[Regular Paper]

Interaction of Hindered Amine Light Stabilizers and Ultraviolet Absorbers

Hiroyuki TAKENAKA, Shigeo MIZOKAWA, and Yasukazu OHKATSU*

Dept. of Applied Chemistry, Faculty of Engineering, Kogakuin University, 1-24-2 Nishishinjuku, Shinjuku-ku, Tokyo 163-8677, JAPAN

(Received December 9, 2005)

The reason is discussed, why ultraviolet absorbers (UVA) having phenolic moiety show the synergism with HALS apparently, on the contrary to phenolic antioxidants. A HALS nitrosonium is a substrate causing the useless oxidation of a phenol, and is formed from HALS more easily in the presence of a phenol. However, 2-hydroxybenzophenone (2-HBP) did not accelerate the formation of the nitrosonium so fast as 3,5-di-*t*-butyl-4-hydroxytoluene (BHT). A HALS nitrosonium, even if formed, did not oxidize 2-HBP so much as BHT. That is, 2-HBP can continue to work longer and more efficiently in the presence of HALS. This fact suggests a weak antagonism of 2-HBP and a strong antagonism of BHT with HALS. On the other hand, quinones, derived from 2-HBP and BHT as result of peroxy radical-catching, were reduced to the corresponding hydroquinones by the action of HALS derivatives, such as HALS hydroxylamine. This reaction occurs strikingly faster and more easily for 2-HBP than for BHT. This fact shows a strong synergism of 2-HBP and a weak synergism of BHT with HALS. The above-mentioned results well explain the apparent synergism of UVA (2-HBP) with HALS, contrarily to the apparent antagonism of BHT with HALS.

Keywords

HALS, UVA, Antagonism, Synergism, Photo-oxidation, Quinone

1. Introduction

Hindered amine light stabilizers (HALS) are important additives for the stabilization and long service-life of polymeric materials. They have many functions to control the degradation of polymeric materials, and their antioxidant action mechanisms have been studied intensively. In particular, a hydroperoxide decomposition by HALS is an important step forming active species of HALS for stabilization. In a previous paper, the authors reported a new fact that a hydroperoxide decomposition by HALS NH proceeds through homolytical chain reactions and is accelerated by the presence of 3,5-di-*t*-butyl-4-hydroxytoluene (BHT), one of phenolic antioxidants¹⁾. In addition, they also reported that a nitrosonium salt of HALS is produced during a hydroperoxide decomposition by HALS, and its formation is accelerated by a phenol. The nitrosonium works as bad species having a considerably high activity of a homolytical hydroperoxide decomposition²⁾, and also oxidizes and consumes a phenol uselessly. Thus, an entirely new antagonism between HALS and phenols was proposed²⁾.

The HALS were developed as light stabilizers, but the decisive explanation, including a direct action on

HALS NH (as one of HALS)

photo-antioxidant activities of HALS, has not been done except for the author's proposal³⁾. A phenol catches peroxy radicals to be a quinone. The quinone absorbs light well to be a photo-excited quinone, which goes into photolysis and accelerates the autooxidation degradation. However, HALS prevent such degradation by reducing the excited quinone to a phenol (see **Scheme 1**). As a result, HALS seem to work as light stabilizer. This is only one photo-stabilizing mechanism explaining a synergism of HALS and phenols³⁾.

The HALS and ultraviolet absorbers (UVA) show synergism. Pickett *et al.*⁴⁾ described that HALS and benzotriazole type UVA do not interact with each other directly, but they apparently work synergistically, because they independently take part in different light stabilization processes: that is, HALS protect UVA from losing the functions by catching peroxy radicals. However, Decker *et al.*⁵⁾ reported that HALS tend to be consumed slowly in the presence of benzotriazole type

* To whom correspondence should be addressed.

* E-mail: ohkatsu@cc.kogakuin.ac.jp

Scheme 1 Synergism between HALS and Phenolic Antioxidant for Polymer Stabilization

UVA, but keep UVA in plastics much longer, although HALS do not affect any photolysis of UVA. However, these mechanisms do not seem to explain the synergism perfectly. On the other hand, the authors reported a good relationship between the inhibition of photo-oxidation by UVA and the initial rate of homolytic decomposition of a hydroperoxide by HALS in the presence of UVA, and concluded no or little antagonism of UVA with HALS⁶⁾. In this study, we confirm it experimentally and propose a new synergism of HALS and UVA by comparing the action of UVA (2-hydroxybenzophenone) with that of phenol (BHT) with respect to both antagonism and synergism with HALS.

