array}\right)$

Sample before
the test
$\left(\begin{array}{l}\text{HHAP 5.0 wt\%}\\ \text{addition}\end{array}\right)$

Sample after the test
(without addition)

Sample before the test
(without addition)
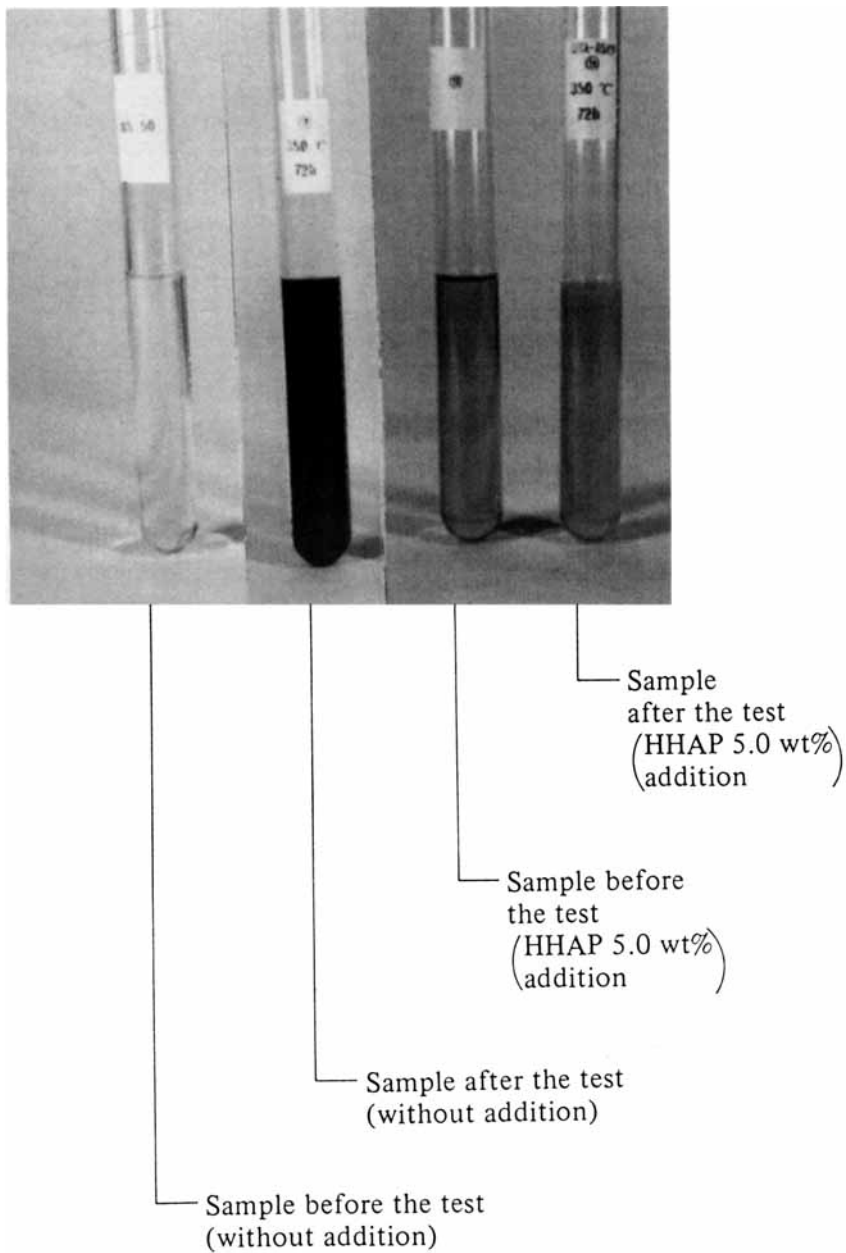
Figure 5 Samples before and after the thermal deterioration test (350°C, 72 h).
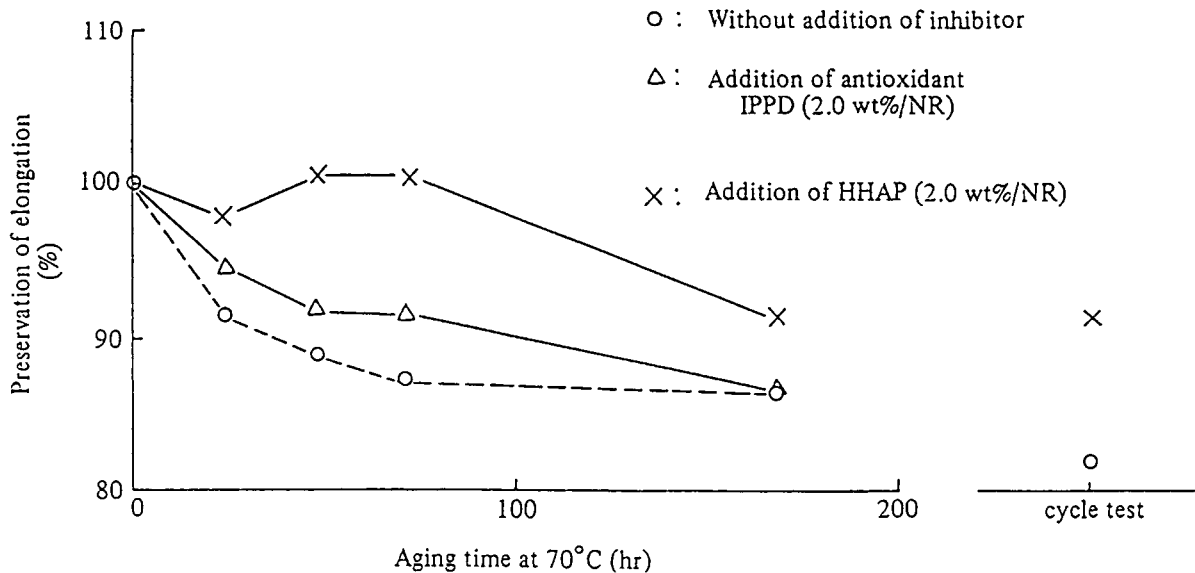
Figure 6 Effects of the addition of HHAP on preservation of elongation (NR).

