[Regular Paper]

Influence of Ultraviolet Absorbers on Decomposition of Hydroperoxide by Hindered Amine Light Stabilizers

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The interaction between hindered amine light stabilizers (HALS), and ultraviolet absorbers (UVA) was investigated, in order to clarify the reason why they generally show synergism, although UVA belong to kinds of phenols. A homolytic decomposition of cumene hydroperoxide (CHP) by amine-type HALS (HALS NH) in the presence of UVA is the antagonism bringing about autoxidation. This antagonism is found considerably weaker for UVA than that of 3,5-di-*t*-butyl-4-hydroxytoluene. This is based on a weak proton-donating ability of UVA to HALS due to their intramolecular hydrogen bond. Furthermore, a good relationship was found between the inhibition of photo-oxidation by UVA and the initial rate of homolytic decomposition of CHP by HALS in the presence of UVA, and a strong synergism of UVA with HALS was observed. As a result, UVA are able to exhibit an apparent synergism in a combination with HALS, because of no or little acceleration (antagonism) of homolytic hydroperoxide decomposition caused by the interaction with HALS, as well as the estimated regeneration (synergism) of new UVA from the corresponding quinoide-type compounds, even if formed, by the action of HALS or the derivatives.

1. Introduction

Hindered amine light stabilizers (HALS), having hindered piperidine moieties, are very important additives that control the photo-degradation of polymeric materials, and their antioxidant action have been studied intensively[1]~[6]. The HALS are known to decompose hydroperoxides, and the decomposition is important as one of the characteristic functions of HALS, giving active species of HALS. On the other hand, HALS exhibit delicate compatibility with other additives. For example, Allen *et al.*[7] reported that, in the stabilization of polypropylene film using both HALS and antioxidant phenols, they show a synergistic interaction for thermal oxidation with some exceptions, but an antagonistic one for photo-oxidation. On the other hand, the authors reported a new antagonism that a hydroperoxide decomposition by amine-type HALS (HALS NH) proceeds according to a homolytical chain reaction, and is accelerated by the presence of 3,5-di-*t*-butyl-4-hydroxytoluene (BHT), one of representative phenolic antioxidants[8]. This homolytical hydroperoxide decomposition is an undesirable reaction that initiates the autoxidation, and accelerates the degra-

dation of polymeric materials. Generally speaking, the interaction between HALS and phenols is understood more or less as antagonism, depending on kinds of phenolic antioxidants.

On the contrary, ultraviolet absorbers (UVA) are reported to show a synergistic interaction with HALS, although UVA belong to a kind of phenol. Pickett *et al.*[9] 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. On the other hand, Decker *et al.*[10] reported that HALS tend to be consumed slowly in the presence of benzotriazole type UVA, and make the UVA work much longer, although HALS do not affect any photolysis of UVA. Therefore, it is preferred to use HALS in a combination with UVA, since UVA are made apparently stable against photolysis, and consequently the synergistic effects are observed. Kurumada *et al.*[11] investigated the preferable mole ratios of HALS to UVA to get suitable photo-stabilization, and reported the following results: about 75 : 25 for polypropylene and high density polyethylene, 90 : 10 for ABS resin, and 80 : 20 for crystalline polystyrene. They explained this result on the basis of the synergistic effect of HALS and UVA: HALS, being present inside, are protected from the harmful UV light by the action of UVA, existing near

the surface of plastics. Broadly speaking, as mentioned above, the interaction between HALS and UVA is recognized as synergism, but the mechanism has not been clarified yet.

In this study, we chose seven kinds of commercial UVA, and investigated their interaction with HALS NH, and found new synergistic phenomena between UVA and HALS NH. This will be discussed.

2. Experiment

2. 1. Materials

Almost stabilizers used in this study were gotten as commercial products, and were purified according to conventional purification methods:

HALS NH: bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate;

UVA: 2-hydroxybenzophenone (UVA-1),
2-hydroxy-5-methylbenzophenone (UVA-2),
2-hydroxy-4-octoxybenzophenone (UVA-3),
2-(2'-hydroxy-5-methylphenyl)benzotriazole (UVA-4),
2-(2'-hydroxy-3'-*t*-butyl-5'-methylphenyl)5-chlorobenzotriazole (UVA-5),
2-(2'-hydroxy-3',5'-di-*t*-butylphenyl)benzotriazole (UVA-6),
2-(2'-hydroxy-5'-*t*-butylphenyl)benzotriazole (UVA-7); and

Reference phenol: 2,6-di-*t*-butyl-4-methylphenol (BHT).

