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Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/0141-3910(89)90008-6
Polymer Degradation and Stability, 26, 2, pp. 185-195, 1989

Polymer Degradation and Stability **26** (1989) 185–195

Photo-stabilizing Efficiency of N-Substituted Hindered Amines in Polypropylene: Effects of Processing Conditions and Exposure to a Protonic Acid*

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(Received 14 August 1988; revised version received and accepted 16 November 1988)

ABSTRACT

The effects of exposure to processing conditions and strongly acidic gases on the photo-stability of polypropylene films stabilized with hindered amine light stabilizers (HALS) have been studied. A series of monofunctional hindered amines based on tetramethylpiperidine containing $>NH$, $>NO>NCOCH_3$, *and* $>N-OC(=O)CH_3$ *substituents in the piperidyl ring was compared with a bifunctional secondary amine. Exposure to heat and shear in a Brabender Plastograph caused loss by volatilization and decomposition of the* $>N-O-C(=O)CH_3$ *additive. All of the HALS derivatives formed salts upon exposure to gaseous HCl and their photo-stabilizing ability was greatly impaired although the monofunctional secondary amine was superior to the bifunctional amine under these conditions. The* $>N-COCH_3$ *additive was extensively decomposed by the HCl exposure.*

INTRODUCTION

Synthetic polymers are used for their excellent properties as films, moldings and fibers. However, most synthetic polymers in air are subject to oxidative deterioration triggered by the action of light, heat and/or mechanical action.

* Issued as NRCC No. 30094.

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Polymer Degradation and Stability 0141-3910/89/$03·50

These chemical and physical changes cause discoloration, crazing and loss of tensile and impact strength.

Recently, a new class of light stabilizer, the hindered amine light stabilizers (HALS), has attracted considerable attention in the plastics and fiber industries because of its excellent light stabilizing efficiency compared with other conventional types of light stabilizer.[1] The original additives were secondary amines based on 2,2,6,6-tetramethylpiperidine and until recently, all commercial products were based on this molecular structure. However, the strongly basic nature of the piperidyl amine function raises the possibility of salt-forming reactions with acidic contaminants. These acids may come from adjacent polymers (for example, volatiles from the thermal ageing of chlorinated resins or rubbers), from various insecticides and herbicides in contact with film in agricultural use, from sulfur-containing compounds etc.[2] In a previous paper[3] we described the influence of acidic species on photo-stabilizing efficiency of HALS in polypropylene photo-oxidation. Among strong acids, HCl and HBr were shown to have the largest effect and extensively decreased the efficiency of commercial stabilizers, all of which contained multiple piperidyl groups in each molecule. At the same time, it was suggested that the less basic N-acylated HALS might be more efficient than using the parent amine in applications where exposure to strong, volatile acids can occur.

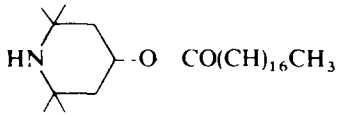
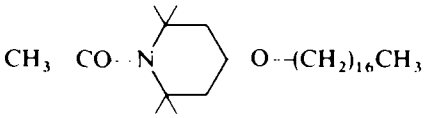
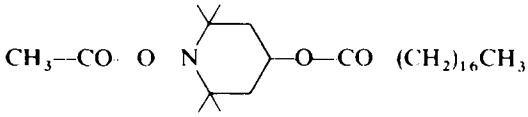
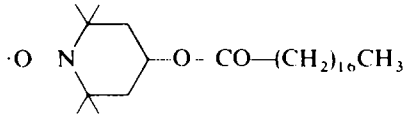
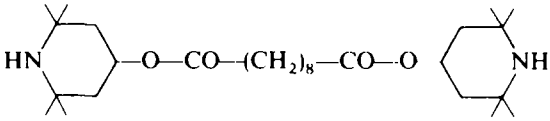
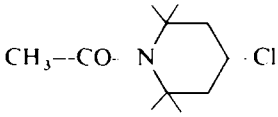
In this work, we discuss the acid-sensitivity of a series of monofunctional HALS carrying various $>$N-substituents including $>$N-oxyl, $>$N-acetyl and $>$N-acetyloxy together with the associated question of the stability of these additives under melt compounding conditions.

