Polypropylene Photostabilization by Hindered Amines in the Presence of Acidic Species*

D. J. CARLSSON, ZHANG CAN,[†] and D. M. WILES, *Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR9*

Synopsis

Some volatile acids were found to dramatically reduce the effectiveness of additives based on 2,2,6,6-tetramethylpiperidine as photostabilizers for polypropylene films. Strong acids such as HCl, HBr, and HNO_3 had the largest effect with sulfurous acid somewhat less detrimental. Weak organic acids did not impair the effectiveness of the hindered amine light stabilizers. The role of acid concentration and contact time were explored for the HCl–piperidyl additive system. Secondary and tertiary amines were included in the study as well as oligomeric additives and an N-oxyl derivative. The latter is less basic than the free amines, and it was correspondingly less effected by acid exposures. The possibilities for acid exposure during the compounding, fabrication, and use of stabilized polyolefin articles is discussed as well as the effects of acids in terms of proposed stabilization mechanisms for the hindered amines.

INTRODUCTION

The hindered amine light stabilizers (HALS) first developed some 10 years ago by Sankyo and Ciba-Geigy are now widely exploited as extremely effective photostabilizers for polyolefins, polystyrene, acrylic coatings, polyurethanes, etc. The original additives were secondary amines based on 2,2,6,6-tetramethylpiperidine. These compounds are still in use, but other additives containing tertiary amine groups, oligomeric structures, and spiro or piperazinone rings have been patented and in some cases commercialized.[1]

With moderate levels of HALS, the useful, outdoor lifetime of a photosusceptible polymer such as polypropylene can be extended by over an order of magnitude, before brittle failure occurs. However, scattered reports of premature failure have suggested problems when HALS-protected polymers are exposed to halogenated species, such as volatiles from the thermal aging of chlorinated resins or rubbers, or from various insecticides in contact with film in agricultural use.[2] The strongly basic nature of the piperidyl amine function raises the possibility of detrimental, salt-forming reactions with acidic species. These acids may come from adjacent polymers, as just mentioned, or from exposure during processing, or fabrication or as a result of in-use degradation. For example, carboxylic acids are well documented products from the oxida-

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[†]Guest Research Scientist; permanent address: Institute of Chemistry, Academia Sinica, Beijing, China.

tion of polyolefins themselves. Furthermore, HALS which contain tertiary amine groups are readily oxidized to secondary amines and carboxylic acids.[3,4]

In order to explore the consequences of salt formation by HALS, we have measured the effectiveness of a series of secondary, tertiary, and oligomeric amines on the photostabilization of polypropylene films before and after exposure to various volatile acidic compounds.

EXPERIMENTAL

A commercial polypropylene (PP) film (30 μm thickness, Profax resins, unoriented) was exhaustively Soxhlet-extracted with acetone to remove processing additives.[5] The hindered amines studied included (Scheme I) bis(2,2,6,6-tetramethyl-4-piperidyl) decanedioate (I, Ciba-Geigy Tinuvin 770), the oligomeric tert.-amine ester from 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol (II, Ciba-Geigy, Tinuvin 622), the oligomeric secondary amine-triazine adduct (III, Chimassorb 944), and bis(2,2,6,6-tetramethyl-4-piperidyl-N-oxyl) decanedioate [IV, prepared by the oxidation of I with H_2O_2 and sodium tungstate[6]]:

I

II

III

IV
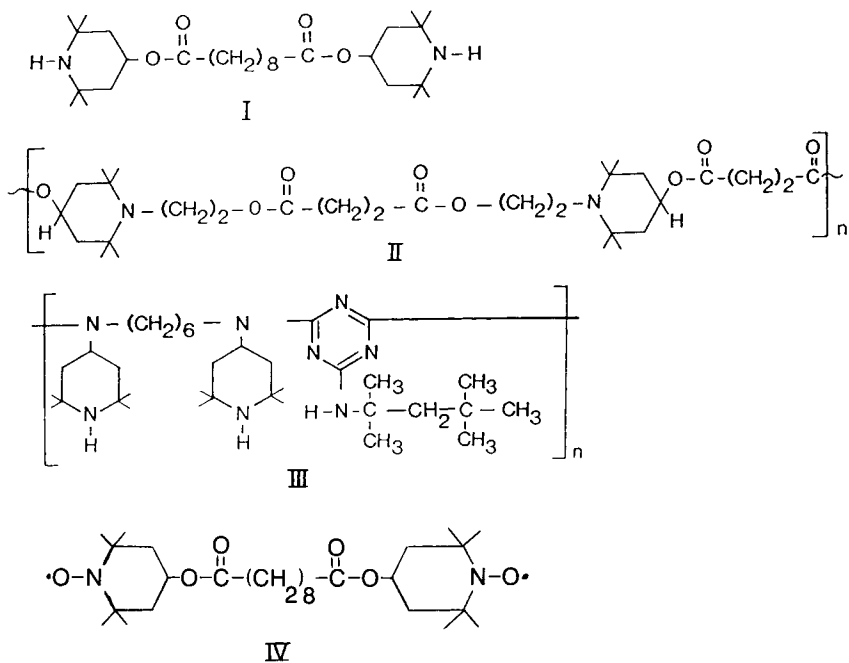
Scheme 1.

Each HALS was diffused into a PP film sample by immersion at 22°C from hexane (I, IV), at 60°C from hexane (III), or at 22° C from carbon tetrachloride (III) solutions. After 24 h of immersion at 22°C, films were removed, briefly rinsed in pure solvent, and vacuum dried.

Before light exposure, some film samples were exposed at room temperature to acidic gases (HCl, HBr, formic acid) or vapors above aqueous acids (HCl, nitric acid, and CO_2 or SO_2 saturated water) for varying times. Light exposure was carried out with an Atlas xenon arc WeatherOmeter (2500 w, Pyrex inner and outer filters, 0.37 w/cm^2/nm at 340 nm, 38°C silver panel temperature,

30% RH, no water spray). The WeatherOmeter accurately simulates the spectral distribution of noon, summer sunlight.

A few film samples were preoxidized by γ-irradiation (A.E.C.L. Gammacell 220, 1.0 Mrad/h) in air prior to the incorporation of HALS and UV exposure.

The accumulation of photo-oxidation products was measured by infrared (IR) spectroscopy (Perkin-Elmer 1500 FTIR), using a polarized IR beam and films tilted at 56° to minimize interference ripples.[7] IR spectroscopy was also used to measure the concentration of additives, I, III and IV (ester absorption at 1738 cm^{-1}) and to monitor salt formation from the amines. The concentration of III was measured by ultraviolet spectroscopy (triazine absorption at 225 nm).

Some film samples were prepared by melt-compounding mixtures of a calcium salt (calcium 4-cyclohexylbutyrate) and I. In these cases, films ($\sim$ 130 μm) were pressed from an additive-free PP powder (Moplen, as polymerized).

For comparison purposes, several salts were synthesized by treatment of hexane–HALS solutions with the appropriate acid. FTIR spectra of these salts were recorded on KBr discs. In addition, some were melt-compounded with PP powder and pressed into films under nitrogen. However, IR indicated that most salts dissociated into the free amine and (usually volatile) acid at the press temperature ($\sim$ 210°C). Only the benzoic acid salt of I was found to survive melt pressing. Some electron spin resonance (esr) spectroscopy measurements (Varian E4 spectrometer) were made on films to detect N-oxyl intermediates from the HALS.