Cumene hydroperoxide (CHP) (Nacalai Tesque Inc.) was used as a hydroperoxide, and chlorobenzene (Takahashi Pure Chemical Co.) was used as solvent after distillation.

2. 2. Procedures

#### 2. 2. 1. Decomposition Reaction of Hydroperoxide

The HALS, CHP, and UVA or BHT were dissolved in chlorobenzene, and the solution was heated at 120°C with stirring under nitrogen atmosphere. A sample was taken out every 4 or 8 h and the remaining hydroperoxide was titrated by an iodometry.

2. 2. 2. Measurement of Intramolecular Hydrogen Bonds

It is well known that a hydrogen bond depends on the concentration of a compound, especially in the case of a compound forming both inter- and intramolecular hydrogen bonds. In order to get information on only intramolecular hydrogen bond, a solution of UVA in carbon tetrachloride was prepared at the concentration of 5×10^{-3} M (1 M = 1 mol·dm^{-3}). The intramolecular hydrogen bond (ν_{OH}) of UVA was measured by means of FT-IR[12].

2. 2. 3. Measurement of Photo-antioxidant Activities

The photo-oxidation of styrene was carried out using azo-bis-isobutyronitrile (AIBN) in oxygen atmosphere
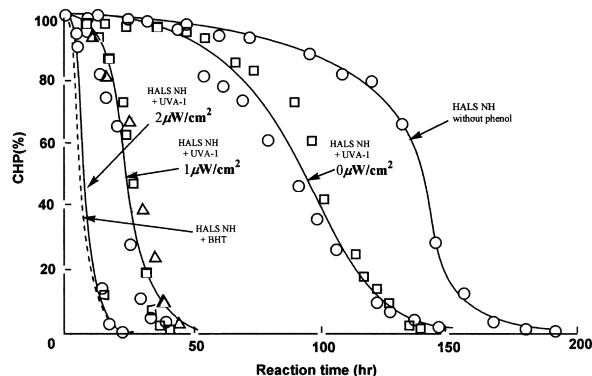
In chlorobenzene under N_2 at 120°C, [HALS NH] = [phenol] = 10^{-3} mol/*l*, [CHP] = 10^{-2} mol/*l*.

Fig. 1 Influence of a Phenol or UV Light on Decomposition of CHP by HALS NH

at 50°C under UV light irradiation: a high-pressure mercury-vapor lamp (500 W), manufactured by Ushio Inc., was used as a light source. Chlorobenzene was used as solvent. The oxidation was pursued recording the amount of oxygen consumed by means of a pressure transducer.

3. Results and Discussion

3. 1. Influence of UVA-1 and Light on Decomposition of Hydroperoxide by HALS

It is known that HALS decompose CHP homolytically. **Figure 1** includes the effect of light on the homolytic decomposition of CHP by HALS in the presence of UVA-1. **Figure 1** also shows the result that the decomposition of a hydroperoxide, CHP, is accelerated by the presence of a phenol, BHT: HALS without the phenol need the induction period (defined later) of about 120 h for decomposition of CHP, but the addition of BHT shortens it to *ca.* 5 h.

The UVA are kinds of phenols, and may be estimated to behave like BHT in the CHP decomposition by HALS. In addition, UVA will be affected by light in the interaction with HALS, because they are sensitive to light to change the chemical structures. Thus, the effect of light should not be ignored in the decomposition of CHP by HALS in the presence of UVA.

Referring to **Fig. 1**, the UVA-1 is found to accelerate the CHP decomposition by HALS, although the acceleration is not so much as that of BHT. Such acceleration also is much affected by light. The light strength of 2 μW/cm^2 corresponds to that on a table at about 2.5 m just below general fluorescent tubes. Such an effect of light strength, however, was not observed in the case of BHT. As shown in **Fig. 1**, all decomposition curves consist of two stages: first slow decomposition and last fast decomposition stages.
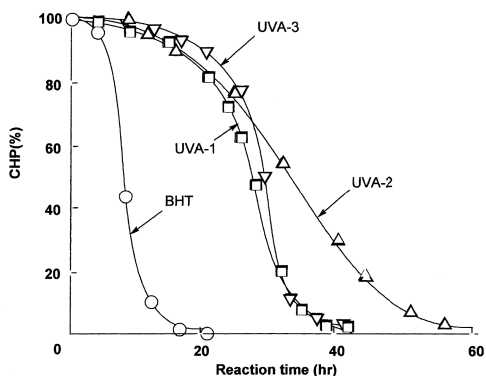
In chlorobenzene under N_2 at 120°C, [HALS NH] = [phenol] = 10^{-3} mol/l, [CHP] = 10^{-2} mol/l.