EXPERIMENTAL

The hindered amines selected for this study were 4-octadecanoate-2,2,6,6-tetramethylpiperidine (I), N-acetyl-4-octadecanoate-2,2,6,6-tetramethylpiperidine (II), N-acetyl-oxy-4-octadecanoate-2,2,6,6-tetramethylpiperidine (III), N-oxyl-4-octadecanoate-2,2,6,6-tetramethylpiperidine (IV) and bis(2,2,6,6-tetramethyl-4-piperidyl) decanedioate (V) (Tinuvin 770, Ciba-Geigy). The preparation of I–IV is described in Ref. 4. Structures are shown in Table 1. HALS were introduced into PP either by diffusion into preformed film or by melt compounding. The stabilizers (I–III) were diffused into PP-film sample by immersion in *n*-hexane solutions of I–III at 40°C. After immersion, films were removed, rinsed in pure solvent and vacuum dried. Prior to use, the commercial PP-film employed (30 μm thickness, Profax resins, unoriented) was exhaustively Soxhlet extracted with acetone to remove processing additives.[5]

For melt compounding, unstabilized PP-powder (Profax 6301) and

TABLE 1

HALS additive		*Abbreviation*
	I	>N H
	II	>N CO CH$_3$
	III	>N O COCH$_3$
	IV	>N O·
	V	HN NH
	VI	

hindered amine derivatives I–V (0·25 w%) were mixed and homogenized in a Brabender-Plastograph (CW Brabender Instruments, Inc. New Jersey, USA) at 175 °C for 5 min under a stream of nitrogen. These compounded polypropylene samples were heated at 200 °C in a small hydraulic press built inside a N_2-filled glove-box and pressed into 100 μm films (total time at 200 °C, 1 min.)

Before light exposure, some films were exposed at room temperature to gaseous HCl for 18 h. Light exposure was carried out with an Atlas Xenon-arc WeatherOmeter (2500 W, Pyrex inner and outer filters, irradiance of $0{\cdot}35 \pm 0{\cdot}05$ W/cm^2/mm at 340 nm, 38 °C silver panel temperature, $30 \pm 5\%$ RH, no water spray). The WeatherOmeter accurately simulates the spectral distribution of noon, summer sunlight.

Fourier Transform Infrared (FTIR) spectroscopy (Perkin-Elmer 1500) was used in the estimation of additives concentration, the changes in additives after HCl-treatment and the accumulation of photo-oxidation products. Film samples were tilted at the Brewster angle in the polarized IR beam to minimize interference ripples.[6] Electron spin resonance (ESR)

spectra were measured on a Varian E-4 spectrometer. Radical concentrations were estimated by double integration of the ESR signal (Adalab A-D converter, Vidichart software-(Interactive Microwave Inc.), and Apple II$^+$ computer) and comparison with the double integral from standard 2,2′-diphenyl-1-picrylhydrazyl solutions in hexane. Nuclear magnetic resonance (NMR) spectra were measured in $CDCl_3$ solutions on a Varian EM 360 NMR spectrometer. Mass spectra were measured with a Hewlett-Packard 5970 mass-selective detector coupled to a Perkin-Elmer Sigma 3B Gas Chromatograph (fused silica column, 30 μm × 0·25 mm, 0·25 micron film of Dura-Bond 5). Extinction coefficient (ε) for the ester group was calculated from IR spectra of model compounds in hexane and found to be 580 (cm mol/liter)$^{-1}$ for all the additives studied.

RESULTS AND DISCUSSION

Effects of melt compounding on HALS

A series of PP films containing 0·25 wt% of each additive was chosen for the photo-stabilization study. These films were pressed from mixtures prepared by melt compounding. (The preparation of PP-films containing the same concentration of HALS by infiltration from *n*-hexane solution was not sufficiently controllable for this study.) The concentration of 0·25 wt% for each additive leads to the calculated molar concentrations shown in Table 2.

