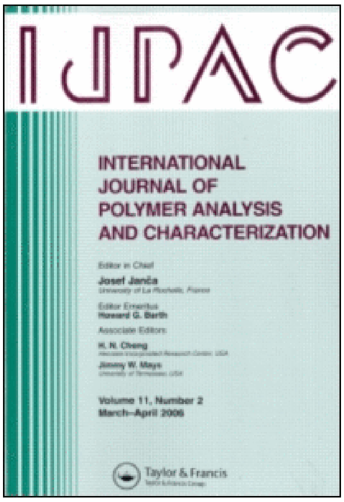

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Characterization by Chemiluminescence of Unstabilized and HALS-Stabilized LDPE Films Exposed to Natural Weathering Conditions

Mustapha Kaci[a]; Naima Touati[a]; Radu Setnescu[b]; Tanta Setnescu[b]; Silviu Jipa[b]
[a] Laboratoire des Matériaux Organiques, Université A. Mira de Béjaia, Algéria [b] Research & Development Institute for Electrical Engineering (ICPE-CA), Faculty of Sciences, Bucharest, Romania; and Valahia State University, Targoviste, Romania

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Mustapha Kaci and Naima Touati
Laboratoire des Matériaux Organiques,
Université A. Mira de Béjaia, Algéria

Radu Setnescu, Tanta Setnescu, and Silviu Jipa
Research & Development Institute for Electrical
Engineering (ICPE-CA), Bucharest, Romania; and
Valahia State University, Faculty of Sciences,
Targoviste, Romania

Photostability of low-density polyethylene (LDPE) films under natural weathering conditions was investigated in the absence and the presence of various structures of hindered amine light stabilizers (HALS) by chemiluminescence (CL) and Fourier transform infrared (FTIR) spectroscopy. The stabilizers studied were Sanduvor PR 31 (as grafted HALS) and Uvasil 299 and Tinuvin 123 (as non-grafted HALS). The HALS were added separately to LDPE at the same concentration, namely 0.3% (w/w). It was found that the weathered stabilized samples exhibited a relative long period during which the CL signal slowly increased, while for unstabilized samples, CL increased after a short induction period. This behavior could be explained by reduction in the rate of hydroperoxide decomposition caused by nitroxyl radicals. However, the very high increase in stability observed in the case of Sanduvor PR 31 sample could be assigned to the grafting effect of the HALS on the polymer chain. At longer exposure times, the oxidation induction time decreased slowly as a result of stabilizer consumption in

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Address correspondence to Mustapha Kaci, Laboratoire des Matériaux Organiques, Université A. Mira de Béjaia 06000, Algeria. E-mail: kacimu@yahoo.fr

the photooxidative process. These changes in CL parameters were found to correlate with carbonyl index determined by FTIR spectroscopy.

Keywords: Low-density polyethylene; Hindered amine light stabilizer; Natural weathering; Chemiluminescence; Fourier transform infrared spectroscopy

INTRODUCTION

In previous work[1], we have shown that the photografting process under natural weathering conditions of hindered amine light stabilizers (HALS) occurred in low-density polyethylene (LDPE) films in a very short exposure period of approximately seven days. This photografting process would possibly avoid the physical loss of the additive through diffusion to the polymer surface during aging[2]. Therefore, it is expected that the permanence of the stabilizer within the polymer matrix should provide better stability to the material by inhibiting the photooxidation process in the early stage of exposure as well as sustaining this inhibition for a longer time[3–5]. In this connection, Malik et al.[6] reported that grafted HALS showed a significantly higher efficiency than the conventional low molecular weight and oligomeric additives in meeting three requirements: high compatibility, minimal diffusion, and high homogeneity distribution of the active functionalities. Several methods have been used to evaluate the effectiveness of light stabilizers according to how much their addition to a polymer improves the resistance of the material against the action of weathering[7–11]. The techniques currently used include Fourier transform infrared (FTIR) spectroscopy[7,8], electron spin resonance (ESR)[9,10], oxygen uptake[11–13], and thermogravimetric analysis (TGA)[14].