Inhibition of Deterioration of Rubbers by HHAP

From the results of the aging tests for NR (Figs. 6 and 7), SBR (Figs. 8 and 9), and CR (Figs. 10 and 11), the following can be understood:

1. Excellent inhibiting ability of HHAP exceeding the conventional inhibitor (IPPD) was found for NR and CR.
2. The inhibiting ability of HHAP toward SBR

was recognized, but it was lower than that of IPPD.

From cycle tests, the following results could be obtained;

1. The inhibiting ability of HHAP toward NR was prominent (Figs. 6 and 7).
2. The inhibition by HHAP toward SBR was not so effective as for NR (Figs. 8 and 9).
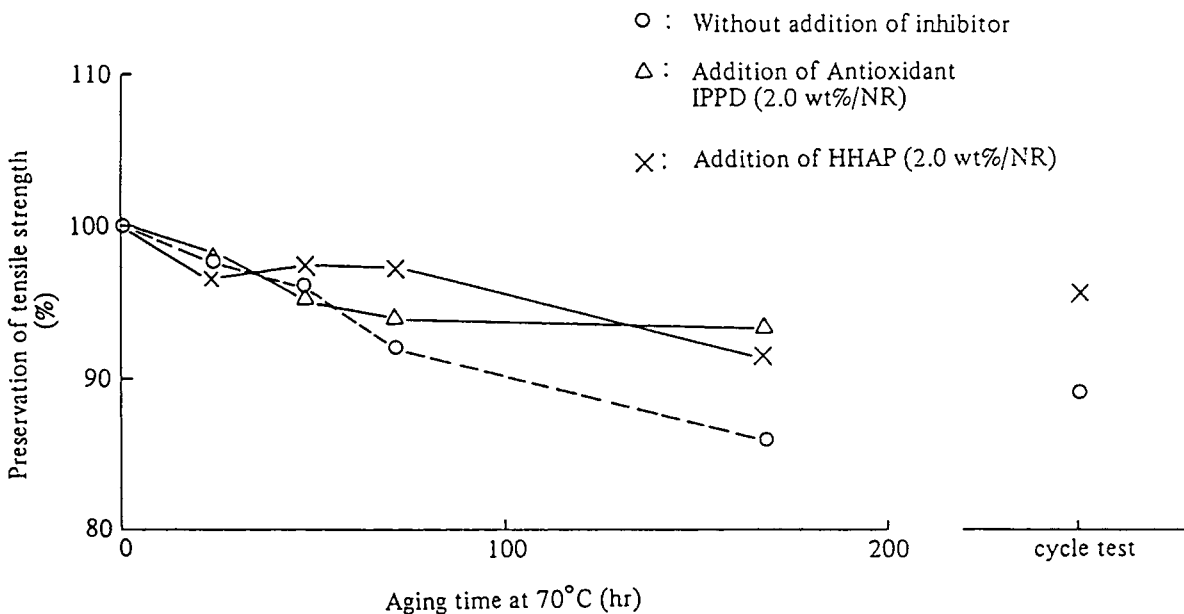
Figure 7 Effects of the addition of HHAP on preservation of tensile strength (NR).
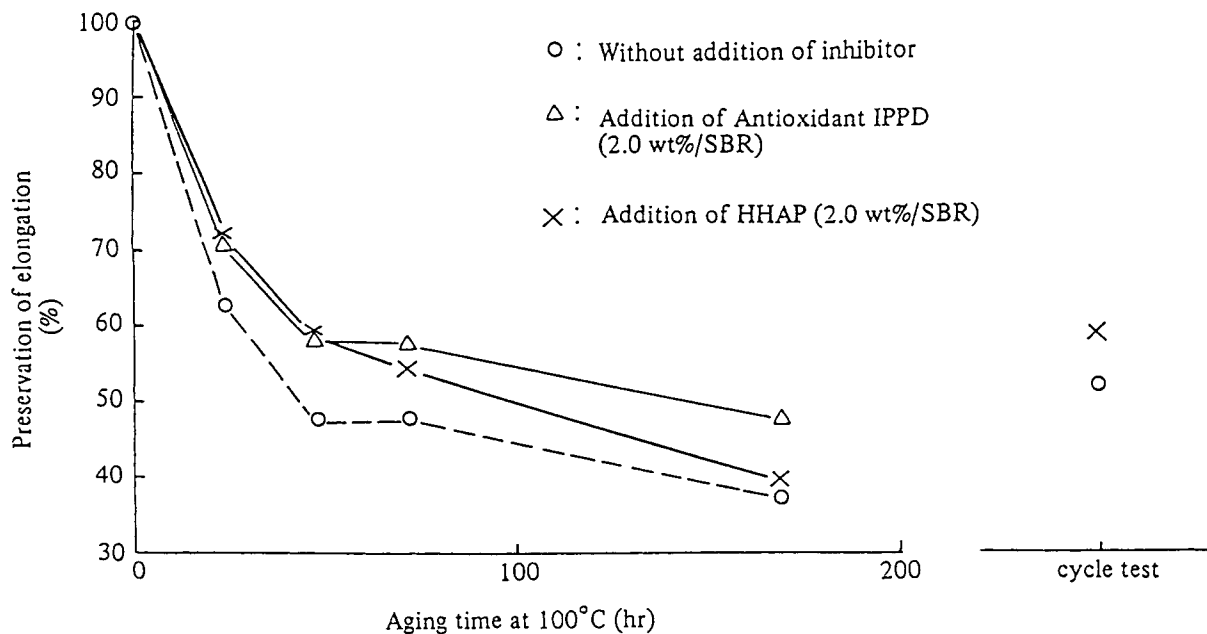
Figure 8   Effects of the addition of HHAP on preservation of elongation (SBR).

It is obvious that HHAP has a prominent inhibiting ability toward the deterioration of rubbers, especially for NR and CR from these results, and the inhibiting ability can be attributed to the hydrogen donation from HHAP.