Mechanical and thermal treatments during melt compounding and during pressing have practically no effect on $>$N—H, $>$N—O· and $>$N—$COCH_3$ derivatives as shown by the FTIR spectra of these samples. For example, the

TABLE 2
Effects of Melt Processing and HCl on Additives in PP Films

Additive	*Additive concentration*		
	Based on gravimetry[a] (*mol/kg* × 10^3)	*After compounding*[b] (*mol/kg* × 10^3)	*After HCl exposure*[b,c] (*mol/kg* × 10^3)
$>$N—H	5·9	6·1	5·7
$>$N—O·	5·7	5·9	5·7
$>$N—$COCH_3$	5·4	5·9	2·1
$>$N—O—$COCH_3$	5·2	3·1	2·6

[a] Calculated from 0·25 wt% initially compounded.
[b] Calculated from IR spectra (1739 cm^{-1}, ε = 580, extinction coefficient obtained from IR spectra of model compounds in hexane).
[c] After 18 h HCl exposure.

ester absorption at 1739 cm^{-1} indicated the presence of the concentrations shown in Table 2. Similarly, ESR spectroscopy indicated that the nitroxide survived unchanged. However, a marked decrease of concentration occurred with the $>N-O-COCH_3$ derivative. The concentration dropped from originally $5{\cdot}2 \times 10^{-3}$ mol/kg to $3{\cdot}1 \times 10^{-3}$ mol/kg as calculated from ester peak ($\varepsilon = 580$), a 40% decrease in ester concentration. In addition, an even more marked decrease occurred for the absorption at 1780 cm^{-1}, attributable to the $>NOCOCH_3$ group which indicated a 60% loss of these groups.

To examine if these changes in III occurred during melt compounding or during pressing, two experiments were carried out. PP-films containing $>N-H$, $>N-COCH_3$ and $>N-O-COCH_3$ were prepared by diffusion of the piperidyl compounds from *n*-hexane solution. These films were then heated at 200°C for 10 min in a nitrogen atmosphere. This treatment caused no loss of $>N-H$ and $>N-COCH_3$ (no decrease in the 1739 cm^{-1} ester absorptions) while for $>N-O-COCH_3$ the 1739 cm^{-1} absorption decreased by ~40%. This loss upon heating in a nitrogen atmosphere could imply a quite high volatility of this derivative despite its high molecular weight. Alternatively, extensive chemical conversion may have occurred.

The second experiment involved the preparation of samples with 1 wt% of $>N-O-COCH_3$ and 1 wt% of $>N-COOH_3$, respectively, by melt compounding, followed by melt pressing into films. The $>N-COCH_3$ sample was again used as a control for comparison purposes. As a result of melt compounding the ester concentration (at 1739 cm^{-1}) dropped by 40% whereas the 1780 cm^{-1} absorption decreased 65% for the $>N-O-COCH_3$ compound. In the case of $>N-COCH_3$, concentrations based upon both 1739 cm^{-1} (C=O ester) and 1650 cm^{-1} (C=O amide) absorptions were still as in the original mixture, 1 wt%. Thus heat alone seems to be responsible for the general concentration decrease of the whole molecule because of volatility whereas mechanical treatment in melt compounding is responsible for the drop at 1780 cm^{-1} either because of a very weak bond in the $>N-O-COCH_3$ group or more likely because of the attack by R· radicals produced from the shearing of the polymer during melt processing. Based on ESR spectroscopy (discussed later) the product from $>NOCOCH_3$ is not a $>N-O\cdot$ radical but most probably a polymer grafting species ($>N-O-PP$).