In recent years, chemiluminescence (CL) has been shown to be a very sensitive technique used for determination of the oxidation rate and even for predicting the long-term stability of polymers[15–18]. CL is the light emitted during some chemical reactions, such as oxidation of organic substances, including polymers and polymeric materials. In the case of oxidation, CL is assigned to deactivation of a carbonyl group that could result by various pathways. Although the reactions responsible for the formation of these carbonyls are still debated[16,19,20], such groups could result from both peroxy radical termination and hydroperoxide thermolysis. In the case of polyolefins (such as polyethylene and polypropylene or their copolymers), oxidation occurs by a long kinetic chain mechanism. As a result, the time dependence of hydroperoxide concentration is a sigmoidal curve that exhibits the three main steps of chain oxidation, namely induction, propagation, and termination. Figure 1 shows a typical CL curve resulting from a CL experiment (under isothermal conditions) on a hydrocarbon polymer (e.g., polyethylene). Typical CL curves, in coordinates of CL signal versus time, are analogous to an oxygen uptake or carbonyl index curve[21]. The oxidation process is spread into the bulk of the material after the end of the induction when all physical barriers (crystallinity) or chemical barriers (inhibitors) are removed. According to the theory of Reich and Stivala[22], the relationship between CL intensity and hydroperoxide concentration is:

$$I_t = C[ROOH]_t$$

where C is a constant. Therefore, we can consider that a CL curve under isothermal conditions should correspond to time dependence of ROOH concentration. If we consider also that the oxidation rate can be related to the hydroperoxide formation (and decomposition, in steady state), we can conclude that the maximum of oxidation rate (v_{ox}) corresponds to the inflection point of the CL curve, and it can be calculated as the slope of the tangent to the CL curve at this point. The stability of a polymer is high when the oxidation induction period is long. The length of the induction period depends on polymer structure, temperature, and antioxidant concentration and effectiveness. If a polymer is subjected to an oxidative stress (temperature, radiation, UV light, mechanical, etc.),

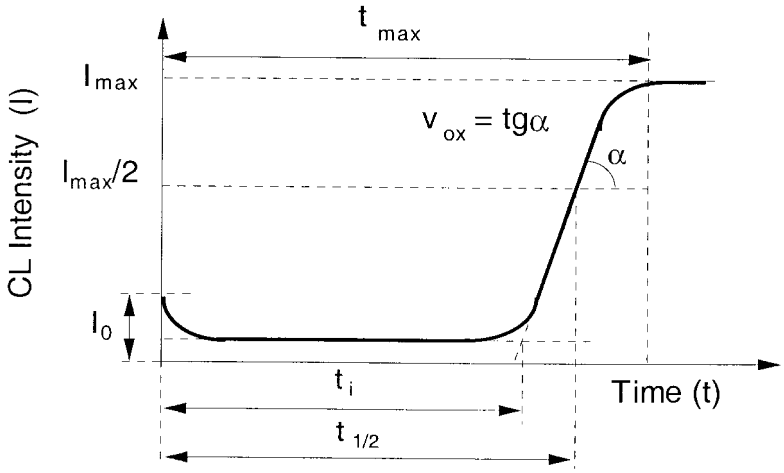


FIGURE 1 Typical chemiluminescence curve describing the kinetics of oxidation of polyethylene and recorded in isothermal mode under oxidative atmosphere and typical CL parameters.

a decrease in stability, as compared to a similar unaged sample, can be observed. This is due to antioxidant consumption and depends on the duration and intensity of stress action. CL parameters related to oxidation kinetics are shown in Figure 1 and Table I as well.

The aim of this work was to examine the stability under natural weathering conditions of LDPE films in the absence and the presence of grafted HALS by using CL technique. The performance of the materials was evaluated by the determination of CL parameters with exposure time, and the data obtained were compared with the unstabilized samples. The stability of the exposed films was also examined on the basis of the formation rate of carbonyl groups determined by FTIR spectroscopy.