Mooney Viscosities

Changes of Mooney viscosities of NR and SBR by adding HHAP were examined (Table X) and found that Mooney viscosities were lowered by the addition
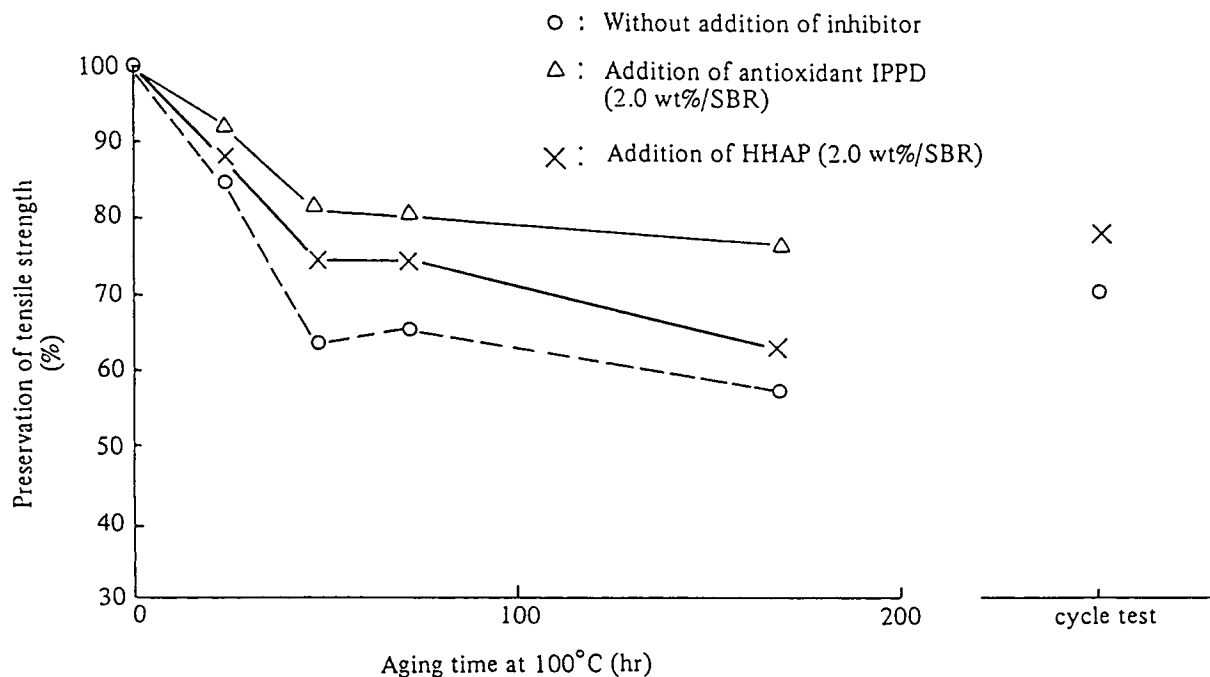