2. Experimental

2.1. Reagents

Bis(2,2,6,6-tetramethyl-4-piperidiny)sebacate (designated HALS NH) (ADK stab LA-77) was purified by a conventional method. Cumene hydroperoxide (designated CHP) (Nacalai Tesque Inc.) was used as a hydroperoxide. Chlorobenzene (GODO Solvents Co.) was purified by a general method. 2-Hydroxybenzophenone (designated 2-HBP) (Tokyo Chemical Industry Co., Ltd.) and 3,5-di-*t*-butyl-4-hydroxytoluene (designated BHT) (Tokyo Chemical Industry Co., Ltd.) was purified by conventional methods.

2.1.1. Syntheses

(a) Bis(1-oxy-2,2,6,6-tetramethyl-4-piperidiny)sebacate (designated HALS NO)

The HALS NH of 13 g was dissolved in 200 ml of methanol, and 7 ml of acetonitrile was added. Then, 3.6 g of sodium hydrogen carbonate, 0.5 g of sodium tungstate, and 20 ml of 35% aqueous hydrogen peroxide solution were added. The mixture was stirred for 4 days at room temperature. After the addition of

200 ml of saturated brine, the solution was extracted with diethyl ether. The solvent was distilled off *in vacuo*, and a product was purified by means of a column chromatography (stationary phase: silica gel, mobile phase: chloroform : acetone = 10 : 1) and by the recrystallization from hexane. A pale orange crystal was obtained.

Yield: 6.2 g (44.4%), melting point: 99.0-99.3°C.

FT-IR(KBr): over 3321 cm⁻¹(>NH) disappeared, 1716 cm⁻¹(ester), 1180 and 988 cm⁻¹(>NO) appeared.

(b) Bis(1-hydroxy-2,2,6,6-tetramethyl-4-piperidiny)sebacate (designated HALS NOH)

The HALS NO 1.0 g (2.0 mmol) was dissolved in slight benzene. Water (20 ml) containing 1.5 g of ammonium chloride was added. Then 1.0 g of zinc powder was added, and the mixture was stirred under nitrogen atmosphere at room temperature until the organic phase became colorless. The benzene phase was separated after zinc was filtered off, washed with saturated brine, and dried over anhydrous sodium sulfate in a glove box purged with nitrogen. Then, the solvent was removed *in vacuo*. The residue was recrystallized from carbon tetrachloride under nitrogen atmosphere to give white crystal.

Yield: 0.46 g (45%), melting point: 116.4-117.4°C.

FT-IR (KBr): 3462 cm⁻¹ (-OH), 1712 cm⁻¹ (ester), 988 cm⁻¹ (NO) disappeared.

¹H-NMR (CDCl₃, TMS): 7.3 ppm (2H, OH), 5.1 ppm (2H, COOCH), 2.4-1.2 ppm (48H, CH₃, CH₂).

(c) 4-Acetoxy-2,2,6,6-tetramethylpiperidine (designated acetate HALS NH)

4-Hydroxy-2,2,6,6-tetramethylpiperidine 9.44 g (0.06 mol) was dissolved in 20.6 ml (0.36 mol) of acetic acid, and 1 ml of concentrated sulfuric acid was added. The mixture was stirred for 4 h at 100°C. After the reaction, the solution was poured into an ice water and made

basic a little with sodium hydroxide. The solution was extracted with dichloromethane. The solvent was removed under a reduced pressure, and pale yellow oil was obtained as product.

Yield: 3.67 g (30%).

FT-IR (NaCl): 3327 cm^{-1} (NH), 3400 cm^{-1} (-OH) disappeared, 1732 cm^{-1} (ester).

$^1\text{H-NMR}$ (CDCl_3 , TMS): 0.94 ppm (1H, NH), 1.5 ppm (1H, OH) disappeared, 2.0 ppm (3H, acetyl) appeared.

