Inhibition of Deterioration of Plastics by Hydroaromatics

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SYNOPSIS

Based on our previous works concluding that the addition of hydrogen-donating hydroaromatics is effective in inhibiting the deterioration of hydrocarbons, heavy hydroaromatics from petroleum (HHAP) that were produced by hydrogenating highly aromatic heavy oil containing partly hydrogenated condensed aromatic rings were examined by the addition to high-density polyethylene (PE), isotactic polypropylene (PP), and poly(vinyl chloride) (PVC, MW: 1300) after confirming its prominent hydrogen-donating ability. The following results were obtained by the deterioration tests and melt-flow tests: (1) Clear inhibiting effects could be found on preservation of elongation and tensile strength by the addition of 0.1% and 0.5% of HHAP to PE. (2) Cross-linking of PE was restricted by the addition of HHAP. (3) Obvious effects could be found on preservation of elongation and tensile strength by the addition of 0.5% of HHAP to PP, but 0.1% of HHAP was not so effective. (4) Melt-flow rate of PP at 270°C supported the results of the deterioration tests at 120°C. (5) Color changes were remarkably improved by the addition of HHAP to PVC (at 160°C, 140 min). From these results, hydrogen donation from hydroaromatics can be considered effective in inhibiting the deterioration of PE, PP, and PVC.

INTRODUCTION

Hydroaromatics (tetralin as an example) have been considered to be easily oxidized in conventional autoxidation studies,[1-3] 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 widely used as radical scavengers to reduce coke formation in coal liquefaction and heavy oil upgrading.[4-6] In view of these facts, hydroaromatics have been examined as inhibitors of the deterioration of hydrocarbon products.

The inhibiting abilities of typical hydroaromatics (tetralin and octahydrophenanthrene) against hydrocarbon oil (lube base oil) were studied by thermal deterioration tests[7,8] where the temperature was high (350°C and 395°C) and oxygen partial pressure was low. From these results, it was confirmed that (1) the addition of hydroaromatics was obviously effective against the deterioration of hydrocarbon oil; (2) the inhibiting abilities of hydroaromatics were

closely related to the hydrogen donation from hydroaromatics; and (3) the inhibiting abilities of hydroaromatics were changed by oxygen partial pressure.

Based on these results, heavy hydroaromatics from petroleum (HHAP)[9-11] were produced by hydrogenating the highly aromatic heavy fraction from petroleum. It has already been reported[10,11] that HHAP were added to rubbers and were found effective as a conventional amine-type inhibitor.

We added HHAP to plastics such as high-density polyethylenea (PE), isotactic polypropylene (PP), and poly(vinyl chloride) (PVC, MW: 1300), and the experimental results are reported here.

EXPERIMENTAL

Properties of HHAP

HHAP (properties are shown in Table I) were produced by the hydrogenation of highly aromatic oil (Table II) that was obtained from the heavy fraction of petroleum by thermal treatment (400–500°C) and distillation. The highly aromatic oil was hydrogenated at 350–400°C, 10–15 MPa (100–150 kgf/cm^2)

Table I Properties of Heavy Hydroaromatics from Petroleum (HHAP)

Density (15°C, g/cm^3)	
Viscosity (100°C, m^2 s^{-1})	2.536×10^{-5} (25.36 cst)
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
^{1}H-NMR of aromatics	
Ha/H	0.16
Hα/H	0.30
Hβ/H	0.37
Hγ/H	0.17
fa (fraction of aromatic carbons)	0.38

in the presence of a commercial desulfurization catalyst, and the nuclear hydrogenation of the aromatic rings was about 55%.

HHAP contain more than 300 components, and, therefore, it is difficult to clarify the chemical structure of the individual components (they cannot be divided by the gas chromatographies), but it was certified that most of the components have partly hydrogenated products of condensed aromatic rings (five rings in a molecule, on average). They are a mixture of heavy hydrocarbons with an average mo-

Table II Properties of Highly Aromatic Oil before Hydrogenation

Density (15°C, g/cm^3)	1.10
Viscosity (100°C, m^2 s^{-1})	1.5×10^{-4} (150 cst)
Elemental analysis	
C	91.1
H	7.9
S	0.6
H/C (atomic ratio)	1.04
Average molecular weight	374

Table III Compositions of the Test Pieces

Components	Composition			
PE	100	100	100	100
HHAP	—	0.1	0.5	—
Irganox 1010	—	—	—	0.1
PP	100	100	100	100
HHAP	—	0.1	0.5	—
Irganox 1010	—	—	—	0.1

HHAP: heavy hydroaromatics from petroleum; PE: high-density polyethylene (density 0.963 g/cm^3); PP: isotactic polypropylene (density 0.90–0.91 g/cm^3).

Table IV Conditions of the Deterioration Tests for Polyolefins

Temperature	120°C
Replacement of the air	3 times/h
Equipment	Gear oven
Test piece	dumbbell #3
No. test pieces	1–3
Straining speed	5 mm/min
Measurement of elongation	By divider

lecular weight of 398, odorless yellowish brown, and at a solid/liquid state at room temperature.