Effects of HCl exposure on HALS and photo-stabilization

The kinetic curves for the increase in carbonyl groups of the irradiated PP-films containing stabilizers I–V (without acid exposure) are shown in Fig. 1. Despite the marked loss and modification of $>NOCOCH_3$ upon

compounding the efficiency of $>N—O—COCH_3$ is still marginally better than that of $>N—COCH_3$ (*cf.* Fig. 1, carbonyl absorption 0·2 at 1180 h and 1130 h, respectively). The best efficiency was obtained with $>N—O\cdot$ (2200 h) followed by $>N—H$ (1620 h). Kuramada *et al.*, using melt compounded 4-benzoate substituted piperidines, obtained the ranking $>N—O—COCH_3 < >N—COCH_3 < >N—H < >N—O\cdot$.[7]

All hindered amines are believed to generate nitroxyl radicals as a result of oxidative reactions. The nitroxide then becomes involved in a regenerative radical scavenging cycle.

$$\text{HALS} \xrightarrow{\text{oxidation}} >NO\cdot \underset{PPO_2\cdot}{\overset{PP\cdot}{\rightleftarrows}} >NOPP \qquad (1)$$

This involves scavenging of the polypropylene macroalkyl radical (PP·) and its peroxyl radical ($PPO_2\cdot$) although the detailed mechanism may be more complex than shown in reaction scheme (1). In the absence of volatility and compatibility effects, the nitroxide is expected to be the most effective photo-stabilizer of the piperidyl family.

The effect of gaseous HCl on stabilization efficiency of the monopiperidyl stabilizers I–IV and V is shown in Fig. 2. From a comparison of Figs 1 and 2, the stabilization efficiencies fell in all cases. The most dramatic decrease occurred with the $>N—COCH_3$ derivative, where photo-oxidation proceeded at the same rate as in the unstabilized control film.

The FTIR spectra of HCl-exposed films gave some information on HALS–HCl reactions which could be compared with products from HCl exposure of the corresponding piperidyl compounds in hexane. Films and solutions containing $>N—COCH_3$ showed a very different behaviour upon HCl exposure. The ester-group absorptions were unaffected by HCl

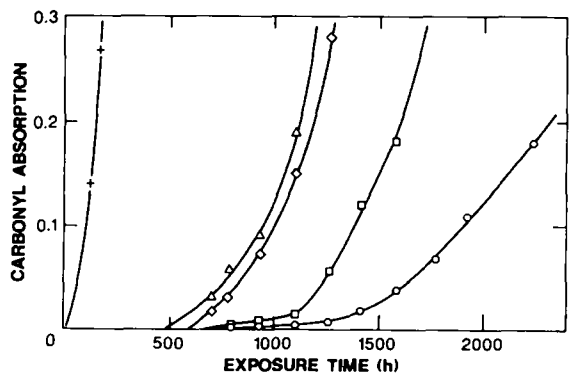


Fig. 1. Rates of photo-oxidation of polypropylene films (*ca.* 100 μm), not HCl treated. + additive free film; ○ $>N—O\cdot$; □ $N—H$; △ $>N\ COCH_3$; ◇ $>N—O—COCH_3$. Concentration of additives 0·25 wt%.

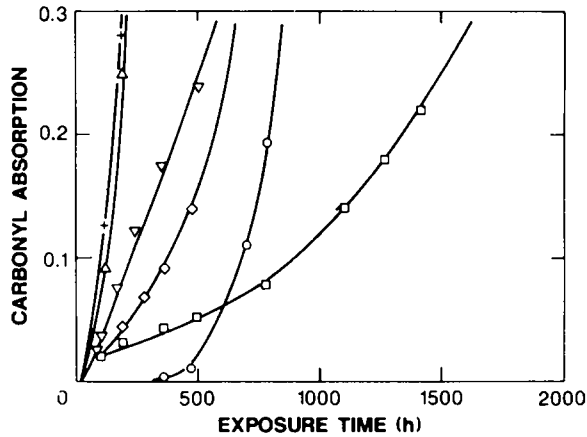


Fig. 2. Rates of photo-oxidation of polypropylene film after 18 h of HCl treatment. Additives and concentrations as in Fig. 1. $>$HN—NH ($2{\cdot}95 \times 10^{-3}$ mol/kg).

