**[Review Paper]**

# Search for Unified Action Mechanism of Hindered Amine Light Stabilizers

Yasukazu OHKATSU*

Special Engineering College of Kogakuin University, 1-24-2 Nishishinjuku, Shinjuku-ku, Tokyo 163-8677, JAPAN

(Received September 10, 2007)

Hindered amine light stabilizers (HALS) possess many functions unlike other additives and are frequently used to extend the service life of polymeric materials, but show particular compatibility with certain other additives. However, combination does not always show synergistic actions, but sometimes has antagonistic effects. Most previous research into the interaction of HALS with other additives has focused on qualitative high synergism to high antagonism, and no common understanding has been reached. HALS and homologs have many derivatives which are classified here as "good" HALS and "bad" HALS, including a new HALS derivative, HALS nitrosonium. The investigation of the antagonism of HALS with other additives has been based on only "good" HALS. The present study discusses the chaotic interactions of HALS with other additives kinetically and thermodynamically by separately considering the synergism of "good" HALS and the antagonism of "bad" HALS. This approach has lead to a new technique for unified evaluation of the interaction semi-quantitatively. The results summarized here clarify the complex and diverse characteristics of HALS and present the possibility that the action mechanism of HALS alone and together with other additives can be discussed based on a unified mechanism. Such united ideas can determine additive formulation much more easily and facilitate the development of new additives, resulting in more stable and functional polymeric materials.

**Keywords**
HALS, HALS nitrosonium, Synergism, Antagonism, Action mechanism

## 1. Introduction

Function-maintaining additives are intended to prevent the deterioration of polymeric materials, and include radical chain stoppers, light stabilizers, peroxide decomposers, and others. In general, these additives have only one function specific to the particular additive structure. For example, a phenolic antioxidant acting as a radical chain stopper is generally used to scavenge peroxy radicals, although alkyl radical scavenging antioxidants have also been developed in recent years. On the other hand, aromatic amine-type stabilizer can scavenge both peroxy and alkyl radicals, and is exclusively used for rubbers because of coloring during use. Light stabilizers includes UV absorbers (UVA) with intramolecular hydrogen bonds such as 2-hydroxybenzophenone.

In contrast, hindered amine light stabilizers (HALS) act as multi-functional stabilizers, with light stabilization, radical scavenging, peroxide decomposing, and heavy metal scavenging functions, although the initial function was that of light stabilizer as suggested by the name. HALS have excellent functions, but also pose some problem. First, HALS may interact in complex ways with other polymer additives, and may show antagonisms in some cases. Second, HALS are basic molecules, so are deactivated by acidic compounds, and cannot be used for materials such as polycarbonates which are hydrolyzed in the presence of basic catalyst. Many studies have tried to clarify the complex phenomena involved in the use of HALS, but only a few behaviors of HALS have been elucidated.

This review tries to identify a unified mechanism to explain the complexity of HALS activity based on the available evidence.

## 2. Individual Actions of HALS

### 2. 1. Light Stabilization Function of HALS

HALS function as light stabilizers, but absorb few UV rays unlike UVA. Therefore, the light stabilization function of HALS seems to depend on effective radical scavenging, but the direct stabilization mechanism of light remained unclear for a long time after HALS were developed. The authors have proposed a light stabilization mechanism of HALS[1),2)], which remains the only mechanism explaining the direct participation of light at present and will be discussed in detail in Chapter **3. 2. 1.**

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

## 2. 2. Radical Scavenging Function of HALS

The radical scavenging function of HALS is mainly mediated by oxidized HALS species, such as HALS nitroxide (HALS NO), HALS hydroxylamine (HALS NOH), and HALS alkoxide (HALS NOR). The proposed antioxidant mechanism of radical scavenging involves scavenging an alkyl radical by HALS NO to form HALS NOR, which is reconverted to HALS NO by reaction with a peroxy radical[3]. This mechanism was later refined to include an intermediate in the pathway between the nitroxide and the alkoxide[4] (**Scheme 1**).

A simplified mechanism[5] based on that proposed by the authors[1] has HALS NOH incorporated in the cycle as shown in **Scheme 2**. Our subsequent kinetic study of the reaction of HALS derivatives with alkyl and peroxy radical supported this mechanism (**Scheme 3**)[6),7)]. That is to say, HALS NOR finally accumulates according to the Denisov-type mechanism, because the rate constant of the alkyl radical scavenging reaction by HALS NO is about $10^{12}$ times higher than that of peroxy radical scavenging by HALS NOR, resulting in stasis of the cycle sooner or later[6),7)]. Therefore, this mechanism cannot explain the effective radical scavenging function of HALS. In **Scheme 3**, HALS NOR conversion to HALS NOH has a rate constant of about $10^{-4}$ $s^{-1}$, which is about 1/200 less than the conversion to HALS NO ($1.9\times10^{-3}$ *l*/mol·s). However, if peroxy radicals are present at a concentration of $10^{-6}$ mol/*l* during the reaction as generally accepted, the reaction releasing an olefin from HALS NOR is faster by 4-5 orders than the reverse reaction to HALS NO.

Rate constants at 50℃ for peroxy radical scavenging reactions are:

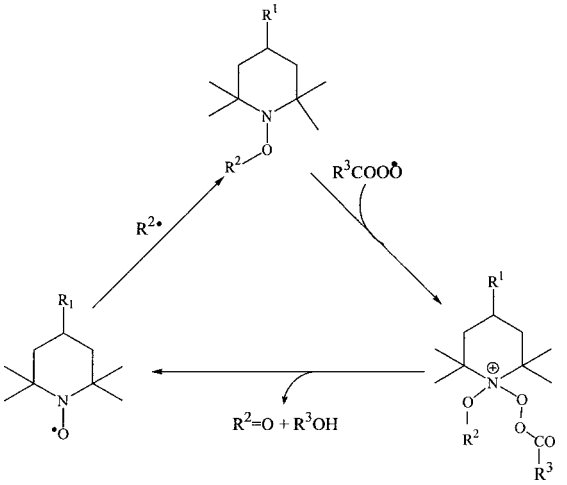
$k$(HALS NH) = $5.1\times10$ *l*/mol·s

$k$(HALS NOH) = $5.5\times10^{2}$ *l*/mol·s

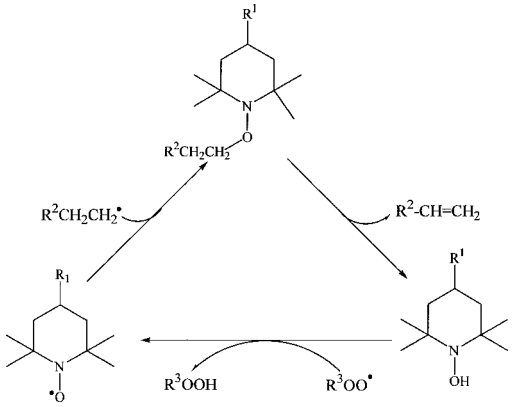
$k$(HALS $NCH_3$) = $2.6\times10^{2}$ *l*/mol·s

in which HALS $NCH_3$ is the *N*-methylated HALS. These values are much larger than the rate constant of HALS NOR to HALS NO. Therefore, the cycle mechanism of **Scheme 3** could operate.

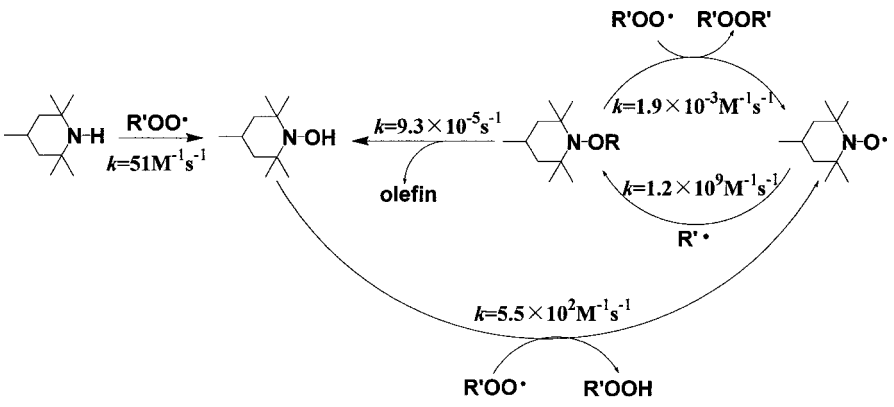
Other radical scavenging mechanisms have also been proposed. HALS NO can react with peroxy radicals in two modes[8], secondary peroxy radicals form inert carbonyl compounds, with HALS NO becoming HALS NH, and HALS NOR is formed through a super-