Thermal Deterioration Test for HHAP

Prior to the addition of HHAP into plastics, the inhibiting ability of HHAP was examined by a thermal deterioration test (350°C, 72 h). The addition of 5 wt % of HHAP to lube base oil (SAE-50) was tested at an atmosphere at which the gas phase was completely replaced with nitrogen and the liquid phase was purged by nitrogen for 20 min prior to heating.

Table V Compositions of the Test Pieces (wt)

|	Sample No.			
	1	2	3	4
PVC ($\bar{P}$ = 1300)	100	100	100	100
Barium stearate	2	2	2	2
Zinc stearate	1	1	1	1
DOP[a]	50	45	40	35
HHAP	—	5	10	15

[a] Dioctylphthalate.

Deterioration Tests for Polyolefins (PE and PP)

The inhibiting effects of HHAP toward PE and PP (both produced by Nippon Petrochemical Co.) were examined. The amount of HHAP added to the base plastics was 0.1 and 0.5 wt %. The compositions of PE and PP test pieces are summarized in Table III.

The test pieces were prepared by the steps of mixing, kneading, and press. The conditions of the individual steps are as follows;

Mixing: Henshel Mixer (2500 rpm, 3 min); HHAP was dissolved in acetone or toluene.
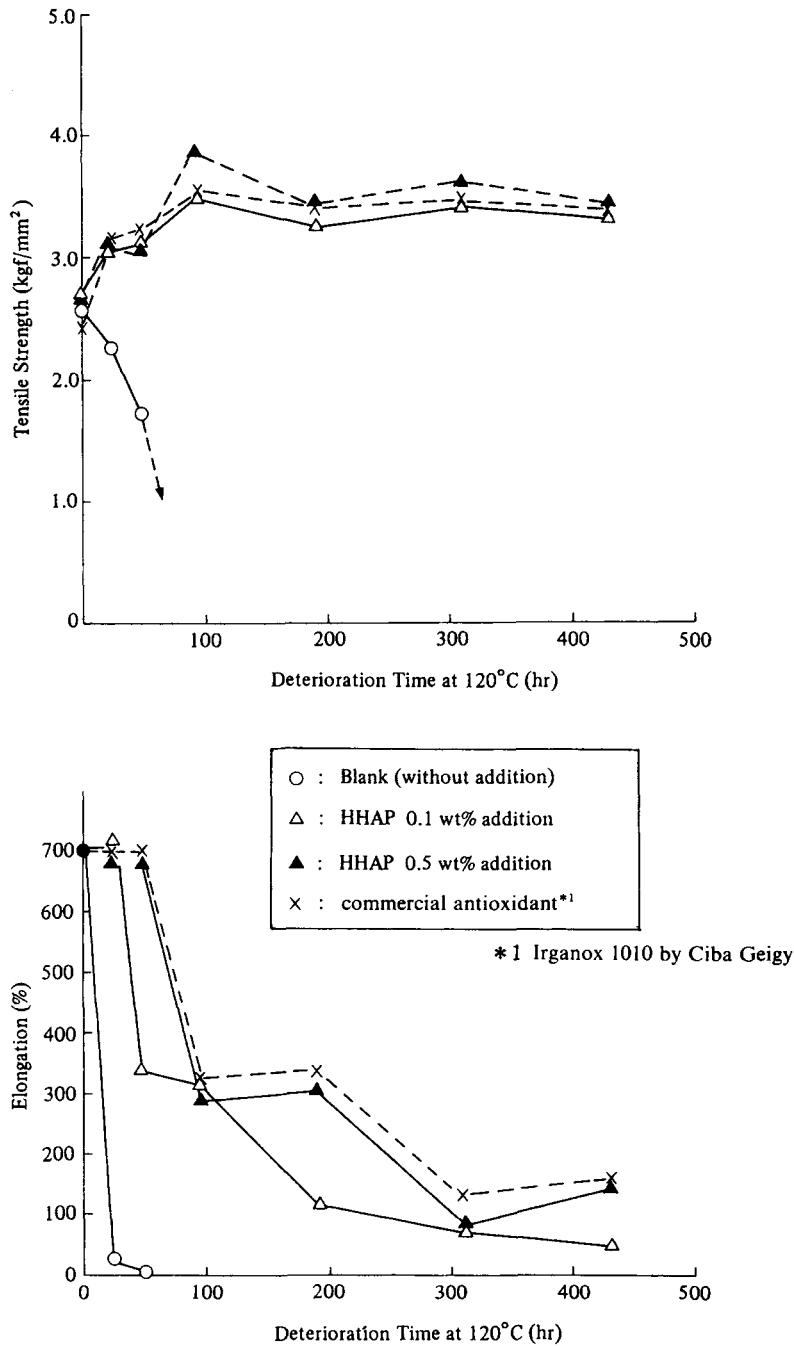
Figure 1   Effects of the addition of HHAP to high-density PE on elongation and tensile strength (120°C).

Kneading: PE 195°C; PP 210°C.