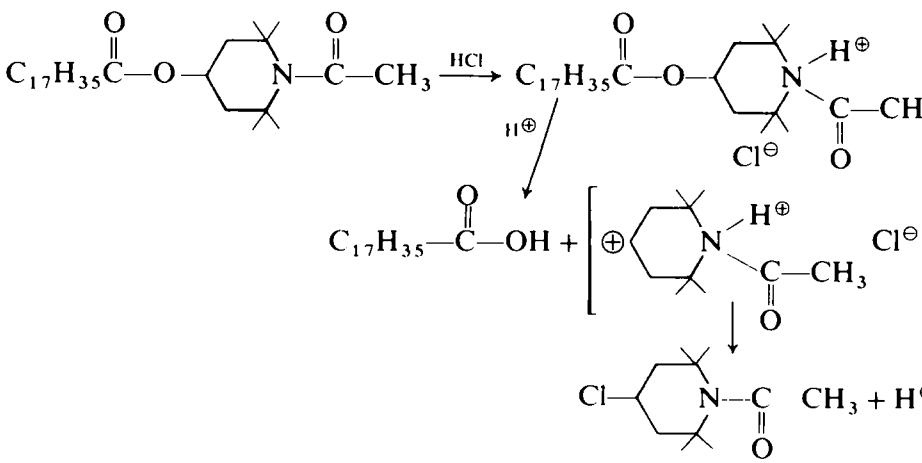
treatment of $>$N—H, $>$N—O—$COCH_3$ and $>$N—O· dispersed in PP films. For the $>$N—H derivative in PP, a new peak appeared at 2466 cm^{-1}, close to that found in the precipitate from *n*-hexane solution. From a comparison of the 1739 cm^{-1} to 2469 cm^{-1} absorbance from PP film with the ratio found for the salt isolated from *n*-hexane system ($A_{1739}/A_{2469} = 2$), 80% of the additive in films was found to be in the form of salt after 18 h of HCl exposure. Films containing $>$N—$COCH_3$ showed a very different behaviour upon HCl exposure. The IR-spectra of PP-films with $>$N—$COCH_3$ after HCl treatment (18 h exposure) showed a dramatic decrease to 1/5 of the original value of the 1739 cm^{-1} ester peak and a complete absence of the 1650 cm^{-1} amide vibration. There were new IR peaks at 1660 cm^{-1} and 1714 cm^{-1}. In contrast, the ester absorption of the $>$N—O·, $>$N—H and $>$N—O—$COCH_3$ additives was constant to within *ca.* 5%.

To follow these reactions in more detail, the reactions with gaseous HCl of the piperidyl compounds was also studied in *n*-hexane solutions. These model experiments also showed that $>$N—$COCH_3$ behaved very differently from $>$N—H and $>$N—O—$COCH_3$. In all cases, the salt was precipitated in the early stages of reaction (after 2 h). For the $>$N—H derivative, the conversion to its salt measured after 18 h was 95% by both gravimetry and the IR of the residual, soluble fraction. In addition, the IR spectrum of the precipitated salt in Nujol showed a sharp peak at 2469 cm^{-1} assigned to the $>NH_2^+$ vibration with $\varepsilon = 200$. The conversion of $>$N—O—$COCH_3$ to its salt was 95% and the IR spectrum of the precipitate contained a broad peak at 2530 cm^{-1} attributable to $>NH^+$.[8]

In the case of $>$N—$COCH_3$ in hexane, the HCl reaction was much more complex as implied by the changes observed in the polymer films. The

precipitate which formed in the first stage of the reaction gradually disappeared until after 18 h, a clear solution remained with an oily product on the bottom of the flask. White crystals (mp 66–68°C) were obtained after evaporation of the clear supernatant. The IR-spectrum of this crystalline product showed a peak at 1715 cm^{-1}. Both the IR-spectrum and mp agree with the formation of stearic acid (mp 67–69°C). Conversion of the ester group to acid was 80% by gravimetry.