(d) 4-Hydroxy-1-oxy-2,2,6,6-tetramethylpiperidine

4-Hydroxy-2,2,6,6-tetramethylpiperidine 6.59 g (0.04 mol) was dissolved in 100 ml of methanol, and 15 ml of acetonitrile was added. Then, 5.01 g (0.05 mol) of sodium hydrogen carbonate, 0.33 g (0.001 mol) of sodium tungstate, and 15 ml of 35% hydrogen peroxide were added. The mixture was stirred for 4 days at room temperature. After the addition of 200 ml of saturated brine, the solution was extracted with diethyl ether. The solvent was distilled off *in vacuo*, and a product was purified by means of a column chromatography (stationary phase: silica gel, mobile phase: chloroform : acetone = 10 : 1) and recrystallized from hexane. A yellow crystal was obtained.

Yield: 7.01 g (97%), melting point: 66.7-67.4°C.

FT-IR(KBr): over 3321 cm^{-1} (NH) disappeared, 1172.6, 991.3 cm^{-1} (NO).

(e) 4-Acetoxy-1-oxy-2,2,6,6-tetramethylpiperidine (designated acetate HALS NO)

4-Hydroxy-1-oxy-2,2,6,6-tetramethylpiperidine 3.5 g (0.02 mol) was dissolved in 40 ml of benzene, and 2.05 g (0.02 mol) of trifluoroacetic acid was added. Acetyl chloride 2.39 g (0.03 mol) in 10 ml of benzene was added dropwisely. The mixture was stirred for 24 h at room temperature, and the reaction solution was filtered. The solvent was distilled off *in vacuo*, and a product was purified by a column chromatography (stationary phase: silica gel, mobile phase: chloroform : acetone = 10 : 1) and recrystallized from hexane. A red crystal was obtained.

Yield: 3.45 g (79%), melting point: 53.1-54.1°C.

FT-IR (KBr): 3415.7 cm^{-1} (-OH) disappeared, 1741.6 cm^{-1} (ester).

(f) 4-Acetoxy-1-oxy-2,2,6,6-tetramethylpiperidinium nitrate/nitrite (designated acetate HALS $\text{N}^+ = \text{O NO}_2^-/\text{NO}_3^-$)

The compound was synthesized by a method of G. Kaupp *et al.*⁷⁾. Nitrogen dioxide (*ca.* 7.2 l at 0°C) was passed through a solution of 4-acetoxy-1-oxy-2,2,6,6-tetramethylpiperidine (0.5 g) in a solvent at -10°C for 2 h. Then, the mixture was stirred for 2 h and remained nitrogen dioxide was removed by warming up to 50°C. High viscous water-soluble crimson oil was obtained.

Yield 0.78 g (98%).

FT-IR (NaCl): 2940, 1620, 1350, 1240, 1160, 1100 cm^{-1} (nitrosonium salt⁸⁾), 1736 cm^{-1} (ester), and

988 cm^{-1} (nitroxide) disappeared.

(g) 2,5-Dihydroxybenzophenone

Methane sulfonic acid (25 g) and 6.65 g (0.05 mol) of aluminium oxide are added to 6.1 g (0.05 mol) of benzoic acid and 5.51 g (0.05 mol) of 1,4-benzenediol, and the mixture was stirred for 1 h at 140°C. The reaction solution was cooled, and dil. HCl was added. The resulting solution was extracted with diethyl ether, and the organic phase was washed with saturated NaHCO_3 aq, water, and saturated brine, and dried over anhydrous sodium sulfate. The solvent was distilled off *in vacuo*, and a product (yellow crystal) was purified by means of a column chromatography (stationary phase: silica gel, mobile phase: dichloromethane : ethyl acetate = 9 : 1) and recrystallized from carbon tetrachloride.

Yield: 1.02 g (9.6%), melting point: 121.8-122.4°C.

FT-IR (KBr): 3298 cm^{-1} (-OH), 1714.6 cm^{-1} (C=O), 875.6 cm^{-1} (C_6H_6).

$^1\text{H-NMR}$ (CDCl_3 , TMS): 11.6 ppm (1H, 1-OH), 8.0-6.9 ppm (4H, C_6H_4), 5.0 ppm(1H, 4-OH).