Press: PE 190°C, 3 min; PP 210°C, 2.5 min.

Deterioration tests at 120°C and 270°C (melt-flow test, according to ASTM D1238) in air were conducted on the test pieces. A commercial antioxidant (hindered phenol type) was tested at the same time for comparison. Testing conditions for PE and PP are shown in Table IV.

Deterioration Tests for PVC

Compositions of PVC test pieces are summarized in Table V. The addition of HHAP was 0, 5, 10, and 15 wt %/PVC. The test pieces were prepared by the steps of mixing, kneading (surface of the roll: 150°C), and press (preheating: 170°C, 3 min).

The properties (hardness, tensile strengths at break and 100% elongation, and elongation at break)
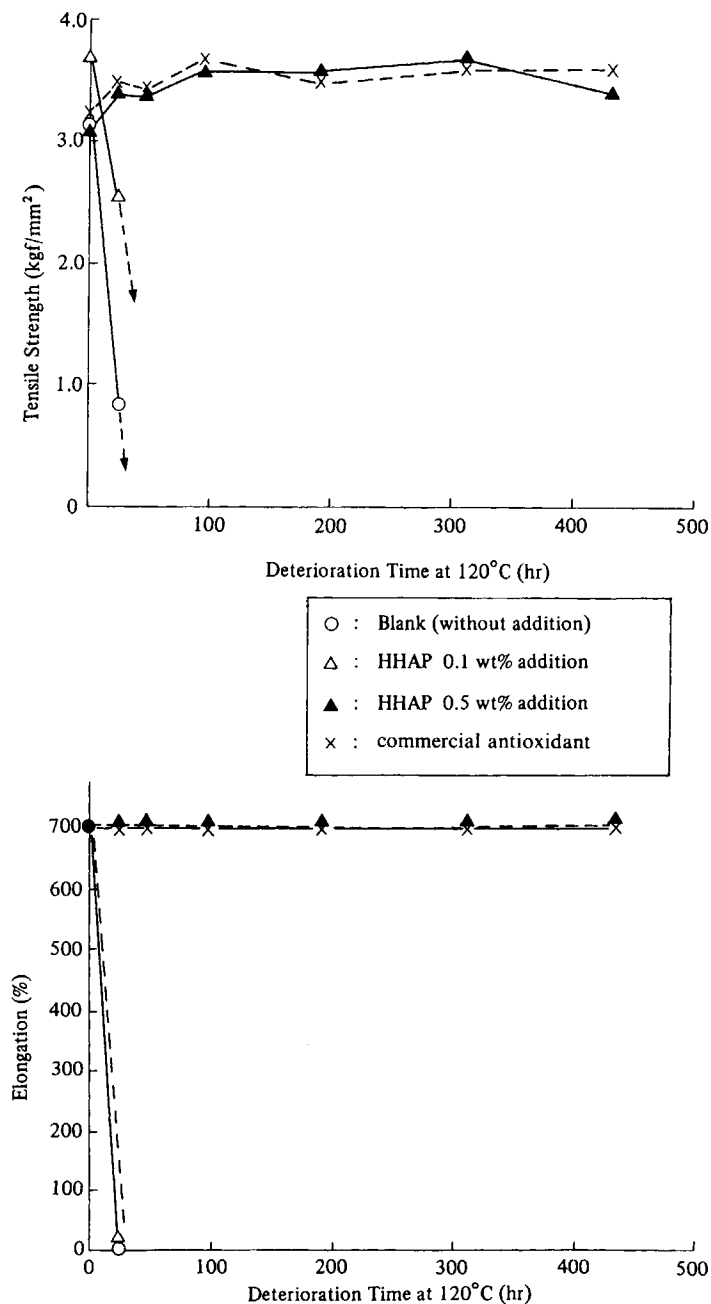
Figure 2 Effects of the addition of HHAP to isotactic PP on elongation and tensile strength (120°C).

were measured before and after the deterioration (100°C, 120 h). The colors of the test pieces before and after the deterioration (160°C, 140 min) were observed and photographed.