Analysis of the oil residue proved to be more complex. The oil was first treated with 5% aqueous NaOH to release the free base. This new oily product was dissolved in $CDCl_3$ and examined by proton NMR. As well as typical peaks for the 2,2,6,6-tetramethylpiperidine ring, the NMR showed a singlet at $\delta = 2{\cdot}1$ and a multiplet at $\delta = 5{\cdot}1$ which corresponds, respectively, to the resonances at the methyl group in $—COCH_3$ and the $\overset{|}{C}H—O—$ of the piperidine ring observed in the NMR of the parent compound. In addition, the NMR spectrum showed a multiplet at $\delta = 4{\cdot}3$ which agrees with the resonance of $\overset{|}{C}H—Cl$ in a synthesized sample of 4-chloro-N-acetyl-2,2,6,6-tetramethylpiperidine (VI). There were also two singlets at $\delta = 6{\cdot}2$ and $\delta = 4{\cdot}7$ which we are unable to assign. From the integration of the NMR spectra, the percentage contents are as follows: $\delta = 4{\cdot}3 \sim 55\%$, $\delta = 4{\cdot}7 \sim 15\%$, $\delta = 5{\cdot}1 \sim 25\%$ and $\delta = 6{\cdot}2 \sim 5\%$. Thus, the neutralized oil contains at least three compounds one of which is the original compound ($\sim 20\%$ of the initial additive based on the stearic acid yield), the second is 4-chloro-N-acetyl-2,2,6,6-tetramethylpiperidine (VI, Table 1, $\sim 55\%$) and at least another unknown product. Gas chromatography confirmed the presence of three components in the oil. The mass spectrum of one component of the mixture separated by gas chromatography showed M^+ peaks at 217 and 219 in the ratio 3:1. These peaks agree with structure VI (natural $^{35}Cl/^{37}Cl$ ratio = 3:1).



(2)

The instability of the amide salt and its rearrangement products are consistent with reported very rapid intramolecular, amide-assisted ester scission reactions.[9,10] Under anhydrous conditions, this may proceed via the carbocation intermediates suggested in reaction (2).

From the ESR of the $>$N—O· derivative in PP film (Fig. 3) it followed that after HCl-treatment only 15% of radicals are in a form detectable by ESR. Rozantsev[11] proposed that the high polarity of nitroxyl radicals leads to reaction with reagents such as proton acids. When dry hydrogen chloride is passed into a solution of nitroxyl radicals in carbon tetrachloride, a coloured agglomerate of the oxammonium chloride (nitroxyl chloride) and the hydroxylamine hydrochloride was reported.[11] However, treatment of HCl exposed PP film containing nitroxide IV with a dilute solution *m*-chloroperbenzoic acid in hexane leads to a rapid ($\sim$ 30 min) reformation of $>$80% of the original nitroxide as measured by ESR. This is consistent with the report of Dulog and Bleher that nitroxide is readily reformed from the HCl promoted reaction products.[12] Similarly, the HCl salts of I and III were converted to nitroxide with peracid. However, neither the parent amide II nor its HCl salt formed more than trace amounts of nitroxide upon peracid treatment.

In Figs 3 and 4, the changes in $>$NO· concentration in PP films with irradiation time are shown. For experimental convenience, the films were irradiated directly in ESR tubes so the degree of photo-oxidation may not correspond exactly with that shown in Figs 1 and 2, although ESR tubes do not absorb light above 280 nm. In all cases, the concentration of $>$NO·

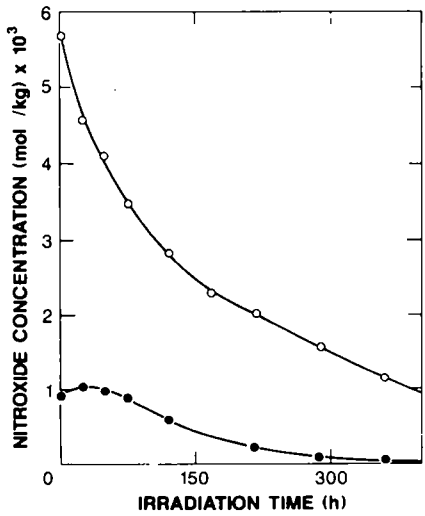


Fig. 3. Concentration of the $>$N—O· radicals in polypropylene films. Initial concentration 0·25 wt% $>$N—O·; ○ film without HCl treatment; ● film after 18 h HCl treatment before irradiation. Films were irradiated in ESR tubes.