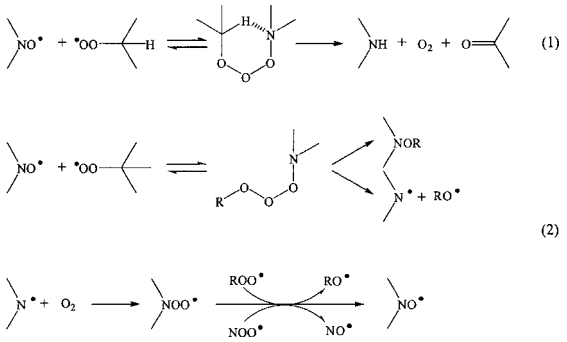

Scheme 1 New Denisov's Cycle



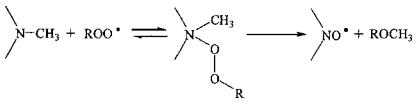

Scheme 2 Scott's Cycle



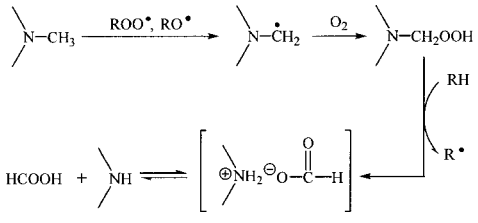

Scheme 3 Kinetics Data of Radical Scavenging Reactions by HALS Derivatives



Scheme 4 Peroxy Radical Scavenging by HALS NO



Scheme 5 Peroxy Radical Scavenging by HALS $NCH_3$



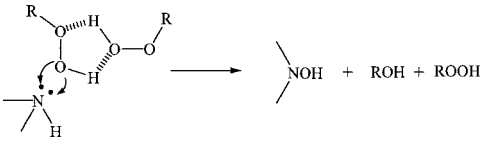
Scheme 6 Reaction of HALS $NCH_3$ with Radicals

peroxide intermediate by the reaction of HALS NO with a tertiary peroxy radical (**Scheme 4**). In addition, HALS $NCH_3$ may scavenge peroxy radicals to form HALS NO as shown in **Scheme 5**[9]. On the other hand, scavenging of oxygen centered radicals may occur according to the mechanism shown in **Scheme 6**[10].

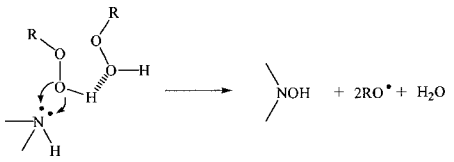
Radical scavenging by HALS may be very complex, and many reactions may occur independently or in combination. The important point is that the radical scavenging function of HALS depends on oxidized HALS derivatives such as HALS NO, NOH, and NOR (called "good" HALS in this paper). Generally phenolic antioxidants are much more effective for peroxy radical scavenging (rate constant of 2,6-di-*t*-butyl-4-methylphenol (BHT) is $1.7\times10^4$ *l*/mol·s at 50℃) than HALS, although alkyl radical scavenging by HALS NO is the greatest feature of HALS.

## 2. 3. Hydroperoxide Decomposition Activity of HALS

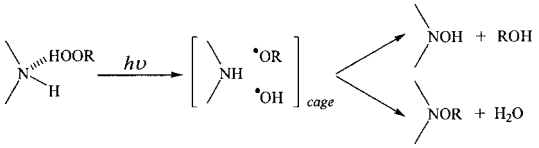
Hydroperoxide decomposition by HALS is an important process for forming oxidized HALS derivatives as active antioxidant species rather than for contributing to the antioxidant action. Various theories have been proposed for the hydroperoxide decomposition mechanism. For example, secondary, tertiary, and hydroxyl amines are proposed to have peroxide decomposition



Scheme 7 Heterolytic Hydroperoxide Decomposition by HALS



Scheme 8 Homolytic Hydroperoxide Decomposition by HALS



Scheme 9 Seldar's Mechanism

activity, with the second order rate constant of decomposition reaction proportional to the acid dissociation constant[11]. The mechanism involves heterolytic or ionic decomposition proceeding trough the nucleophilic attack of a hydroperoxide on the lone pair of an amine nitrogen atom (**Scheme 7**). Homolytic decomposition through a similar nucleophilic reaction starting with the attack of a hydroperoxide on the lone pair has also been proposed (**Scheme 8**)[12].

Another mechanism is based on a reaction forming a complex of HALS and peroxide. Infrared spectroscopy of the interaction of HALS and a number of hydroperoxides detected no ammonium salt, but an aggregated form of HALS and a hydroperoxide, which was finally decomposed to the alcohol (**Scheme 9**)[13]. A similar mechanism involved HALS and hydroperoxide forming a charge transfer complex, which forms the alcohol through a cage reaction[14].

On the other hand, HALS aminyl radical may be formed by HALS reacting with hydroperoxide. The aminyl radical reacts with oxygen and then with a polymeric chain to give HALS NOOR (R = a polymer chain), which finally forms HALS NO[15]. A hydropeoxide decomposition mechanism for HALS NOH generated by oxidation of HALS was also proposed[16]. Piperidine ring cleaving during hydroperoxide decomposition by HALS NOH and HALS NR has been reported[9].

The decomposition of cumene hydroperoxide (CHP) by HALS NH progresses through two continuous stages[17]. The initial slow decomposition stage is regarded as an induction period to generate the active decomposition species, which functions in the last fast

stage. This decomposition does not progress stoichiometrically but catalytically[18], so HALS NH can decompose about 10 moles of CHP more than the stoichiometric amount as described in detail later. Hydroperoxide decompositions by HALS has been assumed to progress either heterolytically or homolytically. However, CHP gives different decomposition products depending on the decomposition mode: heterolytic decomposition forms phenol and acetone, whereas homolytic decomposition gives acetophenone and cumyl alcohol. Therefore, CHP decomposition can be utilized to determine the decomposition mode. In this study, only acetophenone and cumyl alcohol formed in these both stages, and no phenol was detected at all. Therefore, HALS decompose CHP homolytically to form an active species, a HALS nitrosonium salt (sometimes called "bad" HALS), as explained in detail later[18]. This HALS derivative forms the piperidine ring cleaved products after the hydroperoxide decomposition[18]. This cleavage agrees well with the previously reported findings[9].

Many unclear points remain with respect to hydroperoxide decomposition by HALS, but the identification of HALS nitrosonium is important in assessing the proposed action mechanisms of HALS.

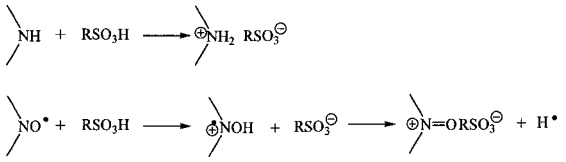
### 2. 4. Other Antioxidant Functions of HALS

Some other functions of HALS include deactivation of heavy metals[19] and quenching action of a photoexcited carbonyl and singlet oxygen which degrade polymeric materials[9]. In addition, HALS can act as an antioxidant of Polypropylene (PP) by scavenging aldehyde derived from ionic decomposition of PP hydroperoxides to control further oxidation to the peracid[20].

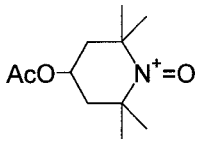
## 3. Interaction of HALS with Other Additives

### 3. 1. Interaction with Acidic Compounds

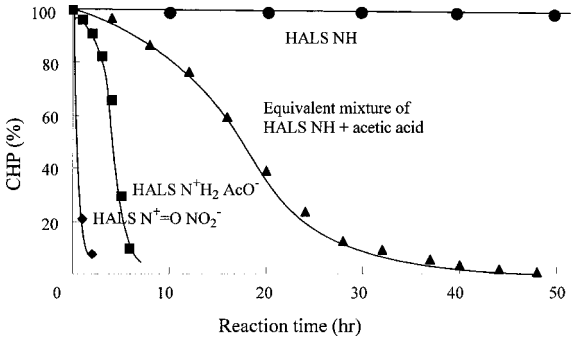
HALS are basic compounds showing antagonism to acidic compounds, such as the antagonism of HALS with sulfur- containing hydroperoxide decomposers. The sulfur-type additive added to stabilize polymeric materials against thermal degradation is believed to decompose hydroperoxides faster than HALS, so the HALS active species, such as the oxidized derivatives, are not formed[21]. On the other hand, the antagonism may be caused by the salt formation of HALS with sulfinic and sulfonic acids derived from the sulfur-type additives, resulting in no formation of HALS active species. Or HALS nitrosonium may be generated and HALS are consumed uselessly (**Scheme 10**), although the nature of the nitrosonium was not investigated[22]. HALS NO may generate free radicals by abstracting hydrogen from sulfur-containing hydroperoxide decomposer[23]. The free radical triggers initiating autoxidation to degrade polymeric materials, but does not cause HALS deactivation.