RESULTS

Exposure of HALS-containing films to acid vapors leads to changes in the IR spectra of the films consistent with salt formation. For example, secondary amine salts (from I and III) showed the $>$NH$_2{}^+$ stretch and deformation absorptions at $\sim$ 2480 and $\sim$ 1600 cm^{-1}, whereas the $tert$-amine salts from II showed the broad $\geqslant$N$^+$H stretch at $\sim$ 2600 cm^{-1}.[8] Carboxylic acid salts showed the —C(=O)—O$^-$ band at $\sim$ 1530 cm^{-1}, except for formate salts where a more complex group of absorptions was formed at 1634, 1612, and 1585 cm^{-1} overlapped with the $>$NH$_2^+$ absorption. HALS III also showed a distinct shift in UV absorption from 225 to 260 nm upon exposure to most acids. This shift was reversed by ammonia exposure, and is attributed to protonation of the triazine ring in III. Exposure of HALS-containing films to CO$_2$/H$_2$O gave no clear indication of salt formation in their IR or UV spectra.

After long exposure times ($\geq$ 18 h) of PP film to strong acids such as HCl, HBr, and HNO$_3$, consistent small decreases in the ester absorption of I and III were observed, implying some cleavage of the ester link.

The effects of a prior exposure to acid gases or vapor for $\sim$ 18 h on photodegradation resistance are shown in Figures 1–4 for HALS I–IV. Oxidation was measured by the buildup of the carboxyl product absorption at $\sim$ 1715 cm.$^{-1}$ Brittle failure of films correspond to a carbonyl absorption of $\sim$ 0.20. In all cases, exposure to carbonic (CO$_2$/H$_2$O) and formic acids did not reduce the stabilizing effect of the HALS. In general, sulfurous acid reduced photostability somewhat whereas HCl, HBr, and nitric acid (NO$_2$/H$_2$O) dramatically reduced stability. In several cases these latter, strong acids reduced the UV stability to below that of the HALS-free, control films.
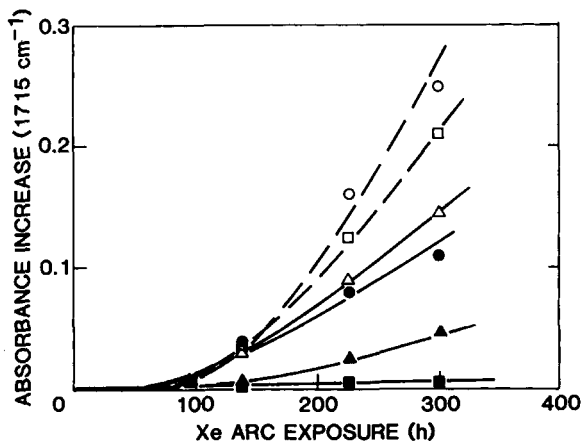
Fig. 1. Effects of exposures to volatile acids on PP film stabilized by additive I. 30 μm films exposed in a WeatherOmeter. (○) No additive or acid exposure. All other samples contain 0.15 wt% of I with the following 18 h acid treatments: (■) none, or CO_2/H_2O or $H—C(=O)OH$ (rapid oxidation and brittle failure at ~ 1200 h); (▲) SO_2/H_2O; (●) HCl; (△) HNO_3 vapor ($NO_x + H_2O$); (□) HBr.
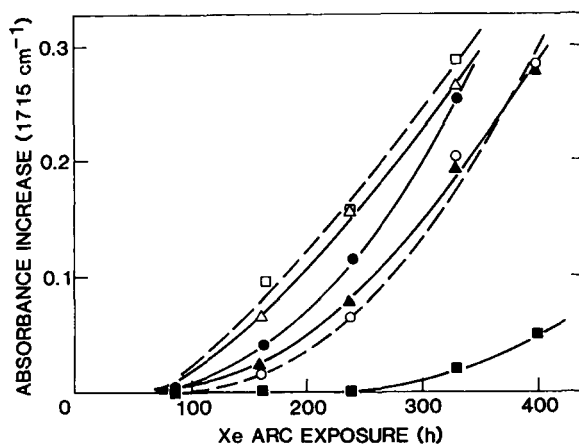

Fig. 2. Effect of exposure to volatile acids on PP film stabilized by additive II. Sample and exposure details as in Figure 2 except additive II concentration 0.07 wt%.