Fig. 2 Decomposition of CHP by HALS NH in Presence of Benzophenones

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

Fig. 3 Decomposition of CHP by HALS in Presence of Benzotriazoles

This suggests that the formation of active species (HALS nitrosonium, sometimes designated bad active species)[13] for fast decomposition needs a period, which is called "induction period" in this paper.
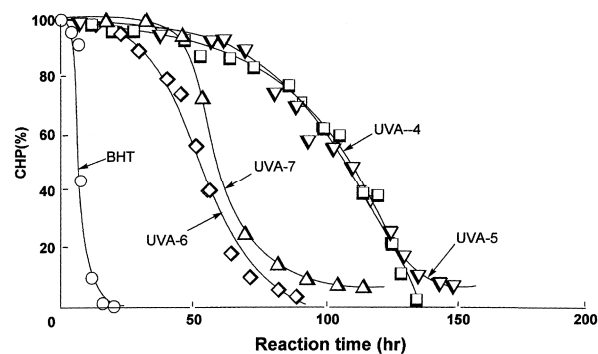
A few compounds are well known to change the acidity under photo-excitation[14]. For example,
(1) a phenolic compound becomes stronger in the acidity under photo-excited state rather than ground state, and
(2) an aromatic carboxylic acid becomes a weaker acid under photo-excited state.
Under UV irradiation, thus, UVA-1 is estimated to hand the phenolic hydrogen as proton more easily to the carbonyl oxygen, the electron density of which rises in the photo-excited state, as mentioned above. Of course, such hydrogen transfer of UVA will occur more frequently under stronger UV light. According to **Fig. 1**, an induction period of the CHP decomposition is more shortened with an increase in the intensity of light, meaning the increase in the quantity of a mobile proton. This fact agrees well with the results reported in a previous paper[8]: CHP decomposition by HALS is accelerated, that is, the induction period is shortened by the addition of BHT as a proton donating substrate. The result shown in **Fig. 1**, thus, is understood by a mechanism that UVA-1 donates a proton to HALS, especially through a light-absorbing process, and accelerates the homolytic decomposition of CHP. However, the proton-donating ability of UVA does not seem so remarkable as that of BHT. The following studies on CHP decomposition, therefore, were carried out under 1 μW/cm² below general fluorescent tubes.

3. 2. Effect of UVA on Decomposition of Hydroperoxide by HALS NH

Shown in **Figs. 2** and **3** is the decomposition of CHP using a combination of UVA and HALS NH. **Figure 2** shows the effect of benzophenones, and **Fig. 3**, that of benzotriazoles. **Table 1** summarises

induction periods, initial velocities, and maximum velocities of the decomposition of CHP in the presence of UVA, which are calculated from **Figs. 2** and **3**. A positive relationship was not observed between initial and maximum velocities, or between initial velocity and induction period. Judging from the induction periods shown in **Table 1**, the fast homolytic decomposition started in the following order: (from earlier) UVA-2, UVA-1, UVA-3, UVA-6, UVA-7, UVA-5, UVA-4
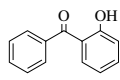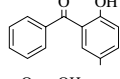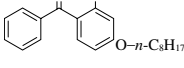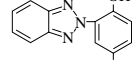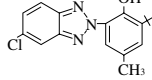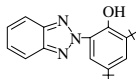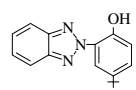This order is interpreted as that of periods necessary for the formation of bad active species of HALS in CHP decomposition: UVA-4, thus, is the best photo-stabilizer of the seven UVA used in this study.

A short induction period would be associated with early formation of the bad active species as discussed above. Both the induction period and the initial velocity, however, could not be connected with each other. This fact implies complicated routes for the formation of bad active species.