(h) 2-Benzoyl-*p*-quinone

2,5-Dihydroxybenzophenone (0.5 g) was dissolved in 40 ml of diethyl ether. Silver oxide (I) (5 g) and 5 g of anhydrous sodium sulfate were added. The mixture was stirred for 3 h at room temperature in dark. Reaction solution was filtered, the filtrate was distilled off *in vacuo*, and a dark brown crystal was obtained as product.

Yield: 0.43 g (86%), melting point: 79.8-80.3°C.

FT-IR (KBr): 3298 cm^{-1} (-OH) disappeared, 1651 cm^{-1} (C=O), 1596.9 cm^{-1} (C=C).

2. 1. 2. Others

Styrene was used after distillation just before use. An initiator, azo-bis-isobutyronitrile (AIBN), was purified by recrystallization from methanol.

2. 2. Procedure

2. 2. 1. Decomposition Reaction of Hydroperoxide

A HALS derivative, CHP, and a phenol were dissolved in chlorobenzene (the total volume: 100 ml). The solution was heated with stirring at 120°C under nitrogen atmosphere. A sample was taken at every 4 h and the remaining hydroperoxide was determined by iodometry or gas chromatography (GC), while reaction products were analyzed by GC and were identified by GC-MS. The reaction was repeated a few times to confirm the reproducibility. All graphs shown in this study show the most reliable one in terms of reproducibility.

2. 2. 2. Iodometry

A solution of 10% acetic acid in 2-propanol was purged with carbon dioxide for two minutes to remove dissolved oxygen. To 5 ml of this solution was added 0.5 ml of an aqueous saturated potassium iodide solution and 1 ml of a sample. The mixture was heated and stirred under carbon dioxide atmosphere at 95°C

In chlorobenzene under N_2 at $120^\circ C$, $[HALS\ NH] = [phenol] = 10^{-3}\ mol/l$, $[CHP] = 10^{-2}\ mol/l$.

Fig. 1 Effect of Phenolic Compound on Decomposition of CHP by HALS

for three minutes. The hydroperoxide content was determined by the titration with 1/1000 N standard sodium thiosulfate solution.

2. 2. 3. Instrumental Analysis

The GC-17A or GC-14B made by Shimadzu Corp. was used as GC with a flame ionization detector (FID). And the GC-MS QP5050A made by Shimadzu Corp. was used as well. The 400-1HT (Quadrex Corp.) was used as column in both systems.

2. 2. 4. Measurement of Photo-antioxidant Activities

Photo-oxidation of styrene was carried out in chlorobenzene under irradiation of UV light (high-pressure mercury-vapor lamp) above 290 nm: a high-pressure mercury-vapor lamp (500 W), manufactured by Ushio Inc., was used as light source. The oxidation was pursued by recording the consumed amount of oxygen by a pressure transducer.

2. 2. 5. Reaction of Quinone and HALS

The HALS NOH or HALS NO and a quinone or hydroquinone were dissolved in carbon tetrachloride, and allowed to react under nitrogen atmosphere and diffused light at $50^\circ C$. A hydroquinone generated or consumed in reactions was measured using a UV-spectrometer.

3. Results and Discussion

3. 1. Influence of UVA on Decomposition of Hydroperoxide by HALS NH

The CHP decomposition by HALS NH was studied in the presence or absence of a phenol. **Figure 1** shows the result. The decomposition curve consists of two stages of an early period showing slow decomposition and a late period, fast decomposition. The slow decomposition period is called an induction period, in which an active species is formed for the following fast decomposition showing maximum velocity. The induction period was about 120 h in the presence of only

HALS, but the coexistence of BHT or 2-HBP shortened the induction period and accelerated the homolytical decomposition of the hydroperoxide (see **Fig. 1**). However, 2-HBP exhibited a longer induction period than BHT. Thus, the benzophenone is found more difficult to produce an active species of hydroperoxide decomposition in comparison with BHT. In the case of BHT, it gives a proton to HALS more easily, and the resulting salt forms active species, namely HALS nitrosonium²⁾. It has not been confirmed yet, however, whether a HALS nitrosonium is an active species in the case of UVA or not.