Exposure of additive-free, PP films to the various acids for 15 h prior to UV exposure had negligible effect on photostability.

Because HCl exposure may occur quite readily during the lifetime of a stabilized article, its effects were explored in more detail with additive I. From Figure 5, HCl effects accumulate progressively with time up to about 1 h. Presumably at this time all amine groups have reacted. Identical results were obtained from anhydrous HCl and vapor from aqueous HCl. Exposure to HCl for a fixed time, but at varying concentrations of anhydrous HCl in N_2 diluent (Fig. 6) show a saturation effect at about 1%.
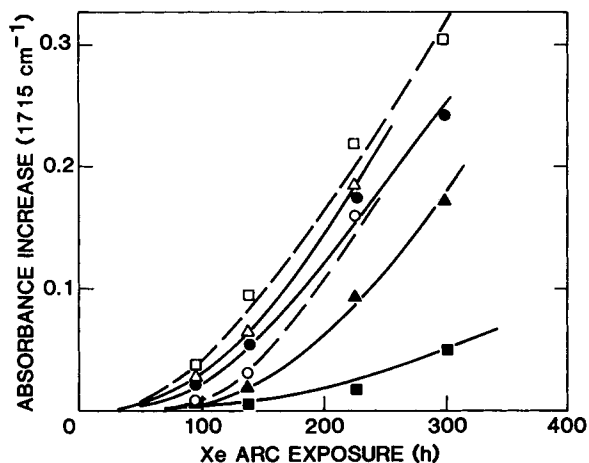
Fig. 3. Effects of exposure to volatile acids on PP film stabilized by additive III. Sample and exposure details as in Figure 2 except additive III concentration 0.06 wt%.
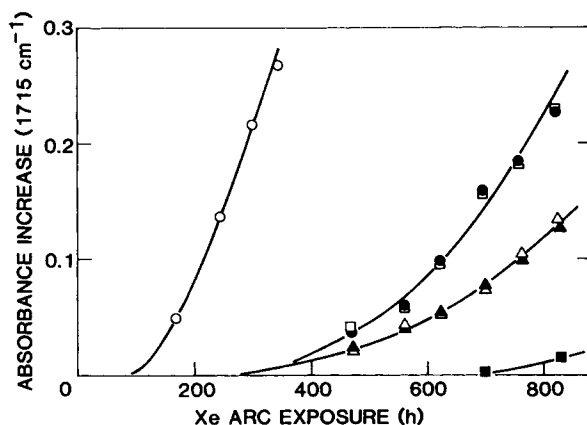

Fig. 4. Effects of exposure to volatile acids on PP film stabilized by additive IV. Sample and exposure details as in Figure 2 except additive IV concentration 0.11 wt%.

Benzoic acid is too involatile and the benzoate salt of I too insoluble in swelling solvents to allow incorporation into the preformed 30 μm film. However, film could be prepared from the benzoate salt of I by melt compounding. Film containing this salt was as photostable as film melt compounded with a similar molar concentration of I. The melt compounding of equimolar quantities (0.01 mol/kg) of the calcium salt and I gave film with the same UV stability as when I was used above. However, the UV stability of the CA^{++}/I-containing film after HCl exposure was, in fact, worse than that of the I-containing film after HCl exposure.