3. 3. Physical Property of the Phenolic Hydroxy Group Affecting CHP Decomposition by HALS NH

It has been reported so far that HALS and phenols are interacted with each other synergistically[15] or antagonistically[16], depending on kinds of phenols, the mole ratio of HALS and phenols, and so on. On the other hand, almost all papers report that UVA are synergistic with HALS, although UVA have similar phenolic moieties. **Figure 4** shows the interaction, with HALS, of phenols, which have similar chemical structures to UVA, but do not belong to commercial UVA. The BHT is a typical antioxidant, while 2-hydroxyacetophenone and o-nitrophenol show little inhibition of autoxidation, if any, due to an electron-withdrawing group on the o-position of phenolic hydroxyl group. In addition, o-methoxyphenol does not exhibit any antioxidant activity at all[17], because of strong intra-

Table 1   Results of Decomposition of CHP by HALS NH in Presence of UVA

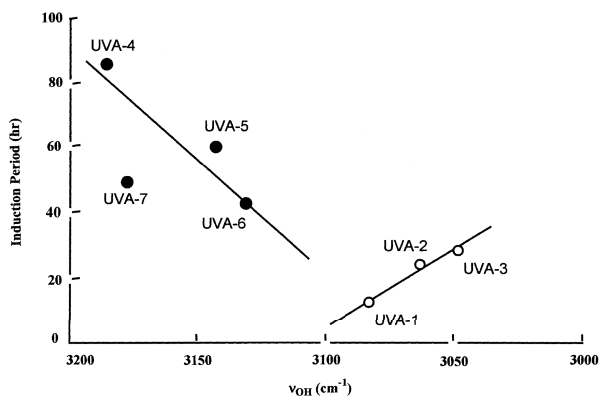|	UVA	Initial velocity [$\times 10^{-8}$ mol/s]	Maximum velocity [$\times 10^{-7}$ mol/s]	Induction period [h]
(benzophenone structure)	UVA-1	1.52	2.63	24.0
(benzophenone structure)	UVA-2	1.29	1.28	12.5
(benzophenone, O–n-C₈H₁₇)	UVA-3	0.97	2.69	28.0
(benzotriazole structure)	UVA-4	0.51	0.49	85.1
(Cl-benzotriazole, CH₃)		0.18	0.36	70.5
(benzotriazole structure)	UVA-6	0.31	0.72	46.5
(benzotriazole structure)	UVA-7	0.32	0.83	49.2
(phenol structure)	AO-1	2.77	2.75	4.0

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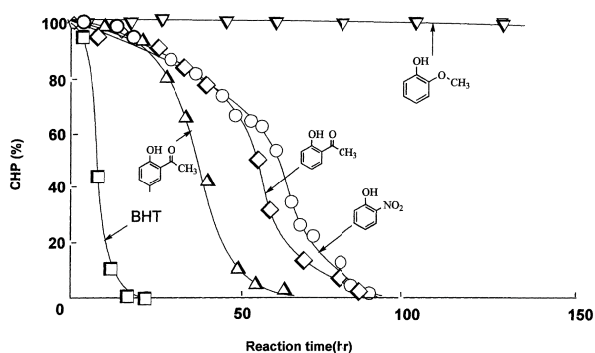
In chlorobenzene under N_2 at 120°C, [HALS NH] = [phenol] = 10^{-3} mol/l, [CHP] = 10^{-2} mol/l.

Fig. 4   Decomposition of CHP by HALS NH in Presence of a Substituted Phenols

v_{OH} of UVA: in CCl_4, [UVA] = 5×10^{-3} mol/l.
Induction period of CHP decomposition: in chlorobenzene under N_2 at 120°C, [HALS NH] = [UVA] = 10^{-3} mol/l, [CHP] = 10^{-2} mol/l.

Fig. 5   Relationship between Induction Period of CHP Decomposition and v_{OH} of UVA

molecular hydrogen bond.   Thus, the degree of antioxidant activity of these phenols is ascribable directly to the intramolecular hydrogen bond.   A phenol having an easily dissociated hydroxy group such as BHT, thus, exhibits high antioxidant activity.   **Figure 4** clearly shows that the induction period of CHP decomposition is much longer for a phenol having a stronger intramolecular hydrogen bond than BHT.   In other words, a phenol having such a hydrogen bond, namely a less proton-donating ability, hardly interacts with HALS.