RESULTS

Inhibiting Ability of HHAP in Thermal Deterioration

An excellent inhibiting effect of HHAP against thermal deterioration of lube base oil was as described in a previous paper.[12] HHAP show a prominent inhibiting ability owing to their hydrogen donation.
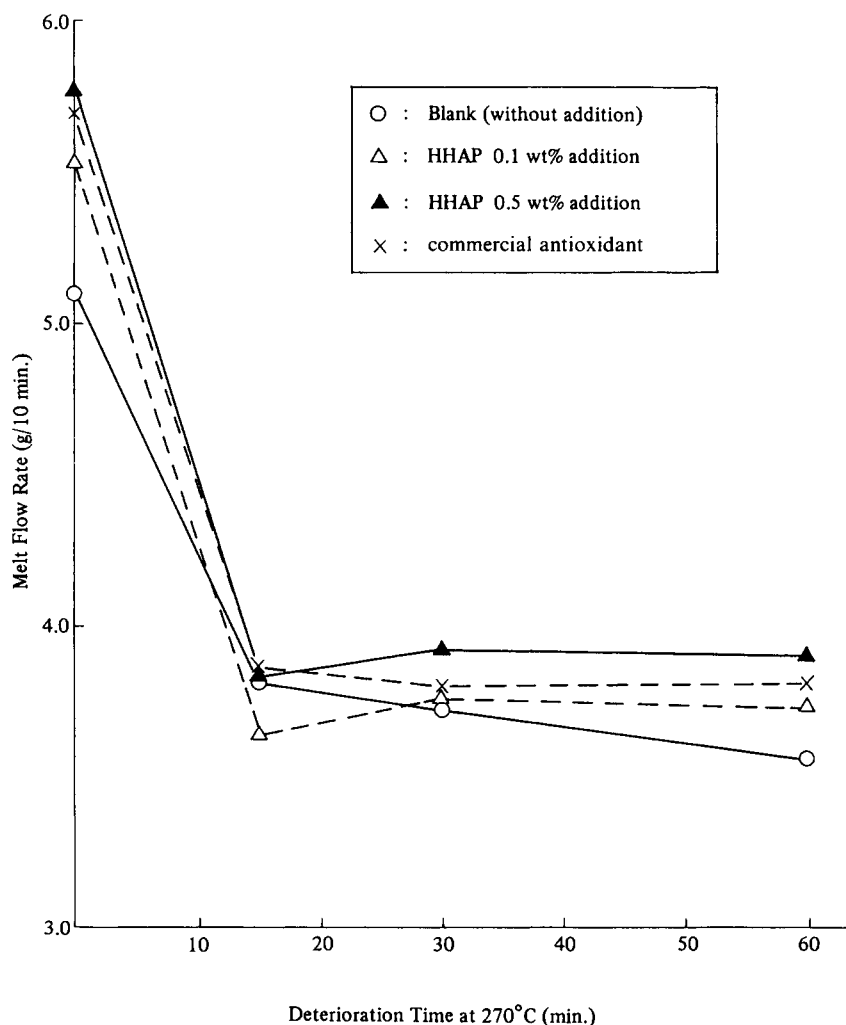
Inhibition of Deterioration of Polyolefins

Obvious effects of the addition of HHAP to PE were found on preservation of elongation at break and tensile strength at yield in the both cases of 0.1 and 0.5 wt % (Fig. 1). A distinction could be observed between 0.1 and 0.5 wt %.

The additive effects of 0.5 wt % HHAP to PP were very clear in preservation of elongation and tensile strength; however, the addition of 0.1 wt % was not so effective (Fig. 2). The addition of the conventional antioxidant (0.1 wt %) was as effective as HHAP (0.5 wt %).

The melt-flow rate (MFR) of the samples deteriorated at 270°C, as illustrated in Figures 3 and 4. The obvious effects can be observed, which are similar to the results at 120°C in the case of PP (Fig. 4). However, such clear effects cannot be found in the case of PE (Fig. 3) because of the cross-linking that occurred during the deterioration, but distinction can be observed after the time that the melt-flow rates reach to constant values.

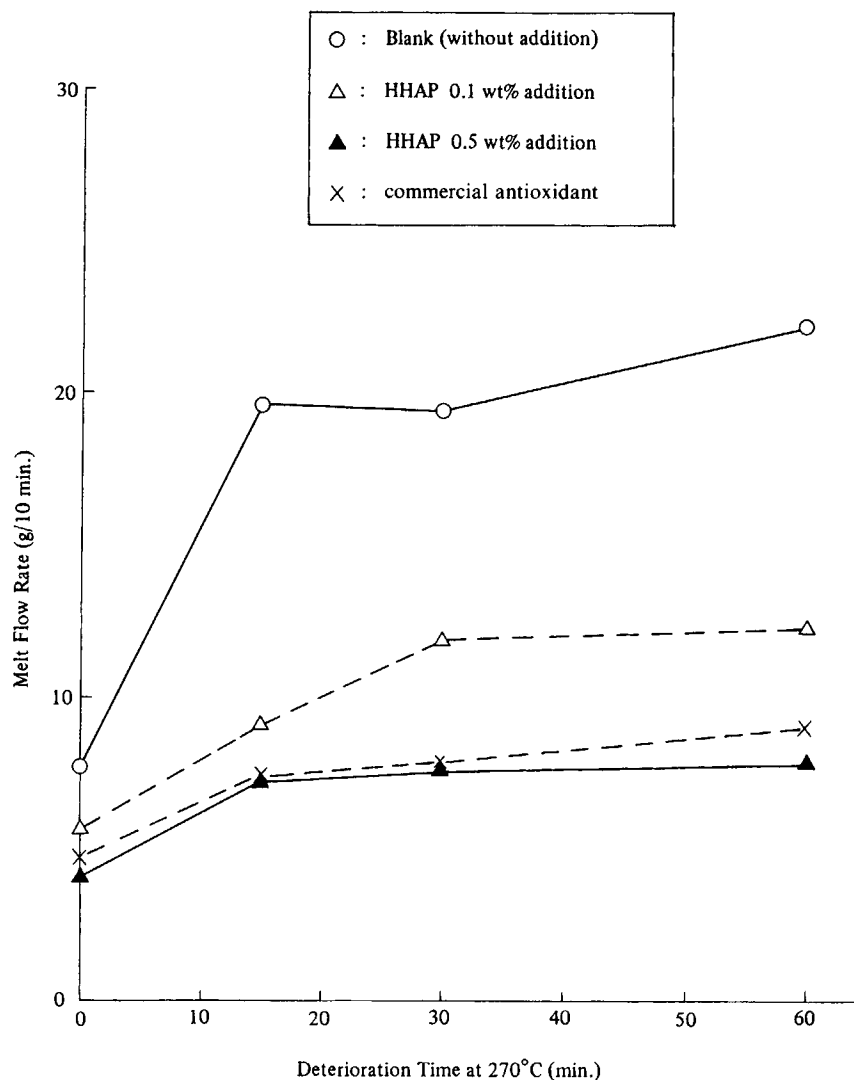**Figure 3**   Effects of the addition of HHAP to high-density PE on MFR (270°C).