A series of measurements were made with 30 μm film that had been preoxidized by γ-irradiation (5 Mrad) prior to the introduction of amine I by diffusion. N-oxyl radical yields were then measured by esr during UV exposure for preoxidized film with I and for preoxidized film with I, after HCl exposure (18 h). This preoxidation step to give a hydroperoxide level of ~ 0.1 mol/kg allowed the use of short UV exposure times (~ 4 h) to give easily
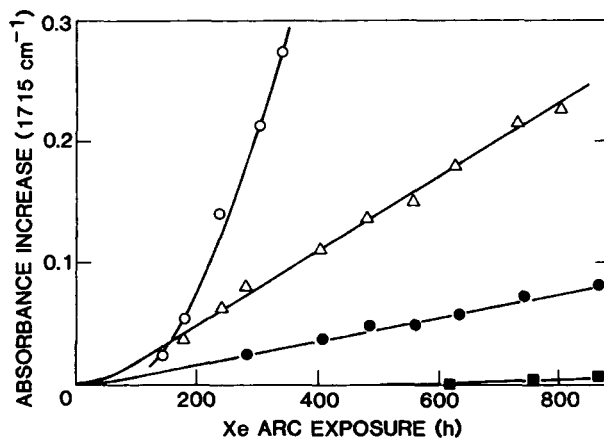
Fig. 5.   Effect of HCl contact time on photostabilization by additive I: (○) additive-free film. Film with 0.10 wt% exposed to HCl gas for: (■) 0 s; (●)60 s; (△)60 min, or 18 h.
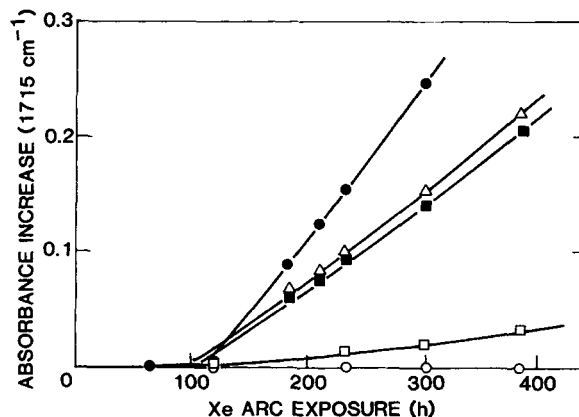

Fig. 6.   Effect of HCl gas concentration of photostabilization by additive I: (●) additive free film. Film with 0.07 wt% I exposed for 18 h to: (○) 0%; (□) 0.1%; (■) 1.0%; (△) 10 and 100% (N_2 inert diluent).

detectable N-oxyl radicals, as compared to 50–100 h with nonoxidized film. After a 4 h UV exposure, N-oxyl was clearly visible in the preoxidized film with I, whereas the N-oxyl yield was an order of magnitude less in the HCl-exposed sample.

Several of the HALS salts were found to be quite water-soluble. This implies that stabilizer loss by water extraction during outdoor exposure will be enhanced by acid exposure.
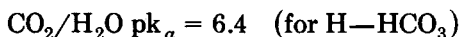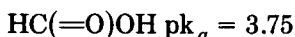
DISCUSSION

Hindered amines are known to be extremely basic compounds. For example 2,2,6,6-tetramethylpiperidine has a pk_b of 2.9 in water, as compared to 3.2 for *tert*-butylamine and 4.7 for ammonia.[9] Salt formation during exposure to acid vapours is clearly shown by the IR spectral changes associated with $>$NH

conversion to $>NH_2^+$ (2480 cm^{-1} growth) and

$$>\!N\!-\!\overset{|}{\underset{|}{C}} \text{ conversion to } >\!\overset{+}{N}H\!-\!\overset{|}{C} \text{ (broad 2600 cm}^{-1} \text{ growth)},$$
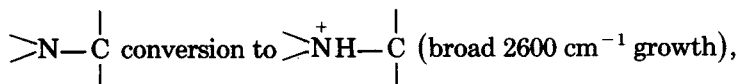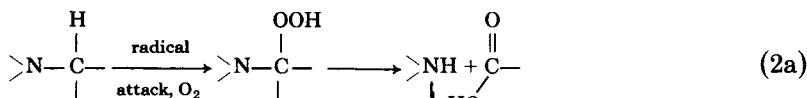
as well as detection of the $-C(=O)-O^-$ species from formic acid (at 1585 cm^{-1}).