EXPERIMENTAL

Materials

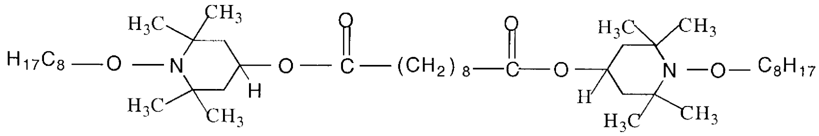
The LDPE used was manufactured by the Algerian Company ENIP "(Enterprise Nationale des Industries Pétrochimiques)" at Skikda (Algeria) and available under the trade name B24/2. The main physical characteristics of the polymer are a density of 0.923 g/cm^3 and a melt flow index of 0.3 g/10 min according to ASTM D 1238/79. The hindered amine stabilizers used were a polymer-bound HALS produced by Clariant Company at Huningue (France) under the trade name Sanduvor PR 31, an alkoxyamine, produced by Ciba Specialty Chemicals (Switzerland) under the trade name Tinuvin 123, and a HALS modified with siloxane, manufactured by Enichem Synthesis (Italy) under the trade name Uvasil

TABLE I CL parameters used for oxidation studies, recorded in isothermal mode under oxidizing atmosphere and their significance

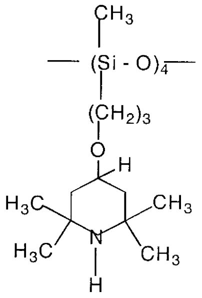
Parameter	Significance
t_i	Oxidation induction time (related to induction period)
$t_{1/2}$	Time observed for reaching half of CL intensity (related to induction period)
V_{ox}	Oxidation rate (related to propagation period)
t_{max}	Time observed for reaching maximum of CL intensity (related to general resistance to oxidation of the polymer)
I_{max}	Maximum of CL intensity (related to concentration of CL emissive species at maximum of hydroperoxide content)

299. The additives were added separately to the polymer at a concentration of 0.3% (w/w). The chemical structure of the stabilizers and their molecular weight are given in Scheme 1.

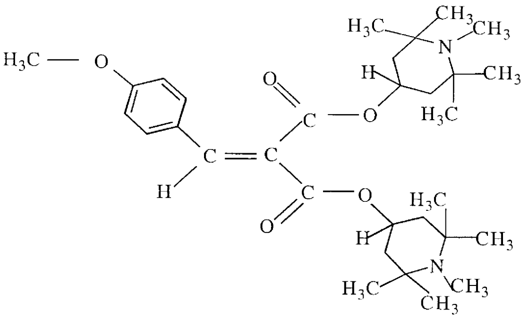
Tinuvin 123: Molecular weight = 737 g . mol^{-1}



Uvasil 299: Molecular weight = 1800 g . mol^{-1}



Sanduvor PR 31 : Molecular weight = 529 g . mol^{-1}



SCHEME 1

Sample Preparation

Films of 80 μ thickness were prepared by blown extrusion process using a Battenfeld SFB 400 extruder with a length/diameter ratio of 24. The temperature in the extruder varied from 160 to 180°C along the barrel; while in the die, it decreased from 180 to 160°C. The films were stretched in the air after leaving the die at a pulling speed of 5 m/min. They were cooled by air passing through the die into the bubble. Finally, the films were cooled with a large volume of air upward over the surface of the bubble.

Natural Weathering Exposure

The natural weathering of both unstabilized and HALS-stabilized LDPE films was carried out according to ASTM D1435. The samples were in the form of rectangular bands (30 × 20 cm) and were mounted on racks, facing southward. The natural exposure was carried out at Béjaia on the east coast of Algeria from December 1999 to October 2001.

Chemiluminescence (CL)

The CL emission of both unstabilized and HALS-stabilized LDPE films were obtained in a CL 931M Chemiluminescence apparatus conceived and made at ICPE - CA Bucharest according to the following experimental conditions. The film samples of 4 to 6 mg were put in a cell having 0.11 mm in thickness, which consists of two cylindrical aluminum disks, as shown in Figure 2. The whole cell was placed inside the apparatus. The use of this type of cell eliminates the shrinking effect induced on film samples by the blown extrusion process. As a result, this method allowed a better reproducibility of the oxidation process and oxidation parameters. All the experiments were carried out at a temperature of 190°C in the presence of air. The chemiluminescence was measured using a conventional cooled photo-multiplier tube. Two experimental tests were performed for each sample.