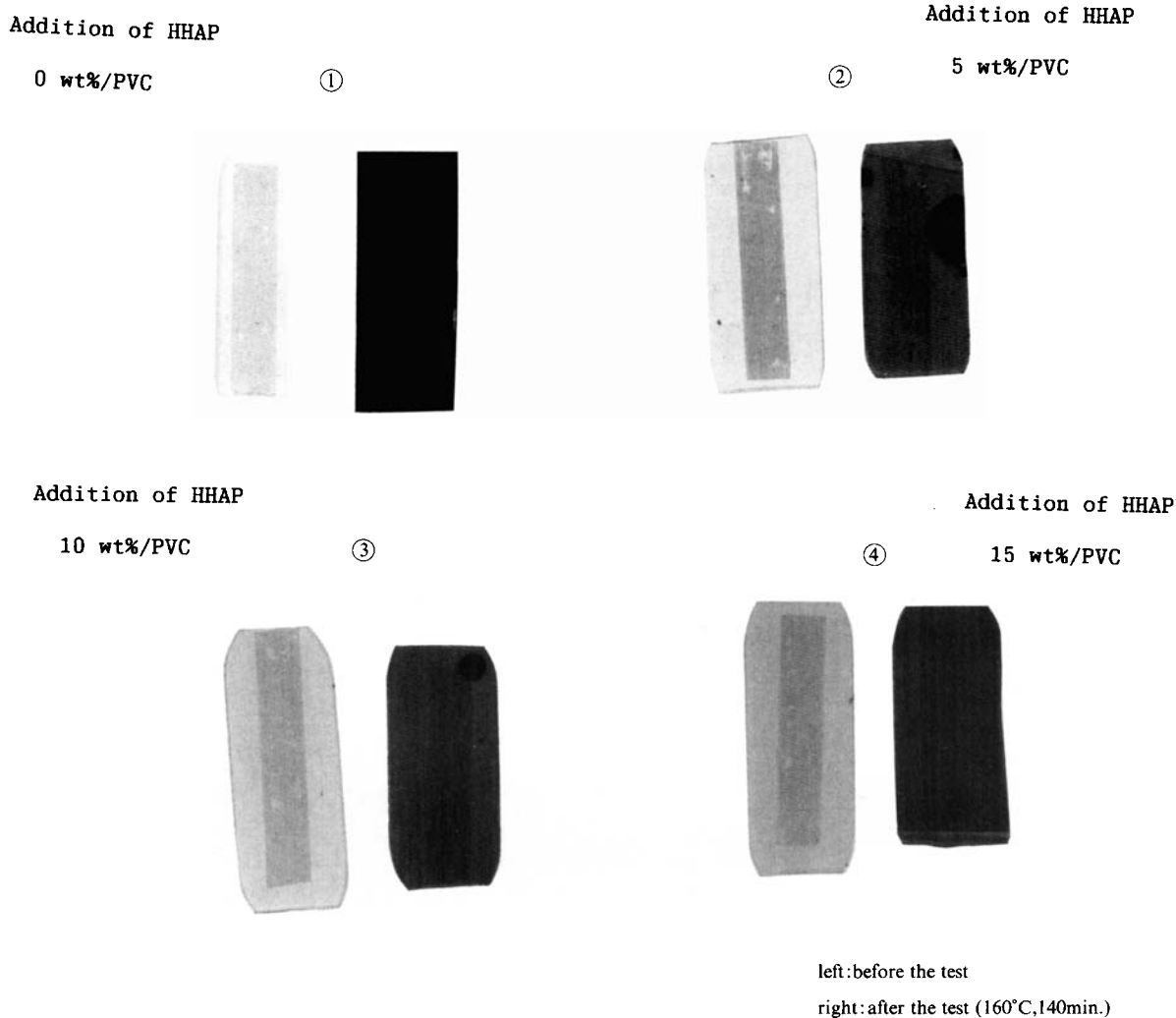**Figure 4**   Effects of the addition of HHAP to isotactic PP on MFR (270°C).