The effect of salt formation on suppressing the UV stabilizing ability of HALS increases in the sequence $SO_2/H_2O \leq HCl \leq NO_x/H_2O \leq HBr$. Formic acid, benzoic acid, and CO_2/H_2O appear to have no detrimental effect. This sequence correlates with the increasing strength of the acids, as measured by pk$_a$ values[9, 10]:

$$HNO_3, HCl, HBr \text{ pk}_a \leq -7$$

$$HC(=O)OH \text{ pk}_a = 3.75$$

$$CO_2/H_2O \text{ pk}_a = 6.4 \quad (\text{for } H-HCO_3)$$
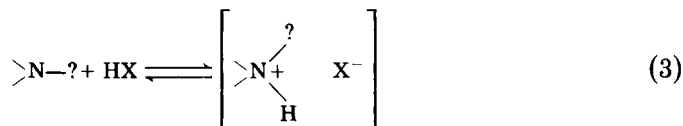
Only SO_2/H_2O is apparently anomalous with pk$_a$ of 1.81 for its first proton. However, pk$_a$ for its second proton is 6.8, which implies that in the multifunctional HALS studied, some amine groups will be bound only very weakly with SO_3^{--} sites.

Before speculating on how acids can deactivate HALS, it is worthwhile to review briefly HALS protective reactions. Although the mechanisms by which HALS photo-protect are still not fully understood, most evidence points to their role as UV-stable, free-radical scavengers by involvement in a regenerative cycle (reaction 1).[4, 11] In this cycle, nitroxide ($>NO \cdot$) and substituted hydroxylamine ($>NOPP$) interconvert by scavenging the two dominant macro-free radicals which carry the oxidative chain degradative process (PP $\cdot$ and PPO$_2$ $\cdot$). The parent amines must be oxidized to nitroxide to allow the occurrence of this cycle. Tertiary amines undergo a rapid free radical attack to form the corresponding secondary amine, possibly via an unstable amine hydroperoxide intermediate (reaction 2a).[3, 4]

$$>\!NO \cdot + PP \cdot \xrightarrow{\quad} >\!NOPP$$
$$\underset{PPO_2 \cdot}{\xleftarrow{\qquad\qquad}} \tag{1}$$

$$>\!N\!-\!\overset{H}{\underset{|}{\overset{|}{C}}}\!-\! \xrightarrow[\text{attack, O}_2]{\text{radical}} >\!N\!-\!\overset{OOH}{\underset{|}{\overset{|}{C}}}\!-\! \longrightarrow >\!NH + \overset{O}{\overset{\|}{C}}\!-\! \tag{2a}$$
$$\underset{HO}{\diagup}$$

peracid, PPOOH attack $\downarrow$

$$>\!NO \cdot \tag{2b}$$

However, the conversion of the secondary amine to $\geqslant$NO · is only poorly understood. Singlet oxygen ($^1O_2$) may oxidize the amine[12] but is probably unimportant in the oxidation of unpigmented polymers. Direct radical attack on the $\geqslant$NH group is faster than $-\overset{|}{\underset{|}{C}}-$H attack, and will be favored by association of the amines with oxidation sites.[11,13,14] Salt formation will disrupt this hydrogen bonding and may also prevent radical attack to give N-oxyl compounds. This is consistent with our esr results on preoxidized films when N-oxyl formation was greatly reduced in the HCl exposed films as compared to those containing the free amine. N-oxyl radicals can be formed also by the slow reaction between $\geqslant$NH and the macrohydroperoxide groups in PP and by the rapid reaction of $\geqslant$NH with per acids (reaction 2b). However, salts can also take part in this reaction as was demonstrated by the rapid $\geqslant$NO · generation when a model peracid (m-chloroperbenzoic acid) was added to a suspension of the HCl salt of I in hexane. Similarly Hiatt has reviewed work which shows that amine salts decompose hydroperoxides as fast as the parent amines.[15]