Scheme 10 Antagonism of HALS with Sulfonic Acid




Scheme 11 Structure of HALS Nitrosonium

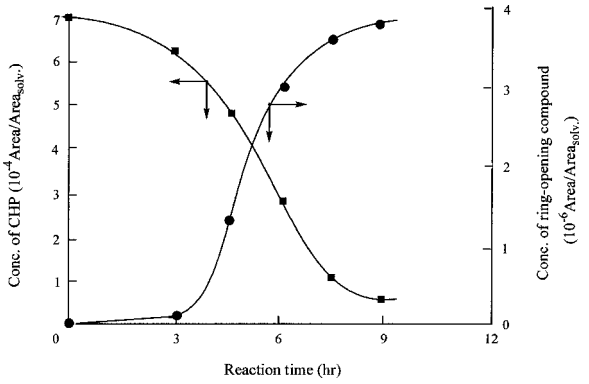



[Ac-HALS] = 1 mmol/*l*, [CHP] = 10 mmol/*l*, in chlorobenzene under $N_2$ at 120℃.

Fig. 1 Decomposition of CHP by Ac-HALS

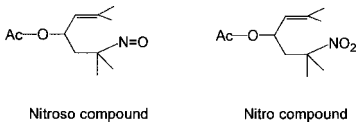
The antagonistic interactions of HALS and acids are complex and unsettled. However, the authors found that an undesirable HALS active species, HALS nitrosonium ("bad" HALS, see **Scheme 11**), is also formed during the hydroperoxide decomposition necessary to produce "good" HALS. Moreover, formation of such "bad" HALS nitrosonium is accelerated by the action of acidic compounds and also induces fast homolytic hydroperoxide decomposition[24]. The effect of acidic compound on hydroperoxide decomposition by HALS is as follows.

**Figure 1** shows the effect of acetic acid on CHP decomposition by a HALS species, namely Ac-HALS (4-acetyl-2,2,6,6-tetramethylpiperidine). Using only HALS for the decomposition, the induction period was about 120 h. Therefore, CHP was hardly decomposed within 50 h. However, the induction period decreased to about 9 h if acetic acid was added to HALS in equimolecular amount. Furthermore, the induction period further decreased to 2.5 h, if HALS NH acetate was used as the HALS derivative[24]. At the same time, some new compounds originating in HALS were observed (**Fig. 2**). The "ring opening compounds" indicates compounds with the chemical structures shown in




[Ac-HALS nitrosonium acetate] = 1 mmol/*l*, [CHP] = 10 mmol/*l*.

Fig. 2 Relationship between CHP Decomposition and HALS Nitrosonium Formation




Scheme 12 Ring-opening Compounds of HALS

**Scheme 12**. These compounds are derived from HALS nitrosonium, which breaks down easily with heat to the nitroso compound which reacts with a peroxy radical to form the nitro compound. Therefore, these two compounds clearly show the presence or formation of HALS nitrosonium during CHP deccomposition. Returning to **Fig. 2**, HALS nitrosonium was generated in correspondence with fast CHP decomposition. The idea that HALS nitrosonium is an active species of hydroperoxide decomposition agrees with the fact that a separately synthesized HALS nitrosonium decomposes CHP without any induction period and very rapidly to give the same ring opening compounds (see **Fig. 1**).

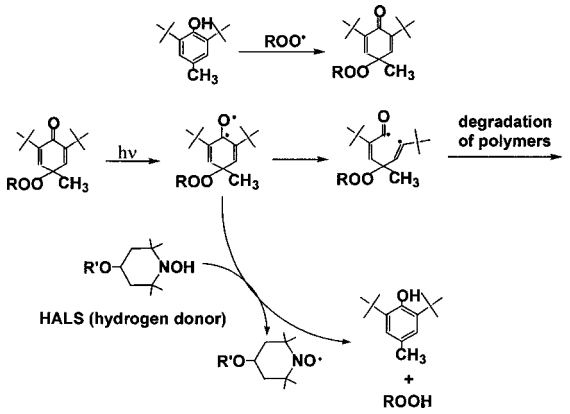
The generally accepted antagonisms of HALS with acidic compounds can be summarized as interfering with the formation of "good" HALS, for instance, HALS NO, HALS NOH, and HALS NOR. However, this idea will have to be reconsidered as acid accelerates the formation of "bad" HALS, rather than generating "good" HALS species.

### 3. 2. Interaction of HALS with Phenolic Antioxidant

#### 3. 2. 1. Synergism

Ohkatsu's mechanism (**Scheme 13**) is the only one proposed for the synergism between HALS and a phenolic antioxidant[2),25),26)]. This mechanism is based on the observation that, in BHT-inhibited autoxidatioin, a small amount of added HALS (1/5 to 1/15 moles per mole of BHT) increased the effect of BHT by 1.5 times.

In addition, UV rays also acted as a promotor. This phenomenon is not based on peroxy radical scavenging




Scheme 13 Ohkatsu's Synergistic Mechanism of HALS and Phenol

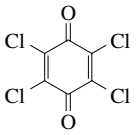
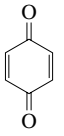
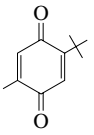
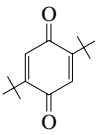
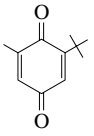
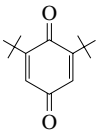
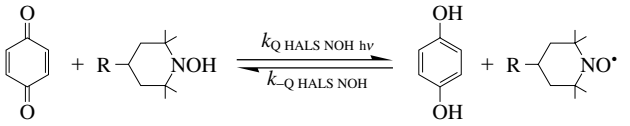
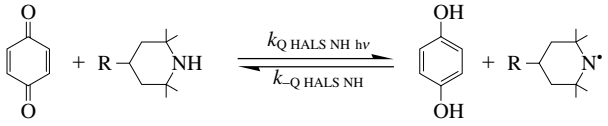
by HALS which have rather poor activity, but is ascribable to the regeneration of a phenolic antioxidant. The phenolic antioxidant forms a quinoid compound after scavenging peroxy radicals, which absorbs UV rays to regenerate the phenolic form. On the other hand, HALS used often with a phenolic antioxidant is oxidized to HALS NOH by reacting with hydroperoxides. Therefore, the HALS NOH will donate hydrogen to the photo-excited quinoid compound to regenerate the phenol, because the photo-excited carbonyl group can easily abstract hydrogen from the surrounding to form the corresponding alcohol[27)]. In fact, such a phenol regeneration reaction depends on the first order of UV rays intensity (**Scheme 13**)[27)]. The result is shown in **Table 1**. This type of reaction also proceeds using HALS NH, but is inferior to that of HALS NOH.

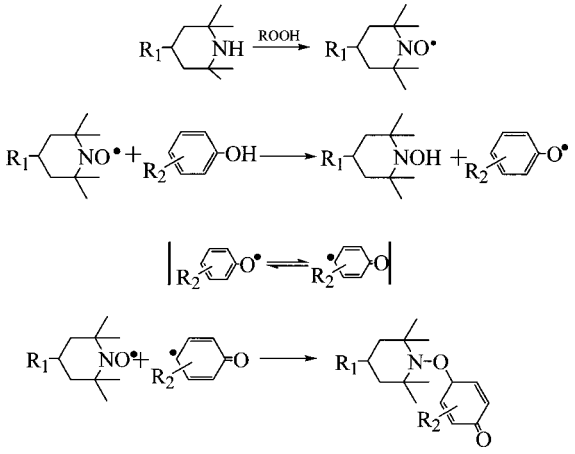
Such synergism also explains the misinterpretation of HALS as excellent light stabilizers. HALS act as the proton donor or reducing agent of the quinoid compound, and prevent the oxidation initiation by light-absorption or photo-excitation of the quinoid. This mechanism accounts for the synergism of HALS and phenolic antioxidants[1),2)]. **Table 1** suggests that a less hindered phenol is better, whereas a hindered phenol is worse (see, equilibrium constant *K*). However, the opposite result is often obtained, if HALS and phenols are kneaded into polymeric materials. This observation will be discussed in detail in the section on the reaction of HALS nitrosonium and phenols.