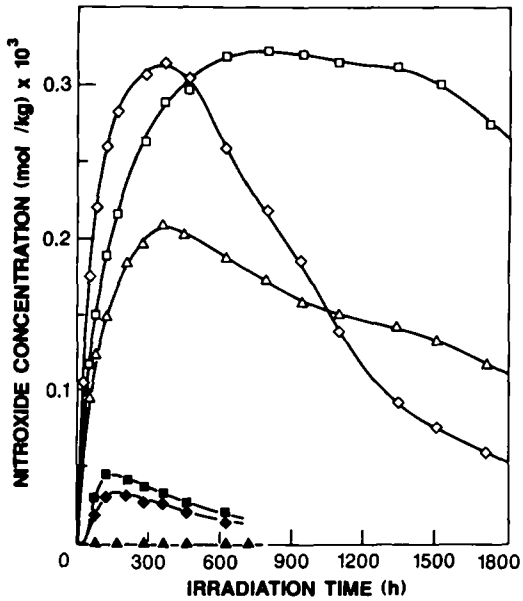


Fig. 4. Generation of $>$N- O· radicals in polypropylene films. Additives and concentration as in Fig. 1; Open symbols: sample without HCl/treatment. Closed symbols: sample after 18 h HCl treatment. Films irradiated in ESR tubes.

radicals was dramatically reduced by HCl treatment. For example, PP-film containing the $>$N—$COCH_3$ derivative after HCl treatment did not show any $>$NO· signal at all (Fig. 4) and this results in photo-oxidation with the same rate as PP-film without a stabilizer (Fig. 2). Starting from the nitroxyl itself, the maximum $>$NO· concentration observed after HCl exposure is less than the concentration of $>$NO· radicals remaining after ~400 h of irradiation of the sample which was not treated with HCl (Fig. 3). Similarly, low yields of $>$NO· radicals were found from $>$N—H and $>$N—O—$COCH_3$ containing films after HCl treatment (Fig. 4).

From Fig. 2 there is a surprising difference between the photo-stabilizing ability of the chemically similar monofunctional stearyl piperidine (I) and the bi-functional, commercial piperidine (V) after HCl exposure. For I, photo-oxidation begins without an induction period, but progresses only very slowly. For V, photo-stabilization is practically non-existent, as we have reported previously.[3] The irradiation time to reach a carbonyl absorption of 0·2 is 1230 h with HCl exposure of I but only 30% higher (~1620 h) for the HCl-free system. However, as mentioned previously, 80% of the $>$N—H groups in I are tied up as the $>NH_2^+Cl^-$ salt (from the 2469 cm^{-1} $>NH_2^+$ absorption) after an 18 h HCl exposure. A very similar value was found for V after HCl treatment which implies equally strong association in the equilibrium reaction (1). The difference in photo-

stabilization ability between the HCl salts of I and V may originate from the close proximity of the $>$N—H sites in V which leads to better retention of HCl in the photo-oxidizing films. Any free HCl evolved from I in reaction (3), may diffuse out of the film whereas in the case of V recombination

$$>N-H + HCl \rightleftharpoons >NH_2^+Cl^- \quad (3)$$

with the adjacent $>$NH group is very likely. This is consistent with the observed $>NH_2^+Cl^-$ level still being ~50% of the initial concentration for V after 100 h of UV exposure whereas for I only ~25% remained tied up as the salt.

CONCLUSIONS

(1) Most substituted piperidyl compounds used as UV stabilizers survive processing conditions, although *N*-acyloxy compounds are degraded both by heat and shear conditions.

(2) Exposure to strong acids results in salt formation from $>$NH, $>$NO·, and $>NOC(=O)CH_3$ containing additives. The N-acyl compound is extensively degraded by HCl which cleaves the ester linkage in the 4-position and introduces chlorine at this point.

(3) Acid exposed piperidyl compounds produce little nitroxide in photo-oxidizing polymers and show impaired UV stabilization.

(4) Monofunctional secondary piperidyl amines are less affected by acid exposure that are multi-functional analogues.

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