Fourier Transform Infrared Spectroscopy (FTIR)

The chemical changes in both unstabilized and HALS-stabilized LDPE films were monitored by measuring the growth in the carbonyl group concentration with exposure time using a Shimadzu FTIR spectrophotometer (model 8000 M) with 2 cm^{-1} as resolution and 40 scans. The carbonyl index was determined by calculating the carbonyl absorption at 1713 cm^{-1} from the FTIR spectra at the different oxidation times using the spectrum of the unoxidized starting material as a reference. All

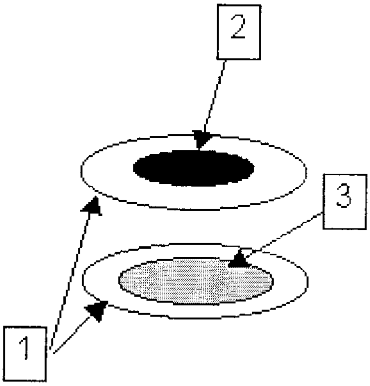


FIGURE 2 Modified cell for chemiluminescence: 1, aluminium plates (diameter = 6 mm, thickness = 0.11 mm); 2, perforation (diameter = 6 mm); 3, sample (diameter = 10 mm).

measured absorbances were normalized for the film thickness by the equation[10]:

$$\text{Carbonyl index (CI)} = [A_{1713}/d] \times 100$$

where A_{1713} is the measured absorbance at 1713 cm^{-1} in the FTIR spectrum at a certain exposure time and d is the film thickness in microns.

RESULTS AND DISCUSSION

CL Analysis

The shapes of CL curves seem to be different, depending on the absence or the presence of the grafted HALS (Sanduvor PR 31) in the LDPE films, as shown in Figures 3 and 4, respectively. In the case of unstabilized samples, CL increases rapidly after a short induction period, while the stabilized samples exhibit a relative long period where the CL intensity remains basically constant. The long induction period observed in the case of the weathered LDPE films containing the grafted HALS could be explained by an antioxidative effect of the grafted stabilizer, while the grafting process could also decrease the number of the active sites susceptible to oxidation. Similar behavior was, however, observed with Tinuvin 123 and Uvasil 299, two HALS that were found to be not grafted under photoexposure[13,23]. Therefore, we assigned the initial

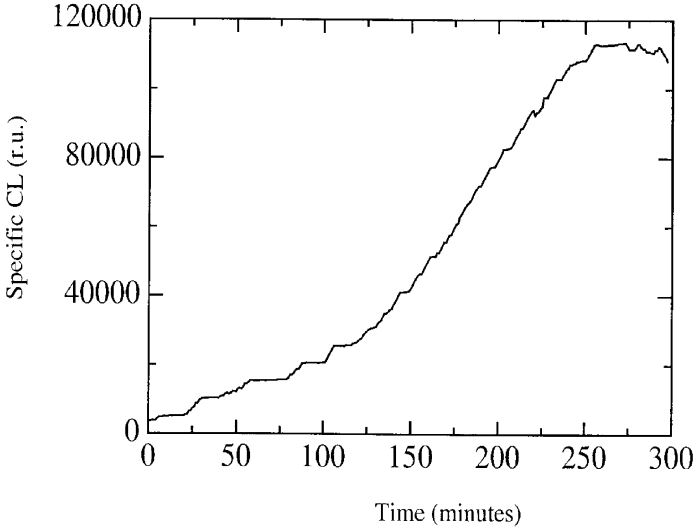


FIGURE 3 CL curve of Sanduvor PR 31-stabilized LDPE film recorded after 225 days of natural exposure.

increase in oxidative stability of weathered samples 190°C, (Figure 5) to the interaction of the polymer hydroperoxides and nitroxyl radicals of the HALS stabilizer. As a matter of fact, Gugumus[24] found a decrease in the