3. 2. HALS Derivatives Formed in Induction Period

The decomposition reaction was carried out in the same manner as described in Paragraph 3. 1. using acetate HALS NH detectable in GC-MS. The reaction solution was analyzed by GC-MS at the middle time of the fast CHP decomposition, namely after 20 h of the reaction.

The gas chromatogram is shown in **Fig. 2**. Products A and B are identified from the MS spectra as reported in a previous paper as follows²⁾.

These products well means the presence of HALS nitrosonium during decomposition reaction²⁾. Thus, an active species for hydroperoxide decomposition is HALS nitrosonium, also in the case of UVA. When UVA and BHT are compared with respect to the nitrosonium formation, UVA do not seem easier to produce the nitrosonium than BHT, because UVA hardly give proton to HALS due to intramolecular hydrogen bond. This explanation coincides well with the argument in Paragraph 3. 1.

3. 3. Oxidation of 2-HBP by HALS Nitrosonium

A HALS nitrosonium is a strong oxidants, and oxidizes BHT to form the oxidized derivatives such as the *p*-benzoquinone, resulting in useless consumption of BHT²⁾. In this study, it was also investigated whether a HALS nitrosonium oxidizes UVA (**Fig. 3**).

On the basis of mass spectra, the reaction product C is identified as 2-benzoyl-*p*-quinone, and the main reaction products D are a mixture of nitro compounds formed by the attack of a counter nitrite anion of HALS nitrosonium.

Judging from the gas chromatogram shown in **Fig. 3**, the reaction product C is formed by the oxidation of

In chlorobenzene under N_2 at $120^\circ C$, $[acetate\ HALS\ NH] = [2-HBPI] = 10^{-3}\ mol/l$, $[CHP] = 10^{-2}\ mol/l$.

Fig. 2 Gas Chromatogram of Reaction Products at 20 h

In chlorobenzene under N_2 at $120^\circ C$, $[acetate\ HALS\ N^+ = O] = [2-HBPI] = 10^{-2}\ mol/l$.

Fig. 3 Gas Chromatogram of Reaction Products of Acetate HALS $N^+ = O$ and 2-HBP at 15 min

In chlorobenzene at 50°C, under O₂ and UV irradiation; [styrene] = 2.0 M (1 M = 1 mol · dm⁻³), [AIBN] = 10⁻² M.

Fig. 4 Synergistic Effect between 2-Benzoyl-*p*-quinone (A) and HALS (B_x)

2-HBP in extremely smaller amount. The BHT donates HALS a proton easily to form HALS nitrosonium, but 2-hydroxybenzophenone is found difficult to donate a proton and very stable against HALS. In other words, UVA do not bring so severe antagonism with HALS as BHT.

3. 4. Synergism in Photo-antioxidation of HALS and UVA

In the past, the synergism between HALS and phenols under UV light was explained by the regeneration of a phenol by the action of HALS on a quinone formed by the radical catching of a phenol (see **Scheme 1**)³. The quinone absorbs UV rays, and the resulting excited quinoid compound is reduced to a phenol by the action of HALS.

Shown in **Fig. 4** is a synergistic interaction of 2-benzoyl-*p*-quinone with HALS in photo-oxidation. A vertical axis shows relative initial velocity of oxygen absorption, and a figure, 100%, means a non-inhibited photo-oxidation. A curve below dotted line shows synergism of two additives, while a curve above the line shows antagonism. Interestingly, both HALS NOH and HALS NH showed similar synergism with the quinone. Either HALS or quinone alone does not prevent any photo-oxidation, but a combination of both additives shows photo-antioxidant activities. In this case, HALS NOH is found to show a higher synergism than HALS NH. This result coincides completely

In chlorobenzene at 50°C, under O₂ and UV irradiation; [styrene] = 2.0 M (1 M = 1 mol · dm⁻³), [AIBN] = 10⁻² M.

Fig. 5 Interaction between 2-HBP (C) and Another Additive (D_x)

with the result obtained in the synergism between HALS and phenols³. Thus, UVA are regenerated by the action of HALS, even if UVA are eventually converted into a quinone due to the attack of peroxy radicals.