Inhibition of Deterioration of PVC

The samples of PVC without the addition of HHAP (No. 1 sample in Fig. 5) turned to black on the whole surface after the test at 160°C, 140 min. But the deterioration in color was distinctly improved by the addition of HHAP, and it can be observed that the black spots of the samples were reduced by the increase of the addition.

Distinct effects of the addition of HHAP on hardness (Fig. 6), tensile strength (Fig. 7), and elongation (Fig. 8) could not be found by these tests. However, tensile strength was raised (Fig. 7) and elongations were almost constant (Fig. 8) with the addition of HHAP.

DISCUSSION

In the case of PE, deterioration proceeds through simultaneous cross-linking and degradation, as earlier investigators indicated.[13] Cross-linking appears to predominate over degradation at an earlier stage of deterioration because MFRs were reduced by the progress of deterioration (Fig. 3). The additive effects cannot be observed during the decline of elongation, but the decrease of MFRs was repressed by the addition of HHAP after they attain nearly constant value (Fig. 3). The addition of HHAP and the conventional antioxidant seems to be effective enough to suppress the degradation, but it is not enough to fully suppress the cross-linking, judged

Addition of HHAP

0 wt%/PVC   ①

Addition of HHAP

②   5 wt%/PVC

Addition of HHAP

10 wt%/PVC   ③

Addition of HHAP

④   15 wt%/PVC

left:before the test

right:after the test (160°C,140min.)

Figure 5   Effects of the addition of HHAP to PVC on changes in color (160°C, 140 min).

from the results that tensile stresses can be preserved nearly constant despite that elongation is reduced by deterioration (Fig. 3).

In the case of PP, deterioration proceeds predominantly by degradation, and the deterioration rates are higher compared to PE (Fig. 2). The deterioration is shown to be remarkably restricted by the addition of HHAP as well as by the conventional inhibitor. However, the addition of 0.1 wt % of HHAP did not considerably affect deterioration, different from it effect on PE. The deterioration rates are so high in PP compared with those of PE that the addition of 0.1 wt % of HHAP probably was not enough to suppress the deterioration. Judged from the results of PE and PP, the addition of 0.5 wt % of HHAP exhibited similar effects and tendencies as did the addition of 0.1 wt % of the conventional

hindered phenol-type antioxidant. This seems to mean that hydrogen donation from HHAP is as effective in inhibiting the deterioration of polyolefins as is the conventional antioxidant and that the hydrogen transfer rate from hydroaromatics is less (roughly estimated one-fifth) than that from the conventional antioxidant in the case of oxidative degradation of polyolefins.

The addition of HHAP clearly exhibited the effects on changes in the color of PVC through the test (Fig. 5), and it is evident that HHAP is effective in inhibiting the deterioration of PVC. However, a clear effect could not be found in elongation and tensile strength by the addition of HHAP because the testing conditions were not severe enough to cause differences in these mechanical strengths.

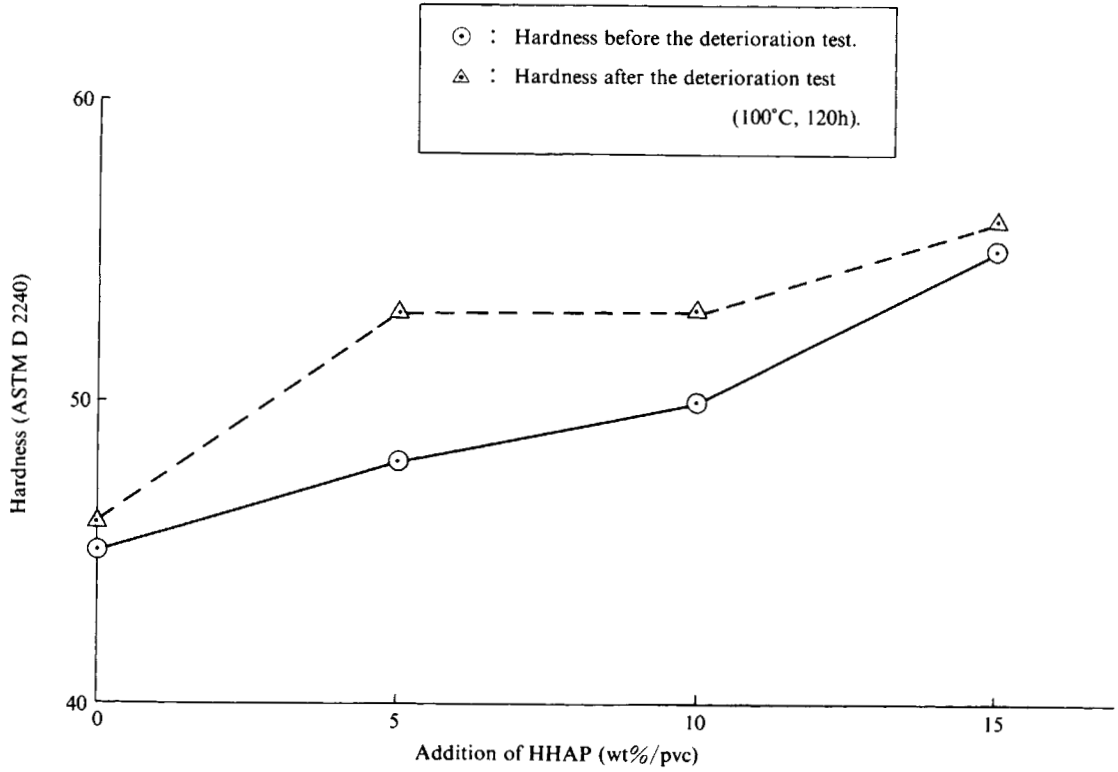Hydrogen-donating hydroaromatics have never