Shown in **Fig. 5** is the effect of intramolecular hydrogen bond on the decomposition of CHP by HALS: the ordinate shows the induction periods of **Table 1**, and the abscissa, v_{OH} of UVA.   Generally speaking, the stronger an intramolecular hydrogen bond, the lower the wave number (v_{OH}).   The figure shows a good correlation, in the case of benzophenone type UVA, that an induction period gets longer with a stronger hydro-
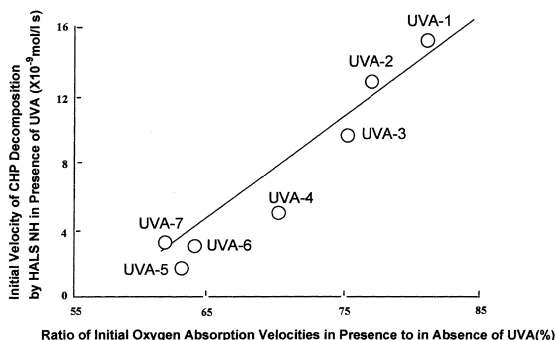
Ratio of oxygen absorption velocities: 50°C; in chlorobenzene [styrene] = 2.0 M (1M = 1 mol·dm^{-3}), [AIBN] = 10^{-2} M, [UVA] = 10^{-4} mol/l.
Initial velocity of CHP decomposition: in chlorobenzene under N$_2$ at 120°C, [HALS NH] = [UVA] = 10^{-3} mol/l, [CHP] = 10^{-2} mol/l.

Fig. 6   Relationship between Initial Velocity of CHP Decomposition and Ratio of Initial Oxygen Absorption Velocities in Presence to in Absence of UVA (%)

Ratio of oxygen absorption velocities: 50°C; in chlorobenzene [styrene] = 2.0 M (1M = 1 mol·dm^{-3}), [AIBN] = 10^{-2} M, [UVA] = [HALS NH] = 5 × 10^{-5} mol/l.
Initial velocity of CHP decomposition: in chlorobenzene under N$_2$ at 120°C, [HALS] = [UVA] = 10^{-3} mol/l, [CHP] = 10^{-2} mol/l.
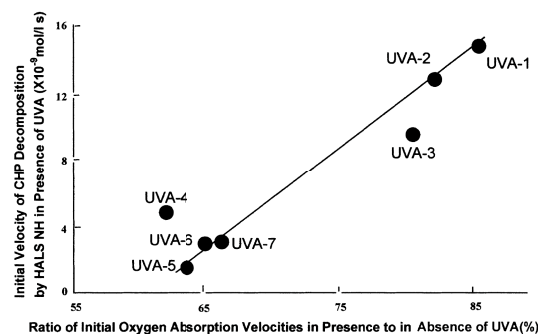
Fig. 7   Relationship between Initial Velocity of CHP Decomposition and Ratio of Initial Oxygen Absorption Velocities in Presence to in Absence of UVA (%)

gen bond.   This result coincides well with our proposal that the antagonism between HALS and BHT is deeply concerned with the proton-donating character of BHT. On the contrary, **Fig. 5** shows, in the case of benzotriazole type UVA, the reverse correlation that the induction period gets longer with a weaker hydrogen bond. However, benzotriazole-type UVA are less antagonistic than benzophenones in the interaction with HALS as judged from induction periods (see **Table 1**).   This fact may be explained by the possible assumption that an intramolecular hydrogen bond in the ground state is not the same as that in excited state, especially for benzotriazoles.

3. 4.   Relationship between Photo-antioxidation and Hydroperoxide Decomposition

Shown in **Fig. 6** is the relationship between photo-antioxidant abilities of only UVA and the effect of UVA on the CHP decomposition by HALS NH.   The ordinate and abscissa show the initial velocity of CHP decomposition shown in **Table 1** and the relative ratio of the initial oxygen absorption rate in the photo-oxidation of styrene in the presence of UVA to that in the absence of UVA, respectively.   The smaller abscissa figure is, the higher photo-antioxidant ability of the UVA.   **Figure 6** shows a good correlation of both velocities, meaning that UVA, exhibiting higher photo-antioxidant activity in the absence of HALS NH, better control the hemolytic decomposition of CHP by HALS NH in the presence of UVA.   This fact coincides well with the above-mentioned result that high photo-antioxidant UVA, namely no or little proton-donating UVA, are difficult to interact with HALS NH.
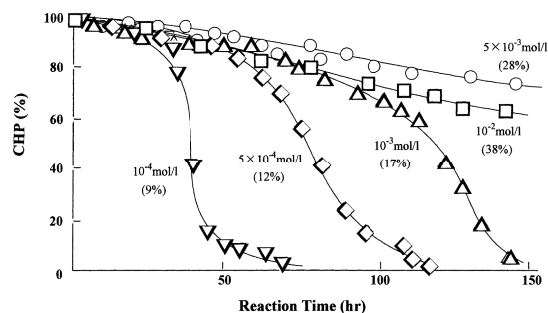
Shown in **Fig. 7** is a similar plot to that of **Fig. 6**, except that the abscissa shows the mole-equivalent mixture of UVA and HALS NH: the total concentration

In chlorobenzene under N$_2$ at 120°C, [HALS NH] = [UVA-4] = 10^{-2}, 5 × 10^{-3}, 10^{-3}, 5 × 10^{-4}, 10^{-4} mol/l, [CHP] = 10^{-2} mol/l.