With strong acids (HX) all piperidyl species (shown as $\geqslant$N—?) in reactions 1 and 2 may be protonated (reaction 3) and prevented from undergoing their essential reactions. With weak acids, this equilibrium will be largely to the left, allowing sufficient free piperidyl species to photoprotect:

$$\geqslant\text{N—?} + \text{HX} \rightleftharpoons \left[\begin{array}{cc} \overset{?}{\underset{H}{\overset{\diagup}{\geqslant\text{N}+}}} & \text{X}^- \\ \diagdown & \end{array} \right] \qquad (3)$$

The extent of salt formation must also depend on the basicity of the piperidyl species, which can be expected to decrease in the sequence

$$tert \ \geqslant\text{N}-\overset{|}{\underset{|}{C}}- \ \geq \ sec \ \geqslant\text{N—H} \ \geq \ \geqslant\text{NOPP} \ \geq \ \geqslant\text{NO} \cdot .^{6,9}$$
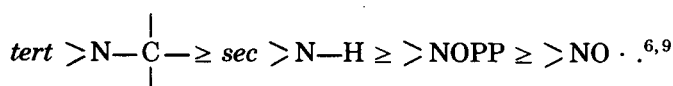
This proposed trend is supported by the lesser effect of acids on the nitroxide IV, as compared to its parent amine I (cf. Figs. 4 and 1). As well as protonation, N-oxyl compounds have been suggested to react directly with acids to form hydroxylamine salts [$\geqslant$N(—OH) H$^+$X$^-$] and oxoammonium salts ($\geqslant$N$^+$ = OX$^-$).[6,16]

Some other piperidyl reactions may play a partial role in stabilization. Formation of a free hydroxylamine ($\geqslant$NOH, an excellent peroxyl radical scavenger) can occur,[15] as can amine complexation with metal sensitizers.[17] Both processes will be hindered by salt formation.

CONCLUSIONS

During compounding, fabrication, storage, and use, HALS-stabilized polymers may be exposed to strong acids which can migrate into the polymer to form strong salts. The deactivation of the photoprotective ability of HALS by strong acids has been experimentally demonstrated, as has the water solubility of the salts. In addition, the useful thermal antioxidant effectiveness of

HALS at moderate temperatures ($\leq 100°C$) can also be expected to be impaired by this acid exposure.

Acidic gases may come from many sources. For example, HCl can be generated from some polymerization catalyst residues or flame retardants in the extruder or during coating operations with the chlorinated rubbers used on some polyolefin fabrics. Similarly HBr can be evolved from bromobutyl rubbers. In addition, the use of halogenated insecticides or fumigants in film-clad greenhouses may generate HCl or HBr during their thermal, photo or hydrolytic breakdown. Oxides of nitrogen are a common product from high temperature combustion processes. With strong acids, their effects can be expected to be cumulative, that is, brief exposures or low concentrations will progressively add up to a significant deactivation of the normally powerful additives.

The presence of a sacrificial acid scavenger might minimize acid effects. However, the requirements of either high concentrations or very highly basic scavengers are implied by the failure of our attempt to protect against HCl by the use of a calcium alkanoate. This compound is analogous to the calcium stearate widely used to minimize corrosion and other problems caused by acidic products from catalyst residues in PP.

Fortunately formic and benzoic acids do not impair HALS performance. This is particularly important because formic acid is the strongest simple, carboxylic acid. Consequently, all other organic carboxylic acids, such as those produced during the oxidation of the host polymer or piperidyl compounds themselves,[3,4,18] from sweat, from foodstuffs, from the biodecomposition of organic matter, etc., are not expected to antagonize HALS effectiveness.

Another aspect of HALS salt formation comes from their use as photo-stabilizers in acid-catalyzed paint systems.[18] The highly basic HALS can tie up the cure catalyst and prevent hardening of the paint film. One proposed solution to this problem is the use of N-acylated HALS [$>$N—O—C(=O)R], which can photostabilize as well as some secondary HALS. It is possible that the N-acylated HALS might be more effective than the free amines in application where exposure to strong, volatile acids can occur.

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