#### 3. 2. 2. Antagonism

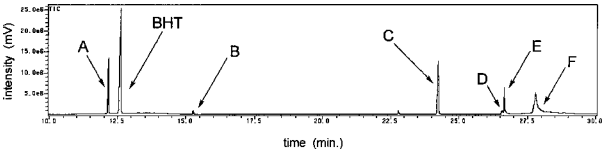
Phenolic antioxidants with HALS are used in many kinds of polymeric materials, but sometimes show antagonism. The antagonistic mechanism involves consumption of a phenol by the HALS NO abstracting the hydrogen[28)]. On the other hand, the deactivation of both additives may occur by the coupling of HALS NO with a phenoxy radical[14)]. The antagonistic mechanism widely accepted at present is a combination of these proposals as shown in **Scheme 14**. However, the former mechanism seems thermodynamically con-

Table 1 Regeneration of Phenol by HALS

| | | | | | | |
|---|---|---|---|---|---|---|
| |  |  |  |  |  |  |
| |  | | | | | |
| $k_{Q\ HALS\ NOH}$ | 33.3 | 15.8 | 6.83 | 3.33 | 2.02 | 0.33 |
| $K_{HALS\ NOH}$ | 0.0978 | 0.409 | 116 | 16 | 2.55 | 1.93 |
| |  | | | | | |
| $K_{HALS\ NH}$ | 0.1 | 0.2 | 3.6 | 1.2 | 1.4 | 1.1 |

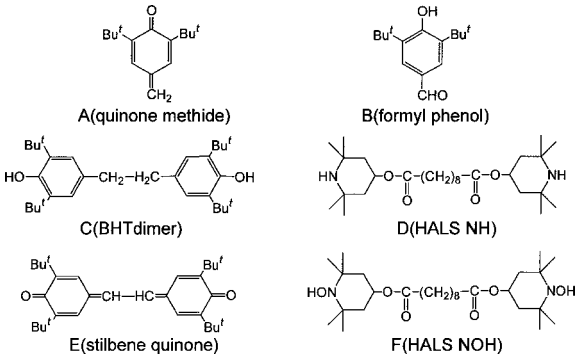


Scheme 14 Antagonism of HALS with Phenolic Antioxidant




[HALS NO] : [BHT] = 10 mmol/*l* : 20 mmol/*l* in chlorobenzene at 120℃.

Fig. 3 Gas Chromatogram of Reaction Mixture of HALS NO and BHT after 6 h

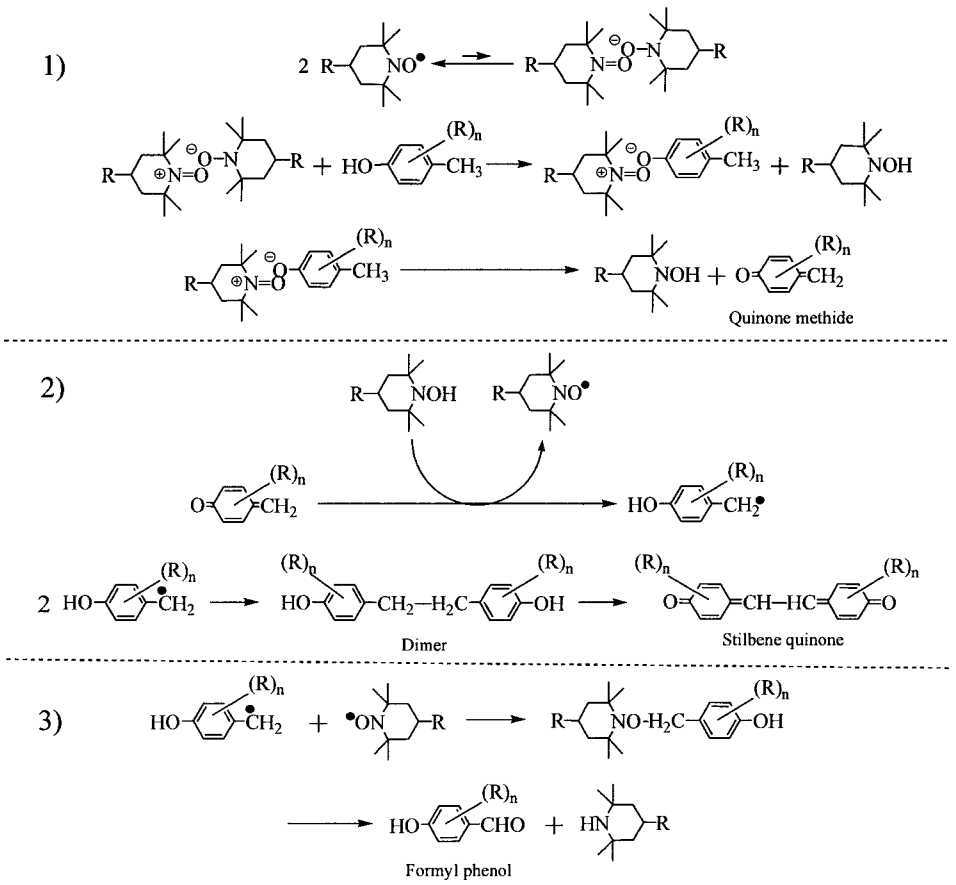



Scheme 15 Reaction Products of HALS NO and BHT

tradictory, because HALS NO is a very stable radical under atmospheric conditions wheresas a phenoxy radical is considerably unstable. Therefore, the formation of the phenoxy radical will need some high driving force, which does not seem present.

The authors have traced the above-mentioned reaction of HALS NO with BHT, and identified the reaction products quantitatively[29]. **Figure 3** illustrates a gas chromatogram of the reaction of HALS NO ($1\times10^{-2}$ mol/*l*) and BHT ($2\times10^{-2}$ mol/*l*) for 6 h at 120℃. Various products (A-F) are shown in **Scheme 15**. The coupling product of phenoxy radical and HALS NO as shown in **Scheme 14** was not detected. Therefore, such antagonism is unlikely. Interestingly, the same color products as formed in the reaction of BHT with $NO_2$ gas[30] are detected. Actually, the reaction solution of HALS NO and BHT becomes yellow during the reaction, and finally orange in the accordance with the generation of compounds A and E. This result suggests the formation of a very strong oxidant, equivalent to $NO_2$ gas, during the reaction of HALS NO and BHT: HALS nitrosonium is very likely to be one of the candidates. As is expected, the separately synthesized HALS nitrosonium has a high oxidant power, and can oxidize BHT to give the same products as shown in **Scheme 15**. This is positive evidence for the formation of HALS nitrosonium, in the reaction of HALS NO and BHT, clearly acting as an active species uselessly oxidizing BHT[29].

The antagonism of HALS NO and BHT can be expressed as in **Scheme 16**. First of all, two moles of HALS NO form HALS nitrosonium by electron trans-

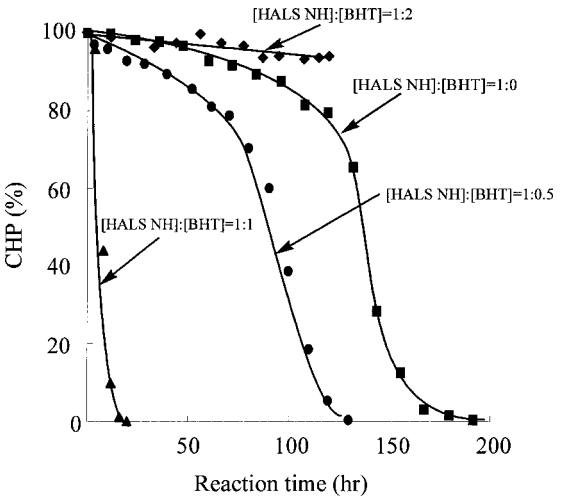



Scheme 16 New Antagonism between HALS NO and Phenolic Antioxidant

fer[31]. This HALS nitrosonium forms HALS nitrosonium phenolate and HALS NOH by anion exchange. Then the former forms HALS NOH and quinone methide. The quinone methide gets one electron to become the radical anion, two moles of which react to form stilbene quinone. Or the quinone methide reacts with HALS NO, in parallel, to form formyl phenol and HALS NH. This mechanism can explain the experimental observations and the products shown in **Scheme 15**.

The interaction of HALS derivatives, in addition to HALS NO, with BHT is also studied[24]. **Figure 4** shows CHP decomposition by HALS NH in the presence of BHT. The induction period of CHP decomposition shortens with the addition of BHT up to the equimolar amount of HALS. This phenomenon results from faster generation of HALS nitrosonium by BHT acting as an acid. Compared with the reaction of other HALS derivatives and BHT (**Fig. 5**), HALS NH shows extreme antagonism with BHT. This fact corresponds well to the phenomenon that HALS NH is less effective for stabilizing polymeric materials than other "good" HALS.