Figure 9   Effects of the addition of HHAP on preservation of tensile strength (SBR).
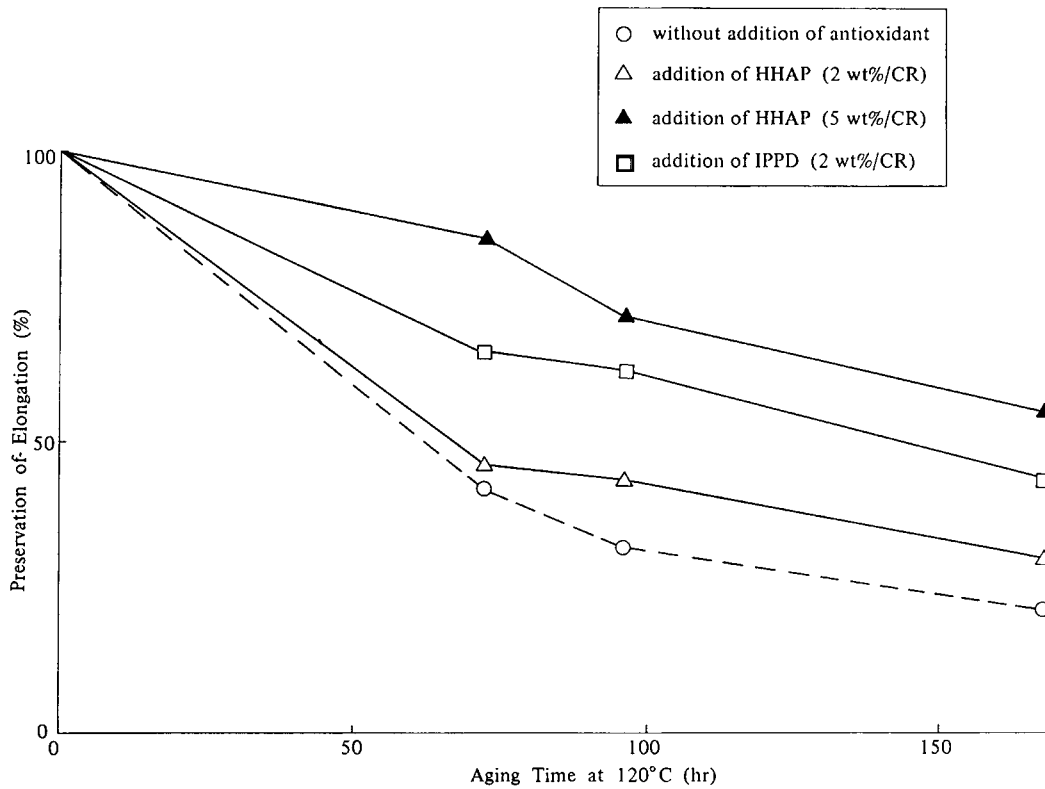
Figure 10 Effects of the addition of HHAP on preservation of elongation (CR).
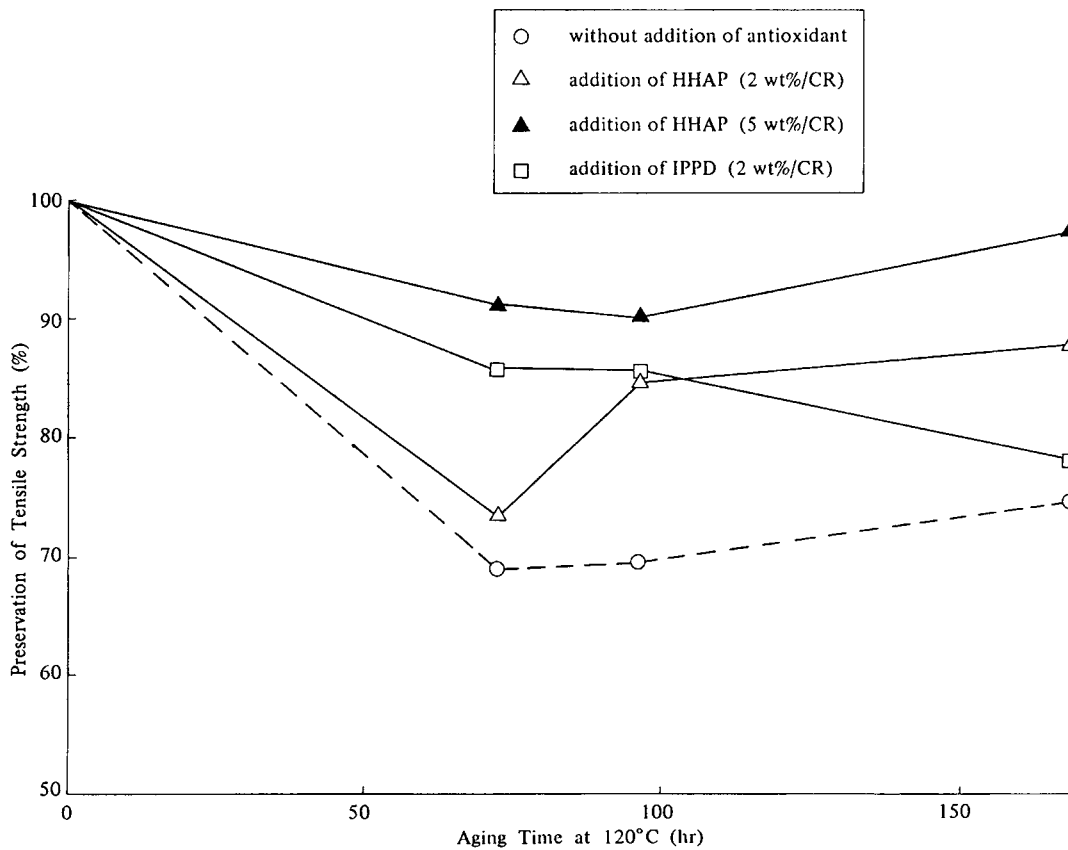

Figure 11 Effects of the addition of HHAP on preservation of tensile strength (CR).

of HHAP. HHAP is expected to be available as softners for rubbers.

Flex Cracking

It was found that the flex cracking was remarkably improved by the addition of HHAP (Table XI).

Contamination

A slight contact staining was observed on the addition of 5 wt % of HHAP, but no staining could be found in other cases. Staining can be expected to be low because of HHAP's pure hydrocarbon constituent.