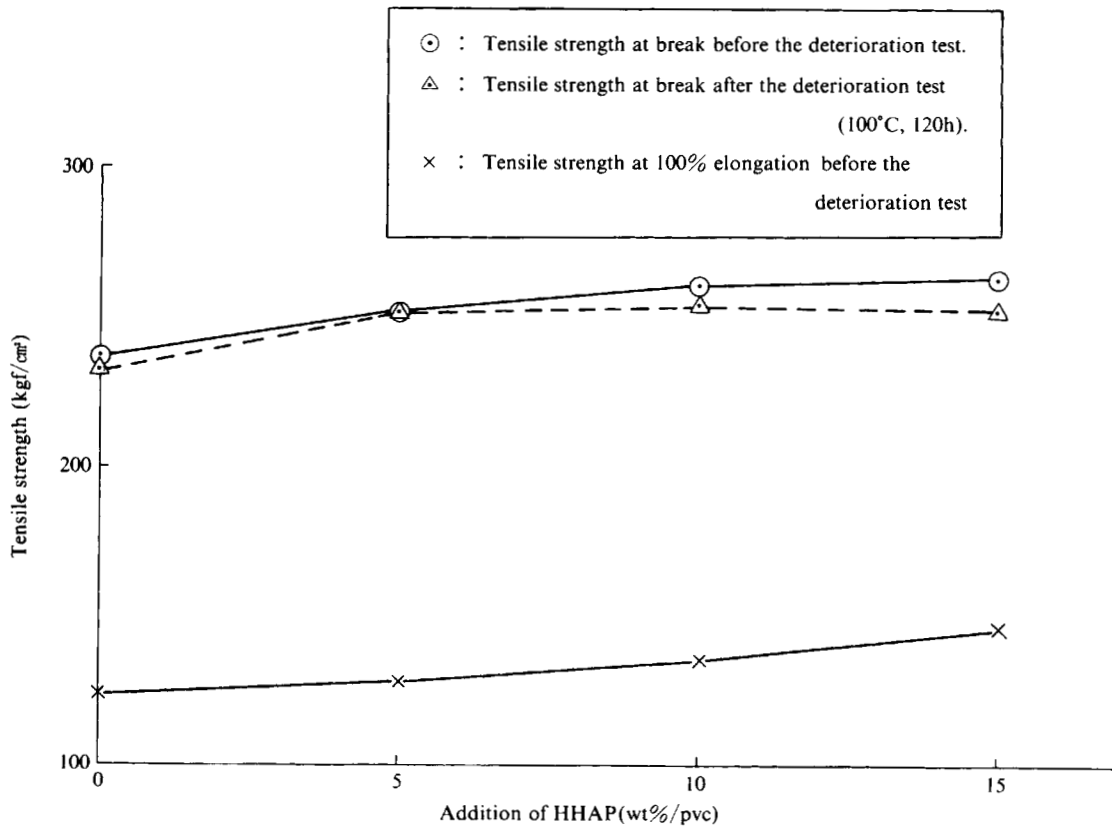**Figure 6**   Effects of the addition of HHAP to PVC on hardness (100°C, 120 h).