Fig. 8   Effect of Absolute Concentration of HALS NH and UVA-4 on Decomposition of CHP by HALS NH in Presence of UVA-4

being same as that shown in **Fig. 6**.   It is very interesting that the mixture of UVA with HALS NH (see **Fig. 7**) shows a little less photo-antioxidant activity than only UVA (see **Fig. 6**), but more activity than that expected on the basis of the fact that in **Fig. 7**, HALS have little UV absorption ability and the amount of UVA is half as much as that in **Fig. 6**.   This may be ascribable partly to the regeneration of UVA by HALS NH as mentioned later.   Especially, UVA-4 is observed to show remarkable synergism with HALS, when **Fig. 6** is compared with **Fig. 7**.

In summary, both **Figs. 6** and **7** suggest that such UVA that do not induce the homolytic decomposition in cooperation with HALS NH are excellent photo-antioxidants as well.

3. 5.   Effect of the Absolute Concentration

Shown in **Fig. 8** is the effect of the absolute concentration of additives, on the decomposition of CHP by

HALS NH in presence of UVA-4: in this case, both additives, HALS NH and UVA-4, were used in the same molar concentration.   The UVA-4 is the most synergetic UV absorber of UVA examined in this study.   As shown in **Fig. 8**, homolytic decomposition of CHP is restrained more, as the absolute concentration is higher.   The quantity of CHP, which is decomposed during the induction period, is also shown as the percent of decomposed CHP in parenthesis under the concentration.   This value shows the quantity of CHP needed to generate the bad active species of HALS as CHP decomposer.   On the other hand, the hydroperoxide decomposition by HALS NH is known also to form various good active species of HALS NH, which contribute to the stabilization of plastics.   Therefore, HALS NH is estimated to exist in various species during induction period of CHP decomposition.   Considering the relative concentration ratio of CHP to HALS NH, in the case of the higher ratio (the lower absolute concentration of HALS NH), the HALS can be estimated to be oxidized more easily to form the bad active species and to make the induction period shorter for CHP decomposition.

The UVA are considered sometimes to behave similarly to BHT, and occasionally to loose phenolic hydrogen during repeated UV absorption processes to become the corresponding quinoid compounds.   However, they will be reduced to new UVA, such as 2-benzoyl-*p*-hydroquinone, by HALS NH or the derivative, similarly to the case of the synergism between HALS and phenol, such as BHT[15].   The resulting hydroquinone can exhibit photo-stabilizing activity again.

On the other hand, HALS and UVA exhibit only a little antagonistic interaction, due to a little proton-donating ability of UVA, and, as a result, are not ease to induce the homolytic decomposition of a hydroperoxide.

A combination of both above-mentioned phenomena can well explain the synergism of UVA with HALS.

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要　　旨

ヒンダードアミン系光安定剤の過酸化物分解能に及ぼす紫外線吸収剤の影響

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ヒンダードアミン系光安定剤（HALS）および紫外線吸収剤（UVA）間の相互作用を検討して，UVA がフェノールの1種でありながらなぜ HALS と相乗作用を示すのかを明らかにした。UVA 存在下におけるアミン型 HALS によるクメンヒドロペルオキシド（CHP）のラジカル分解は，自動酸化を誘発する UVA と HALS の拮抗作用である。この作用は UVA の場合，フェノール系酸化防止剤 3,5-di-*t*-butyl-4-hydroxytoluene（BHT）に比べて非常に弱いことが分かった。これは，UVA のプロトン供与性の弱いこと，すなわち分子内水素結合によるものと推定できた。一方，UVA による光酸化の防止と UVA 存在下における HALS による CHP のラジカル分解の初速度との間には良好な関係が見出され，UVA と HALS の強い相乗作用が観察された。結論として，UVA は HALS との相互作用によってヒドロペルオキシドのラジカル分解を誘発（拮抗作用）する能力がない，またはほとんどなく，また UVA のキノイド化合物が生成したとしても HALS またはその誘導体の作用によって新しい UVA に再生（相乗作用）されるために，HALS との組合せにおいて見かけ上相乗作用を示すことができる。

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