DISCUSSION

Hydrogen-donating hydroaromatics have never been applied as inhibitors to the deterioration of rubbers. In conventional autoxidation studies, hydroaromatics (tetralin, for example) have been considered to be easily oxidized.[11-13] However, most of the experiments involving hydroaromatics have been conducted at high oxygen partial pressures at the reaction sites to exclude the effects of oxygen partial pressure. There have been some experiments conducted at lower oxygen partial pressure to investigate the effects of oxygen partial pressure on oxidation reaction rate[14,15]; however, the reaction pathways of hydroaromatics at lower oxygen partial pressure have not yet been clarified.

As reported in our previous papers,[4-6] it was found that hydrogen donation from hydroaromatics (tetralin and octahydrophenanthrene) are obviously effective in inhibiting the deterioration of hydrocarbons, where oxygen partial pressure at the reaction sites is low, and that the inhibiting abilities

Table X   Mooney Viscosities

Polymer / Addition of Inhibitors	Mooney Viscosity ML_{1+4} (100°C)	
	NR	SBR
None	40	67
HHAP		
2.0 wt %/NR & SBR	33	67
5.0 wt %/NR & SBR	—	61
Antioxidant		
2.0 wt %/NR & SBR	46	64
5.0 wt %/NR & SBR	45	58

Table XI   Flex Cracking Tests for NR

Sample No.	1	2	3	4	5
Number of bending	6500	11,000	17,000	9700	12,000

of the hydroaromatics are changed by oxygen partial pressure. In other words, reaction pathways of hydroaromatics at lower oxygen partial pressure can be considered to be similar to the ones in coal liquefaction and heavy oil upgrading:
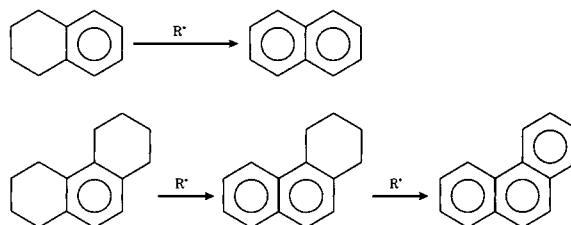
Based on these results, synthetic H/D which contains various hydroaromatics as its main components was tested, and obvious effects could be confirmed by the practical deterioration tests. From these consequences, it can be considered that the hydrogen-donating abilities of hydroaromatics can be applicable to the inhibition of the deterioration of rubbers. However, the physical properties, especially volatility, of the synthetic H/D was proved to be improved, and HHAP of higher molecular weight was produced from heavy fraction of petroleum.

HHAP contains many more components than the synthetic H/D, and their chemical structures are more complicated. It is very difficult to clarify the chemical structure of the individual component; however, it is evident that HHAP has excellent inhibiting ability toward rubbers, which can be attributed to the hydrogen donation from HHAP.

The reason why the hydrogen-donating abilities of hydroaromatics can be applicable to rubbers is as follows: In rubbers, the oxygen partial pressure at the reaction sites can be estimated to be very low because the diffusion coefficient of oxygen in rubbers is very low, reported to be 2×10^{-6} cm s at 30°C,[16] and the permeability of oxygen in rubbers was reported to be 18×10^{-13} cm s Pa^{-1} (NR, 25°C).[17] Therefore, hydroaromatics exhibit their inhibiting abilities against the deterioration of rubbers.

The reason for the difference in the effects of HHAP among NR, CR, and SBR cannot be made

clear yet. It can be supposed that the difference is dependent on the chain reactions in these rubbers, but it is not certified. The relation between the effect of hydroaromatics and the chemical structure of the base rubber should be the problem to be investigated.

Conclusively, the hydrogen-donating abilities of hydroaromatics were confirmed to be available as radical scavengers toward the deterioration of rubbers, and various possibilities can be expected from these results.

CONCLUSION

Hydrogen-donating hydroaromatics were applied to the inhibition of the deterioration of rubbers, and the following results could be obtained:

1. The synthetic inhibitor containing various hydroaromatics as its main components produced from coal tar fraction was found to be as effective as the conventional amine-type inhibitor (IPPD).
2. Heavy hydroaromatics (HHAP) was produced by the hydrogenation of highly aromatic oil from petroleum to improve the physical properties of the synthetic hydroaromatics from coal tar fraction. It was confirmed that HHAP has prominent inhibiting abilities toward rubbers, especially NR and CR.
3. It was found that the hydrogen-donating abilities of hydroaromatics are effective in inhibiting the deterioration of rubbers.

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