Figure 7   Effects of the addition of HHAP to PVC on tensile strength (100°C, 120 h).
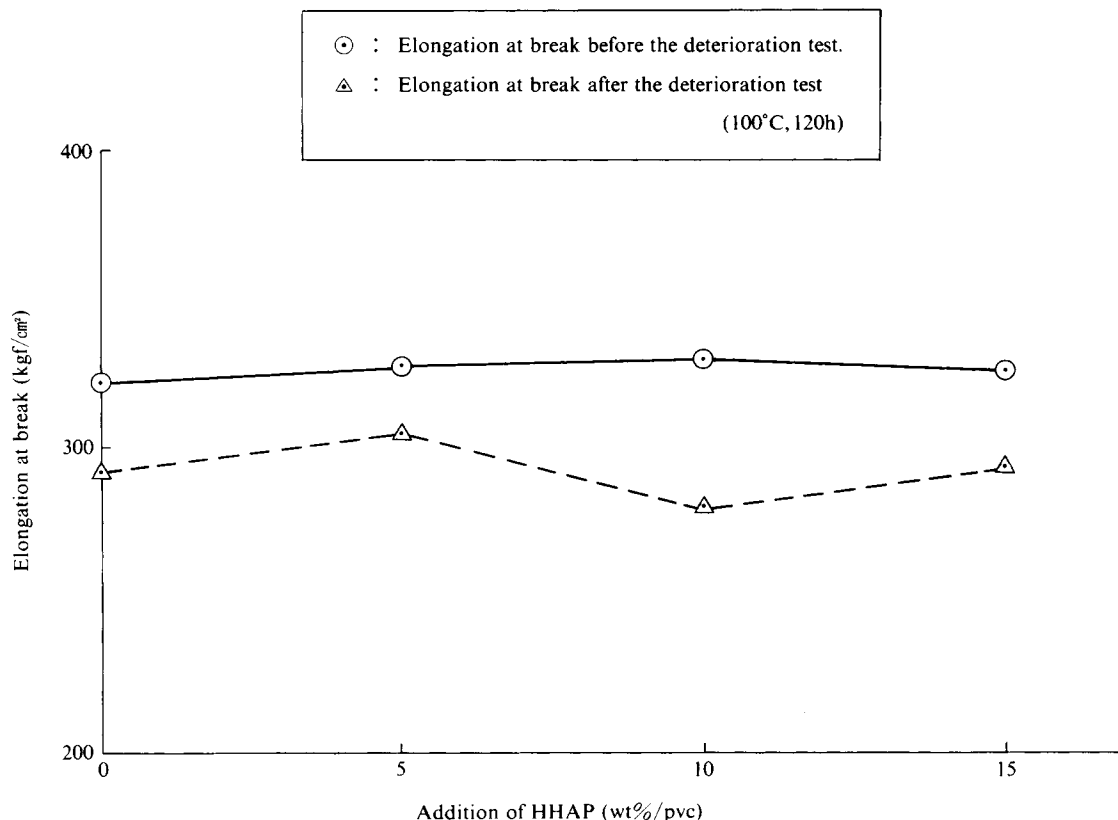
Figure 8 Effects of the addition of HHAP to PVC on elongation (100°C, 120 h).

been applied as inhibitors to plastics, but from these results, they can be seen to be as effective as is the conventional inhibitor.

As reported in our previous papers,[7,8,14] hydrogen donation from hydroaromatics (tetralin and octahydrophenanthrene) was found to be obviously effective in inhibiting the deterioration of hydrocarbons. Based on these results, an additive containing various hydroaromatics as its main components that was produced from coal tar fraction (main components were reported in our previous paper) and one that was produced from heavy fraction of petroleum (HHAP, more components are contained and chemical structure of the individual component is more complicated and unknown) have been examined by their addition to rubbers. Both were found to have excellent inhibiting abilities to rubbers, especially to natural rubber and chloroprene rubber.

From these series of experiments, hydrogen donation from hydroaromatics appears to be available as radical scavengers toward the deterioration of hydrocarbon products, similar to the reactions in coal liquefaction and heavy oil upgrading.

In conventional autoxidation studies, many reports can be found referring to the effects of aro-

matics and hydroaromatics on the restriction of oxidation, such as on the inhibition of oxidation of cumene by tetralin[15] and on the addition of tetralin-hydroperoxide,[16] tetralin, or methylnaphthalene to sulfur compounds[17] oxides of aromatics, and hydroaromatics.[18] However, hydrogen donation from hydroaromatics has never been discussed in relation to the inhibition of the deterioration of hydrocarbon products.

Hydroaromatics were easily oxidized in earlier autoxidation studies, but the reaction pathways of hydroaromatics at lower oxygen partial pressure at the reaction sites have not been clarified. The deterioration of plastics appears to be inhibited by the addition of HHAP because the oxygen partial pressure inside the plastics can be estimated to be low.

Boss and Chien[19] indicated that the rate of oxidation increases with the reciprocal of film thickness until 0.2 mil^{-1} (7.9 mm^{-1}) in PP. Diffusion coefficients of oxygen in polymers were also reported.[20] From these data, oxygen partial pressure in PE and PVC can be estimated to be low, the same as in rubbers.

In our previous experiments[7,8,14] it was concluded that the addition of hydroaromatics was effective at

relatively low oxygen partial pressure and that the inhibiting effects were changed by oxygen partial pressure. From these conclusions, HHAP appear to exhibit prominent effectiveness toward PE, PP, and PVC because the oxygen partial pressures inside plastics can be estimated to be low, the same as in rubbers.[12]

CONCLUSIONS

The effects of the addition of heavy hydroaromatics from petroleum (HHAP) on the deterioration of high-density polyethylene (PE), isotactic polypropylene (PP), and poly(vinyl chloride) (PVC) were examined and the following results were obtained:

1. The addition of HHAP is obviously effective in inhibiting the deterioration of polyolefins (PE and PP).
2. The changes in color of PVC can be remarkably improved by the addition of HHAP.

From these results, hydrogen donation from hydroaromatics can be considered effective in inhibiting the deterioration of PE, PP, and PVC.

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