The basic characteristics of HALS are important for the practical use of HALS. The antagonism of HALS

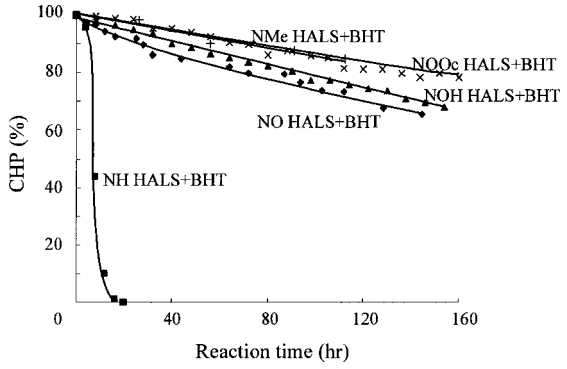



[HALS NH] = 1 mmol/*l*, [CHP] = 10 mmol/*l*, in chlorobenzene under $N_2$ at 120℃.

Fig. 4 Decomposition of CHP by HALS NH in the Presence of BHT

shown in **Fig. 5** is in the order of

HALS NH≫HALS NO>HALS NOH>HALS $NCH_3$ = HALS NOOc,




[HALS] = [BHT] = 1 mmol/*l*, [CHP] = 10 mmol/*l*, in chlorobenzene under $N_2$ at 120℃.

Fig. 5 Decomposition of CHP by HALS Derivatives in the Presence of BHT

Table 2 Basicities of HALS Derivatives

| HALS | $pK_b$ in this study | $pK_b$ reported |
|---|---|---|
| HALS NOOc | 10.2 | |
| HALS NOR | | 9.6 |
| HALS NO | 9.4-9.9 | |
| HALS NOH | 9.5-9.7 | |
| HALS $NCH_3$ | 6.5 | 5.1 |
| HALS NH | 5.7-5.9 | 5.0 |

where HALS NOOc is *N*-octyloxylated HALS. This order indicates "bad" HALS nitrosonium generation or roughly corresponds to the degree of HALS basicities (see **Table 2**), except for HALS $NCH_3$. This very interesting series explains the superiority of HALS with a lower basicity.

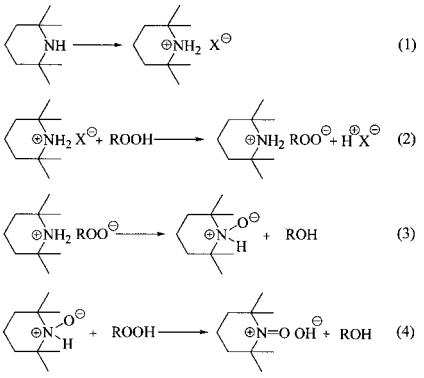
### 3. 3. Characteristics of HALS Nitrosonium Salt

#### 3. 3. 1. General Character of Organic Nitrosonium

About 40 years ago, a nitrosonium compound was synthesized by reacting chlorine or bromine with the nitroxyl radical of tetramethylpiperidine. Nitrosonium is also formed by reacting hydrochloric acid with a nitroxyl radical[32]. Furthermore, HALS nitrosonium is formed by equilibrium electron transfer between two HALS NO molecules[31]. All nitrosonium species seem to originate in the corresponding nitroxyl radicals.

The reactivities of nitrosonium compounds are well reported[33),34)], in particular the oxidation of alcohols. Nitrosonium can oxidize primary and secondary alcohols to the aldehyde and the ketone respectively. However, oxidation of phenols is not well known. Oxidation of 2,4-di-*t*-butylphenol with nitrosonium compound forms the quinone dimmer, but the mechanism is not dicussed in detail[35].

Oxidation of compounds other than alcohols is also reported. For example, a nitrosonium can oxidize a ketone to $\alpha$-diketone[36]. Electron transfer occurs when triethyl amine reacts with nitrosonium, resulting in the formation of triethylaminyl cation radical and the nitroxide[32].




Scheme 17 Formation Mechanism of HALS Nitrosonium

Piperidine nitrosonium compound can undergo the ring-opening reaction. For example, a reaction like Hoffman decomposition takes place under the action of a base to produce a nitroso compound, if a double bond with oxygen or nitrogen is present at the 4-position of the piperidine ring[31),34),37)]. If a nitrosonium has chloride ion as the counter anion, ring cleavage also occurs under the action of sodium benzoate and silver benzoate, even if the 4-position has no double bond[33].

#### 3. 3. 2. Generation of HALS Nitrosonium from HALS NH

The formation mechanism of HALS nitrosonium is shown in **Scheme 17**[24]. In general, less basic HALS have less antagonism with phenols, as explained by step (1). Then, an anion exchange occurs between the salt and excess hydroperoxide to give the intermediate shown in step (3). This intermediate undergoes two-electron oxidation by another hydroperoxide to form the HALS nitrosonium in step (4).

The induction period of CHP decomposition by HALS should be longer, due to the hindered approach of less hydrophilic CHP, if a more hydrophilic substrate such as an acid coexists in large amounts. This phenomenon is observed if twice the amount of BHT per HALS is added (see **Fig. 4**). The addition of cumyl alcohol also retards CHP decomposition.

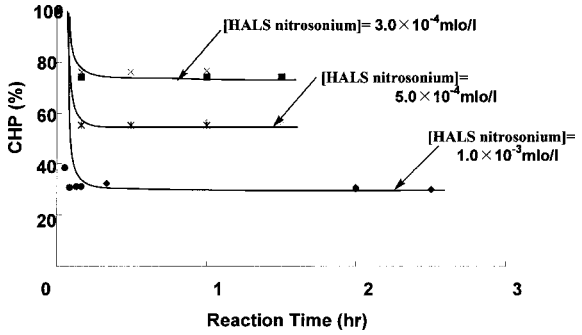
As shown in **Fig. 5**, acid-sensitive HALS are just HALS NH. Therefore, HALS derivatives other than HALS NH should be used to exclude "bad" HALS behavior. However, HALS NH may form, in some cases, during HALS reactions, even if other HALS are used at the beginning. "Good" HALS always has the potential into a "bad" HALS nitrosonium.

#### 3. 3. 3. Hydroperoxide Decomposition by HALS Nitrosonium

**Figure 6** shows the CHP decomposition by HALS nitrosonium, with duplicated runs indicated separately[18]. The concentration of CHP was fixed as $10^{-2}$ M (1 M = 1 mol·dm$^{-3}$). HALS nitrosonium nitrite decomposed

CHP very promptly and catalytically: one mole of the nitrosonium decomposed 15-25 times moles of CHP, suggesting a redox mode of decomposition. The products originating in HALS nitrosonium in this reaction are also ring opening products as mentioned before. Therefore, HALS nitrosonium is presumed to function as an active hydroperoxide-decomposing species, although the ring-opening compound like a nitroso derivative may also be active species[17].

CHP decomposition by HALS nitrosonium is very sensitive to the solvent polarity[24]. Changing the solvent from chlorobenzene to more polar benzonitrile




[CHP] = 10 mmol/*l*, in chlorobenzene under $N_2$ at 120℃.

Fig. 6 Decomposition of CHP by HALS Nitrosonium

remarkably retards CHP decomposition, also by substituting chlorobenzene with acetophenone with polarity between chlorobenzene and benzonitrile. The polar HALS nitrosonium and CHP probably form aggregates in a less polar solvent, resulting in immediate CHP decomposition, explaining the low CHP decomposition in the presence of twice the moles of BHT compared to HALS NH, because some excess BHT gathers around the HALS to prevent the approach of CHP (see **Fig. 4**)[17].

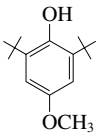
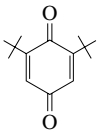
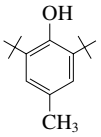
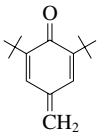
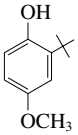
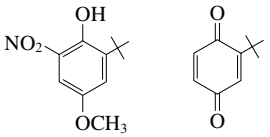
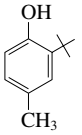
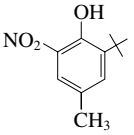
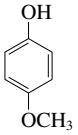
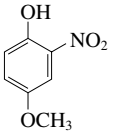
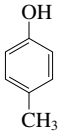
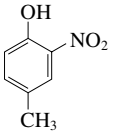
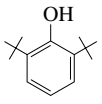
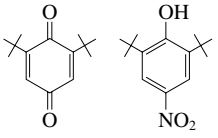
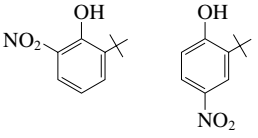
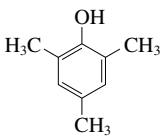
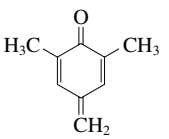
### 3. 3. 4. Reaction of HALS Nitrosonium with Phenol

**Table 3** shows the reaction of HALS nitrosonium nitrite with phenols at room temperature[24]. The reaction modes can be classified into three groups:

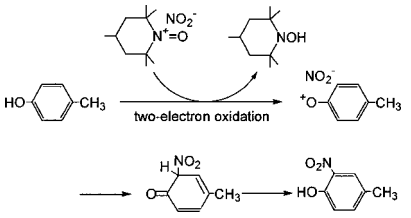
(1) oxidation to quinoid compound,
(2) nitration, and
(3) a combination of these reactions.