Shown in **Fig. 4** also is the actual photo-antioxidant activity of a regenerated UVA, for example 2-benzoyl-hydroquinone, which is the most plausible UVA regenerated from the quinoid compound. The concentration of 2-benzoyl-*p*-quinone was made same as that of A in A + B_x shown in **Fig 4**. The similar oxidation-suppressing curves are observed at a less concentration than 5 × 10⁻⁵ mol/l of 2-benzoyl-hydroquinone, on comparing the result of the combination of 2-benzoyl-*p*-quinone and HALS NOH with that of 2-benzoyl-hydroquinone. This fact can be fully explained by the mechanism that 2-benzoyl-*p*-quinone is reduced to 2-benzoyl-hydroquinone by an equivalently excess of HALS under UV irradiation. On the contrary, 2-benzoyl-hydroquinone is not produced sufficiently at a less concentration of HALS than that of 2-benzoyl-*p*-quinone. Therefore, a photo-antioxidant activity is decreased over 5 × 10⁻⁵ mol/l of 2-benzoyl-*p*-quinone.

Shown in **Fig. 5** is the interaction of UVA with various radical trapping substrates. Interestingly, 2-HBP is found to show the synergism with HALS NH having little UV-absorbing ability by itself. Furthermore, HALS NOH also shows the almost same synergism as HALS NH. If the synergism is based on the radical catching ability of HALS, HALS NO, having a high radical catching ability, would show higher synergism, compared with that of HALS NH. However, the result shown in **Fig. 5** clearly exhibits no interaction between HALS NO and 2-hydroxybenzophenone. In addition, a strong radical-catching substrate, BHT, showed antagonism instead of synergism. Therefore, the above-mentioned synergism is not ascribable to such radical trapping of HALS as proposed by Pickett

In CCl_4 under N_2 and diffused light at 50°C , $[\text{quinone}] = [\text{HALS NOH}] = 10^{-4} \text{ mol/l}$.

Fig 6 UV Spectra of the Mixture of 2-Benzoyl-*p*-quinone and HALS NOH with Time

In CCl_4 under N_2 and diffused light at 50°C , (a) $[\text{quinone}] = [\text{HALS NOH}] = 10^{-4} \text{ mol/l}$, (b) $[\text{hydroquinone}] = [\text{HALS NO}] = 10^{-4} \text{ mol/l}$.

Fig 7 Relationship between Formation (a) and Consumption (b) of Hydroquinone

*et al.*³⁾.

3. 5. Interaction of HALS Hydroxylamine with Quinone

In Paragraph 3. 4., UVA show the synergism with either HALS NOH or HALS NH in photo-antioxidation. This phenomenon may be ascribed to the regeneration of a new UVA by the action of HALS, even if UVA are converted into corresponding quinones. Shown in Fig. 6 are UV spectra of the interaction of HALS NOH with 2-benzoyl-*p*-quinone under diffused light. At first, only one peak of the quinone is observed at 265 nm, but a new peak which is assigned to 2,5-dihydroxybenzophenone appears at 372 nm. The latter peak increases, while the former quinone peak decreases with time. It is confirmed, therefore, that the hydroquinone is formed by the interaction of HALS with a quinone under diffused light. Figure 7 shows both the formation of the hydroquinone from a quinone by the reaction with HALS NOH and the consumption of hydroquinone by the reaction with HALS NO. The formation and consumption amounts of the hydroquinone became constant with the progress of time. This result means the following equilibrium reaction (see Scheme 1):

Thus, the equilibrium constant can be calculated.

$$K = k_{\text{Q,NOH}}/k_{\text{Q,NO}} \quad (2)$$

Table 1 shows the rate and equilibrium constants of the reaction concerning 2-hydroxybenzophenone, together with that concerning BHT. 2-Benzoyl-*p*-

Table 1 Kinetic Parameters in Interaction of a Phenol with HALS at 50°C

		Kinetic parameters concerning 2-HBP		Kinetic parameters concerning BHT
$k_{\text{Q,NOH}}$	$[\text{M}^{-1} \cdot \text{s}^{-1}]$	11.09		0.33
$k_{\text{Q,NO}}$	$[\text{M}^{-1} \cdot \text{s}^{-1}]$	1.68		0.173
K		6.60		1.93

quinone has a much higher rate constant ($k_{Q,NOH}$), compared with 2,6-di-*t*-butyl-*p*-quinone. That is, the quinone of UVA is more easily reduced to the corresponding hydroquinone, namely a new type of UVA.