The oxidation of phenols by HALS nitrosonium completely depends on the oxidation potentials of the phenols. 2,6-Di-*t*-butyl-4-methoxyphenol and 2-*t*-butyl-4-methoxyphenol with lower oxidation potentials are oxidized to the corresponding benzoquinones more easily, but such an oxidation reaction does not progress for a phenol with a higher oxidation potential. On the other hand, the nitration by attack of $NO_2^-$, the counter anion of HALS nitrosonium, seems not to depend on the oxidation potential of the phenol (**Scheme 18**). This re-

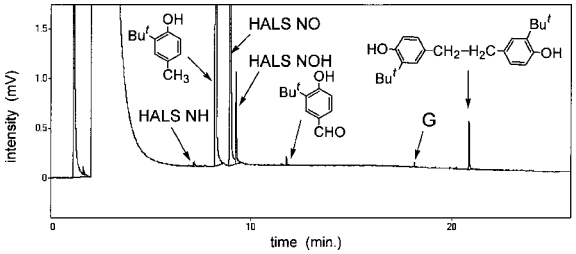
Table 3 Influence of Oxidation Potential of Phenol on Reaction Products in the Reaction of Phenol with HALS Nitrosomiun Nitrite

| Phenol | Oxidation potential [v] | Reaction products | Phenol | Oxidation potential [v] | Reaction products |
|---|---|---|---|---|---|
|  | 0.94 |  |  | 1.24 |  |
|  | 0.98 |  |  | 1.29 |  |
|  | 1.05 |  |  | 1.40 |  |
|  | 1.15 |  |  | 1.52 |  |
|  | 1.21 |  | | | |

[HALS $N^+ = 0$] = $5.0 \times 10^{-4}$ mol/*l*, [Phenol] = $5.0 \times 10^{-4}$ mol/*l*, in chlorobenzene under $N_2$ at 120℃.
Oxidation potential: [Phenol] = $1.0 \times 10^{-3}$ mol/*l* in 0.1 M tetrabutylammonium perchlorate solution in acetonitrile under $N_2$.

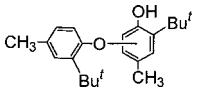



Scheme 18 Estimated Formation Mechanism of Nitrated Phenol




[HALS NO] : [cresol] = 10 mmol/*l* : 20 mmol/*l* in chlorobenzene at 120℃.

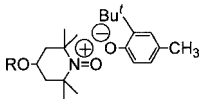
Fig. 7 Gas Chromatogram of Reaction Mixture of HALS NO and 2-*t*-Butyl-*p*-cresol after 23 h



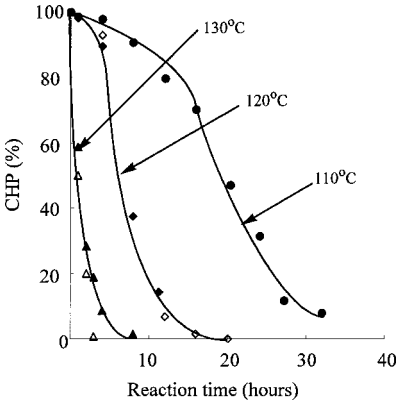
Scheme 19 Phenolic Dimmer

action progresses preferentially for phenols with no substituent(s) on the *o*- and/or *p*-position(s), with nitration at the *o*-position being easier than that at the *p*-position. Similar reaction using HALS nitrosonium bromide formed the corresponding brominated phenol. These results may suggest that the reaction depends on the stability of the phenoxy cation formed from the phenol by two-electron oxidation by HALS nitrosonium. In summary, the intermediate phenoxy cation undergoes two-electron oxidation to the *p*-benzoquinone for a phenol with a low oxidation potential, or becomes a quinone methide by releasing a proton for a phenol with a medium potential. The rather stable phenoxy cation is not oxidized further, but reacts with the counter anion of HALS nitrosonium.

**Figure 7** is a gas chromatogram obtained from the reaction of HALS NO ($1\times10^{-2}$ mol/*l*) and 2-*t*-butyl-*p*-cresol ($2\times10^{-2}$ mol/*l*) for 23 h at 120℃[29]. Similar products to the case of BHT were formed except for a few differences. The generation of dimers originating in 2-*t*-butyl-*p*-cresol could be identified, but the quinone methide regarded as a precursor of the dimer and stilbene quinone was not confirmed. Interestingly, the product G of **Fig. 7** with the structure shown in **Scheme 19** was detected for 2-*t*-butyl-*p*-cresol. This is a different dimer of the phenol from that just mentioned, with unspecified substitution position, but probably on the *o*-position as the ease of nitration. Moreover, such a dimer suggests the existence of an intermediate shown in **Scheme 20**, and provides important evidence for the formation of the similar intermediate shown in **Scheme 16**.



Scheme 20 HALS Nitrosonium Phenolate




[HALS] = [BHT] = 5 mmol/*l*, [CHP] = 50 mmol/*l*, in chlorobenzene under $N_2$.

Fig. 8 Effect of Temperature on Decomposition of CHP by HALS in the Presence of BHT

The non-hindered phenol, *p*-cresol, did not react with HALS NO at all at 120℃ for 50 h. The reactivity of HALS NO with phenols is in the order of

BHT＞2-*t*-butyl-*p*-cresol≫*p*-cresol

which is the same as that of the reactivity of HALS nitrosonium with the phenol. Therefore, a phenol with a low oxidation potential antagonizes HALS NO, whereas a phenol with a high oxidation potential has good compatibility with HALS NO.

In practical use, a hindered phenol is often considered to be more compatible with HALS than a less-hindered phenol. If HALS and phenols are used together, both synergism and antagonism occur at the same time. For example, the synergism is higher for a less-hindered phenol, but this phenol is consumed antagonistically by coupling as shown in **Scheme 19**. Therefore, the actually recognized synergism or antagonism in the interaction of HALS with phenols will depend on the balance of the these synergistic and antagonistic reactions.

This review has proposed a new mechanism of antagonism of HALS with phenols. **Figure 8** shows the temperature dependence of this antagonism[17]. The induction period of the CHP decomposition shortens

remarkably with increased temperature, and is not observed at 130℃. Based on this result, HALS nitrosonium must be produced rapidly at a practical processing temperature (>200℃) of polymeric materials, so will promote the deterioration of polymeric materials and cause deterioration in the service life. In general, a hydroperoxide decomposer such as phosphorus-type antioxidant is added to make hydroperoxides harmless during processing. This decomposition reaction will compete with the homolytic decomposition by HALS nitrosonium. Under practical conditions, the free radicals and hydroperoxides produced will continue to remain active after processing, if the ionic or heterolytic decomposition does not sufficiently surpass the homolytic decomposition. Therefore, processing under severe conditions requires the use of low basicity HALS or no "bad" HALS, because HALS may adversely affect the processing in the presence of a phenolic antioxidant, depending on the formulation of the additives.

Even if an acidic compound accelerates the homolytic decomposition by HALS, such decomposition will not become antagonistic if the HALS can scavenge the formed radicals efficiently. Thus, the ESR method was used to measure the amount of HALS NO, which forms as a result of HALS NH ($5\times10^{-3}$ mol/*l*) scavenging both peroxy and alkoxy radicals at 120℃. The maximum concentration of HALS NO was evaluated as $2\times10^{-6}$ mol/*l*, corresponding to only 0.04% of the initial concentration of HALS NH. Therefore, HALS does not function as a radical scavenger effectively enough to counteract the homolytic hydroperoxide decomposition.

### 3. 4. Interaction of HALS with UV Absorbers

#### 3. 4. 1. General Aspects of the Interaction

No accepted explanation including the direct participation of light had been proposed for the photostabilizing ability of HALS. This present review proposed the photo-interaction of HALS with benzoquinones originating from added phenols. The mechanism is explained well, in **Scheme 13**, as a synergism of HALS with phenols. However, HALS and phenols sometimes show antagonism as mentioned in the preceding section.

UVA show a synergism with HALS regardless of the type of phenols. HALS and benzotriazole type UVA do not interact directly, but apparently work synergistically, because of independent involvement in different light stabilization processes, while the antioxidant activity of HALS protects useless consumption of UVA[38]. HALS tend to be consumed slowly in the presence of benzotriazole type UVA, so the UVA continues to be effective much longer, although HALS do not affect any photolysis of UVA[39]. That is, HALS in combination with UVA is preferred because of apparent stabilization of UVA against photolysis, resulting in synergism. On the other hand, the preferable mole ratios of HALS to UVA to achieve photo-stabilization were about 75 : 25 for polypropylene and high density polyethylene, 90 : 10 for ABS resin, and 80 : 20 for crystalline polystyrene[40]. This synergistic effect is explained as HALS, being located inside, protected from the harmful UV light by the UVA near the surface of the plastics. Broadly speaking, as mentioned above, the interaction between HALS and UVA is synergistic without exception, but the mechanism has not been totally understood yet.

Table 4 Synergism of HALS with UVA or UVA *p*-Quinone

| | Relative ratio of synergism | | |
|---|---|---|---|
| | UVA 1 | UVA 2 | UVA 3 |
| Photo-antioxidant by UVA + HALS NOH | 2.45 | 1.41 | 1.00 |
| Photo-antioxidant by UVA *p*-quinone and HALS NOH | 2.02 | 1.24 | 1.00 |

UVA 1: 2-(2'-hydroxy-5'methoxy)-phenylbenzotriazole.
UVA 2: phenyl 5-hydroxysalicylate.
UVA 3: 2-hydroxy-benzophenone.

#### 3. 4. 2. Synergistic Interaction of HALS and UVA

The authors consider that the synergistic effect of HALS and UVA can be explained using the relationship between photo-antioxidant ability and hydroperoxide decomposition ability of HALS and/or UVA. UVA, exhibiting higher photo-antioxidant activity in the absence of HALS NH, can better control the homolytic CHP decomposition by HALS NH together with the UVA. High photo-antioxidant UVA, namely no or little proton-donating UVA, is unlikely to show antagonism with HALS NH.

Interestingly, an equimolar mixture of UVA and HALS NH shows similar or greater photo-antioxidant activity compared with that of a double amount of only UVA[41]. This synergism is ascribable to the regeneration of UVA, because HALS has no particular photo-antioxidant functions. Thus, the interaction of HALS with UVA can be characterized by weak antagonism and strong synergism. If such an interaction is evaluated semi-quantitatively by the kinetic approach, for instance, a benzophenone UVA promotes homolytic CHP decomposition by HALS, although the promotion degree is much lower than that of BHT. HALS nitrosonium forms in the presence of benzophenone similarly to BHT, but does not oxidize the benzophenone as much as BHT[42]. In addition, even if HALS nitrosonium oxidizes benzophenone to 2-benzoyl-*p*-quinone, this is promptly reduced to a new UVA by HALS NOH.

**Table 4** summarizes the semi-quantitative evaluation of the interactions of HALS and UVA[43]. The upper line shows the synergistic effect of both additives in the photo-oxidation of styrene in the presence of UVA and HALS NOH. The numerical values are ratios based

on 1.00 for benzophenone. On the other hand, the lower line shows the synergism obtained in the same photo-oxidation of styrene except for substituting UVA with UVA *p*-quinone derived from UVA scavenging peroxy radicals. This comparison shows how the *p*-quinone is reduced to a new UVA during the photo-oxidation. The values in both lines agree well, indicating that the essence of the synergistic action of HALS with UVA in photo-oxidation is to generate new UVA from UVA *p*-quinone by HALS NOH. In summary, UVA show apparent synergism due to the low antagonism and very high synergism with HALS.

### 3. 5. Proposal of Unified Action Mechanism of HALS

Many action mechanisms of HALS have been proposed, but there is little consistency. In this paper, HALS are divided into two groups of "good" HALS and "bad" HALS, by which the authors have tried to clarify various uncertain points concerning the functions of HALS. The "good" HALS include HALS NH, HALS NR, HALS NO, HALS NOH, HALS NOR, and their desirable functions are demonstrated for polymer degradations as follows:

HALS NH: scavenging oxygen-centered radicals, reducing photo-excited species, deactivating metal ions,
HALS NR: scavenging oxygen-centered radicals, deactivating metal ions,
HALS NO: scavenging carbon-centered radicals
HALS NOH: scavenging oxygen-centered radicals, reducing photo-excited species,
HALS NOR: scavenging oxygen-centered radicals, producing HALS NOH.

Previous study have tried to explain all functions of HALS using such "good" HALS, but have generally failed because the "bad" behavior of HALS cannot be explained using "good" HALS. Here, the author have suggested that "bad" HALS, namely HALS nitrosonium, exists in addition to "good" HALS, and is responsible for the bad following characteristics:

homolytically decomposing hydroperoxides, and
oxidizing phenolic compounds, such as phenolic antioxidants and UVA.

The actual HALS behavior must be discussed by considering the functions of both "good" and "bad" HALS. So, can "good" and "bad" HALS provide a unified explanation of the entire HALS action. There are two important points for establishing the unified action mechanism. First is the problem concerning the synergistic action of HALS and phenolic additives. The synergistic actions of these additives are not supported by reliable positive evidence. On the contrary, the authors believe that the synergistic action is based on regenerating a phenol by the action of HALS, especially HALS NOH, on a benzoquinone.

The second problem is the antagonistic interaction of HALS with phenols. The clue to resolve this problem

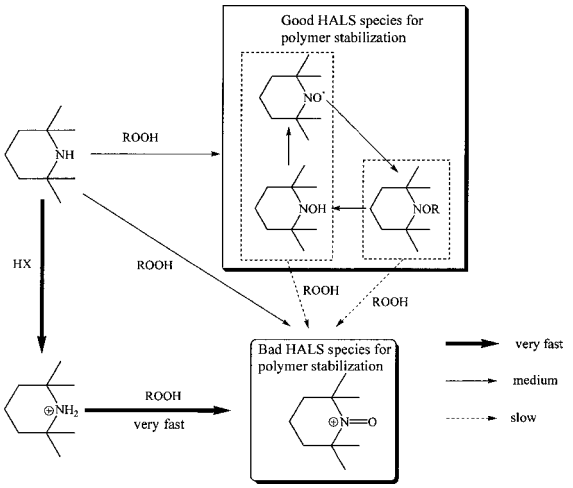



Fig. 9 HALS Nitrosonium Formation

is to regard a phenol as acid. As a result, the interaction of HALS with a phenol has been found to accelerate the formation of HALS nitrosonium, which is the cause of the "bad" HALS behavior. Thus, the antagonism of HALS and phenols can be clarified semi-quantitatively.

In the past, the interaction of HALS with other additives has not been studied by the consideration of synergism and antagonism. A large number of interactions covering high synergism to high antagonism have been adopted as a convenient way to explain experimental results. In contrast, a semi-quantitative method combining the interaction of HALS and phenols as synergism and antagonism can interpret or explain almost all phenomena.

How HALS NH is changed into "good" HALS or "bad" HALS is summarized in **Fig. 9**. HALS nitrosonium is acceleratedly formed by the action of an acidic compound, which results in the useless consumption of phenols and UVA as well as homolytical and catalytical decomposition of hydroperoxides. These HALS actions are most undesirable for the stabilization of polymeric materials. Thus, measures to control the formation of and decompose HALS nitrosonium will be the main key to the use of HALS.

Finally, **Fig. 10** summarizes the new action mechanism of HALS together with previously accepted mechanisms. Polymeric materials friendly to the global environment can be developed by effectively stabilizing with additives, resulting in better functions and longer service lives. For this purpose, additives must be investigated without preconceived ideas, which prevents us knowing their real functions. This is an effective way to improve the defects of additives and to make use of the advantages.