On the other hand, the reaction of hydroquinone with HALS nitroxide, namely the reverse reaction seems harder to proceed in the case of UVA. These results shows that 2-benzoyl-hydroquinone is much more stable than 2,6-di-*t*-butyl-hydroquinone. That is, 2-hydroxy-benzophenone can continue to maintain its function of UV absorption over a longer period.

4. Conclusions

In general, an ultraviolet absorber, one of phenolic antioxidants, is different from an antioxidant phenol in terms of the interaction with HALS. In this study, the interactions of UVA or phenol with HALS are compared with each other (see **Table 2**). The UVA do not accelerate the formation of HALS nitrosonium so easily as phenol. Even if a HALS nitrosonium is formed, it can hardly oxidize UVA. On the other hand, if UVA are eventually converted to quinones, they are reduced by HALS promptly to the corresponding hydroquinone-type UVA.

In conclusion, an antioxidant phenol apparently

Table 2 Apparent Interaction of Phenols with HALS

	Interaction of phenols with HALS		Apparent interaction
	antagonism	synergism	
Benzophenone	○	◎	synergism
BHT	◎	△	antagonism

◎ strong, ○ medium, △ weak.

shows the antagonism with HALS due to higher antagonism than synergism, while UVA shows the synergism in a combination of strong synergism and weak antagonism.

References

- 1) Yamashita, H., Ohkatsu, Y., *Polym. Deg. Stab.*, **80**, 421 (2003).
- 2) Yamashita, H., Banno, K., Ohkatsu, Y., *J. Appl. Poly. Sci.*, **102**, 1310 (2006).
- 3) Ohkatsu, Y., Yamaguchi, K., Sengoku, T., Sato, T., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **37**, (4), 405 (1994).
- 4) Pickett, J. E., Moore, J. E., *Polym. Deg. Stab.*, **42**, 231 (1993).
- 5) Decker, C., Zahouily, K., *Polym. Mater. Sci. Eng.*, **68**, 70 (1993).
- 6) Mizokawa, S., Ohkatsu, Y., *J. Jpn. Petrol. Inst.*, **50**, (1), 1 (2007).
- 7) Kaupp, G., Schmeyer, J., *J. Org. Chem.*, **60**, 5494 (1995).
- 8) Miyazawa, T., Endo, T., Shiihashi, S., Okawara, M., *J. Org. Chem.*, **50**, 1332 (1985).

要 旨

ヒンダードアミン系光安定剤と紫外線吸収剤の相互作用

竹中 宏行, 溝川 茂雄, 大勝 靖一

工学院大学工学部応用化学科, 167-8677 東京都新宿区西新宿1-24-2

フェノール系酸化防止剤がヒンダードアミン系光安定剤 (HALS) と拮抗作用を示すのに、紫外線吸収剤 (UVA) がフェノール構造を持っているにもかかわらず、なぜ HALS と見かけ上相乗作用を示すのかを議論する。HALS と 2,6-di-*t*-butyl-4-hydroxytoluene (BHT) の拮抗作用をもたらす原因物質の HALS ニトロソニウムは、2-ヒドロキシベンゾフェノン (2-HBP) の場合に生成しにくかった。さらに、HALS ニトロソニウムはたとえ生成しても BHT ほど 2-HBP を酸化せず、2-HBP がより長くかつより効率よく働き続けることができた。これらの結果は、2-HBP の HALS との弱い拮抗作用および BHT と HALS の

強い拮抗作用を示す。一方、2-HBP と BHT のペルオキシラジカル捕そくによるキノンハルは HALS 誘導体、たとえば HALS ヒドロキシルアミンの作用によって対応するヒドロキノンへ還元された。2-HBP は BHT よりも非常に速く、かつ容易に還元されて新しい UVA となった。この事実は、2-HBP の HALS との強い相乗作用および BHT と HALS の弱い相乗作用を示す。これらの結果を総合すれば、BHT と HALS の拮抗作用に対して、UVA (2-HBP) と HALS が見かけ上相乗作用を示すことがよく説明できる。