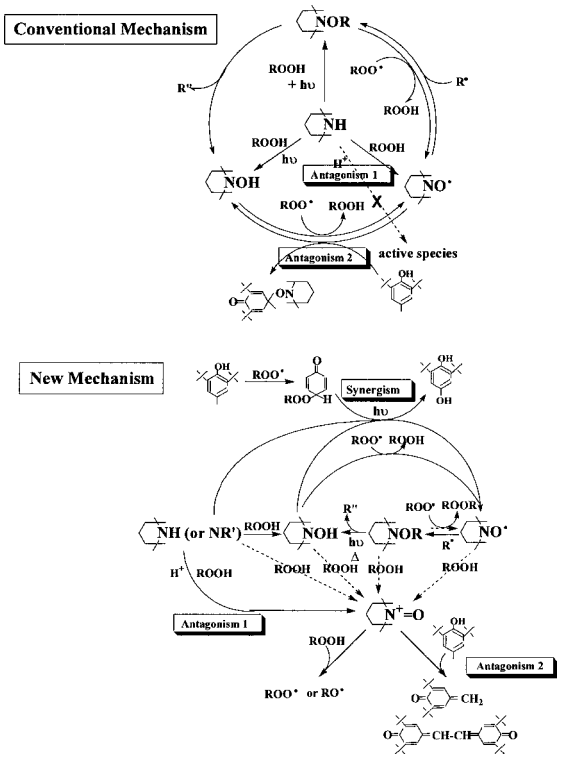



Fig. 10 Unified Action Mechanism of HALS

## References


1) Ohkatsu, Y., *Res. Rep. Kogakuin Univ.*, **61**, 42 (1986).
2) Yamaguchi, K., Ohkatsu, Y., Kusano, T., *Sekiyu Gakkaishi (J. Jpn. Pertol. Inst.)*, **34**, (5), 458 (1991).
3) Denisov, E. T., *Polym. Degrad. Stab.*, **25**, 209 (1989).
4) Klemchuk, P. P., Gande, M. E., Codora, E., *Polym. Degrad. Stab.*, **27**, 65 (1990).
5) Al-Malaika, S., Omikorede, B. O., Scott, G., *J. Appl. Polym. Sci.*, **23**, 703 (1987).
6) Ohkatsu, Y., Yamaguchi, K., Kubo, K., Sengoku, T., *Sekiyu Gakkaishi (J. Jpn. Pertol. Inst.)*, **37**, (4), 395 (1994).
7) Ohkatsu, Y., Yamaguchi, K., Kawada, Y., *Sekiyu Gakkaishi (J. Jpn. Pertol. Inst.)*, **37**, (4), 400 (1994).
8) Schwetlick, K., Habicher, W. D., *Polym. Degrad. Stab.*, **78**, 35 (2002).
9) Yang, X., Chen, Y., Dickinson, L. C., Chien, J. C. W., *Polym. Degrad. Stab.*, **20**, 1 (1988).
10) Vyprachtick, D., Pospisil, J., Sedlar, J., *Polym. Degrad. Stab.*, **27**, 49 (1990).
11) Ball, S., Bruice, T. C., *J. Am. Chem. Soc.*, **21**, 6499 (1980).
12) Carlsson, D. J., Chan, K. H., Durmis, J., Wiles, D. M., *J. Polym. Sci. Poly. Chem. Ed.*, **20**, 575 (1982).
13) Sedlar, J., Petruj, J., Pac, J., Navratil, M., *Polymer*, **21**, 5 (1980).
14) Lucki, J., Rabek, J. F., Ranby, B., *Polym. Photochem.*, **5**, 351 (1984).
15) Allen, N. S., Chirinos-Pardon, A., Appleyyard, J. H., *Polym. Degrad. Stab.*, **6**, 149 (1984).
16) Allen, N. S., *Polym. Degrad. Stab.*, **2**, 179 (1980).
17) Yamashita, H., Ohkatsu, Y., *Polym. Degrad. Stab.*, **80**, 421 (2003).
18) Yamashita, H., Banno, K., Ohkatsu, Y., *J. Appl. Polym. Sci.*, **142**, 1310 (2006).
19) Fairgrieve, S. P., MacCallum, J. R., *Polym. Degrad. Stab.*, **8**, 107 (1984).
20) Gisman, P., Gitton-Chevalier, M., *Polym. Degrad. Stab.*, **8**, 483 (1984).
21) Chakroborty, K. B., Scott, G., *Chem. Ind.*, **7**, 237 (1978).
22) Kikkawa, K., Nakahara, Y., Ohkatsu, Y., *Polym. Degrad. Stab.*, **18**, 237 (1987).
23) Bigger, S. W., Delatycki, O., *J. Polym. Sci. A: Polym. Chem.*, **27**, 63 (1989).
24) Yamashita, H., Kawaguchi, A. W., Ohkatsu, Y., *J. Jpn. Petrol. Inst.*, **49**, (6), 294 (2006).
25) Ohkatsu, Y., Yamaguchi, K., Yamaki, A., Maruyama, Y., Kusano, T., *Sekiyu Gakkaishi (J. Jpn. Pertol. Inst.)*, **34**, (3), 280 (1991).
26) Ohkatsu, Y., Yamaguchi, K., Sengoku, T., Sato, T., *Sekiyu Gakkaishi (J. Jpn. Pertol. Inst.)*, **37**, (4), 405 (1994).
27) Bortolus, R., Dellonte, S., Faucitant, A., Grantani, F., *Makromol.*, **19**, 2916 (1986).
28) Allen, N. S., *Polym. Photochem.*, **1**, 243 (1984).
29) Ohkatsu, Y., Fujiwara, T., *J. Jpn. Petrol. Inst.*, **50**, (2), 87 (2007).
30) Smeltz, K. C., *Textile Chem. Color.*, **15**, 52 (1983).
31) Abakumov, G. A., Tikhonov, V. D., *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 724 (1969).
32) Golubev, V. A., Rozantsev, E. G., Neiman, M. B., *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1898 (1965).
33) Bobbitt, J. M., Flores, M. C. L., *Heterocycles*, **27**, 509 (1988).
34) de Nooy, A. E. J., Besemer, A. C., van Bekkum, H., *Synthesis*, **8**, 1153 (1996).
35) Bobbitt, J. M., Ma, Z., *Heterocycles*, **33**, 641 (1992).
36) Liu, Y., Ren, T., Guo, Q., *Chin. J. Chem.*, **14**, 253 (1996).
37) de Ilarduya, J. I. M., Krzyczmonik, P., Scholl, H., Grabowski, G., *Electroanalysis*, **3**, 233 (1991).
38) Picket, J. E., Mooire, J. E., *Polym. Degrad. Stab.*, **42**, 231 (1993).
39) Decker, C., Zahouily, K., *Polym. Master. Sci. Eng.*, **68**, 70 (1993).
40) Kurumada, T., Ohsawa, H., Yamazaki, T., *Polym. Degrad. Stab.*, **19**, 263 (1987).
41) Mizokawa, S., Ohkatsu, Y., *J. Jpn. Petrl. Inst.*, **50**, (1), 1 (2007).
42) Takenaka, H., Mizokawa, S., Ohkatsu, Y., *J. Jpn. Petrol. Inst.*, **50**, (1), 8 (2007).
43) Ohkatsu, Y., Takenaka, H., *J. Jpn. Petrol. Inst.*, **51** (2), 88 (2008).


……

## 要　　旨

### ヒンダードアミン光安定剤の統一的作用機構の模索

大勝　靖一

工学院大学専門学校，163-8677 東京都新宿区西新宿1-24-2

ヒンダードアミン光安定剤（HALS）は他の添加剤と異なって多くの機能を有し，高分子材料の長寿命化に頻繁に使用されているが，それは併用する添加剤のえり好みが激しい。その組合せは必ずしも相乗作用ではなくて，拮抗作用を示すことがしばしばある。結果としてHALSを中心とした他の添加剤との相互作用については，多くの研究が報告されている。しかし，その成果の多くは相互作用を大きな相乗作用から大きな拮抗作用までの多様な局面に対して定性的に議論し，相互に統一性を欠いている。

HALSおよびその同族体には多くの誘導体が知られている。本論文では，これらの誘導体を「良いHALS」と分類し，一方で著者らが新しく発見したHALS誘導体，すなわちHALSニトロソニウムを「悪いHALS」として表記する。過去の研究はこの良いHALSを用いてHALSの他の添加剤との悪い拮抗作用を説明しようとした。ここに問題があった。本論文は，HALSと他の添加剤の混とんとする相互作用を，これもまた著者らが発見した良いHALSによる相乗作用と悪いHALSによる拮抗作用とに分けて動力学的，かつ熱力学的に議論する。その結果として，上述したような広範にわたる相互作用を半定量的，かつ統一的に説明する研究手法を提案する。

本論文で総括する成果は，諸事実の発見によりHALSの複雑で多岐にわたる性質を明らかにし，これらに基づいてHALSの単独でのおよび他の添加剤共存での作用機構を統一的に議論しうる可能性を提示することである。この統一的な考えに基づいて高分子材料の安定化および機能化を行えば，従来よりも非常に容易に添加剤処方が決定でき，かつさらには新添加剤の開発が可能となるであろう。

……