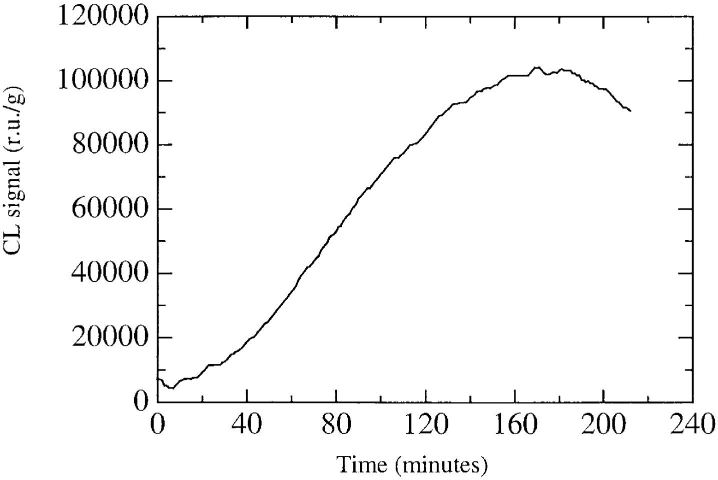


FIGURE 4 CL curve of unexposed Sanduvor PR 31-stabilized LDPE film recorded before exposure.

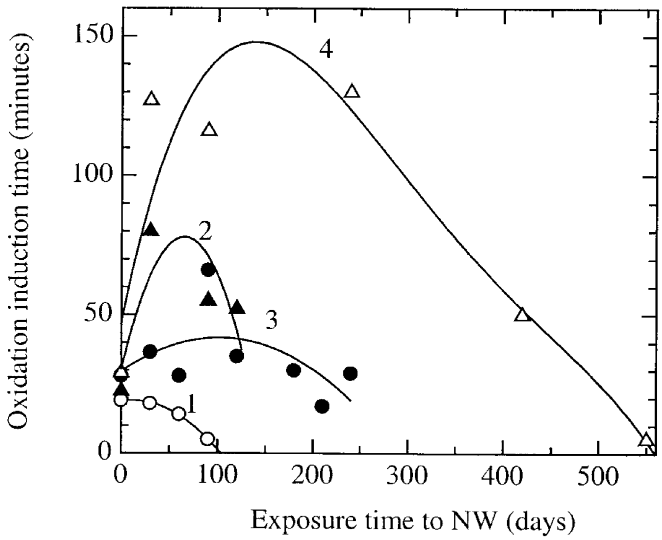


FIGURE 5 Oxidation induction time (OIT) at 190°C as a function of exposure time for unstabilized and HALS-stabilized (0.3%) LDPE films: 1, LDPE free of additives; 2, Tinuvin 123; 3, Uvasil 299; 4, Sanduvor PR 31.

decomposition rate of hydroperoxides in the presence of nitroxyl radicals. The maximum in stability that is reached after more or less the same duration (starting from CL measurement) could be therefore related to a maximum in concentration of nitroxyl radicals. In the case of unstabilized LDPE films, such a maximum is not observed, and the stability decreased as the weathering duration increased.

The very high increase in stability observed with Sanduvor PR 31 seems to be related not only to the interaction of its nitroxyl radicals with the hydroperoxides formed in the LDPE films, but also to a grafting process that could enhance the oxidative resistance of the polymer. The occurrence of such a grafting process has been proved by spectroscopic data[1,25] and could result in blocking of some reactive sites toward oxidation of the polymer. Oxidation rate values are basically constant with the LDPE films containing PR 31 as reported in Table II, but they seem to increase slowly as the weathering time for the unstabilized samples increases (Table III). CL intensity corresponding to the maximum of the signal increases from unexposed samples to exposed ones, reaching a maximum of 60 days of exposure. However, above 90 days the unstabilized samples become less emissive. Initial CL signal (I_0) from 90-day weathered samples suggested that the hydroperoxide content is

TABLE II CL parameters from Sanduvor PR 31-stabilized LDPE films as a function of exposure time

Exposure time (days)	t_i (min)	$t_{1/2}$ (min)	t_{max} (min)	V_{ox} (%/min)	I_{max} (r.u./g)
0	20	130	168	0.75	276 000
30	144	194	292	0.57	612 000
90	150	199	290	0.79	560 000
225	26	105	147	0.86	332 000
420	12.5	106	122	0.69	300 000
550	0	51.5	90	0.72	299 000

considerably higher in the case of unstabilized samples as compared to HALS-stabilized samples as shown in Table IV. The lowest values were obtained with Sanduvor PR 31 and Tinuvin 123, which seem to be more effective than Uvasil 299 upon natural weathering exposure. This result is in agreement with previously reported data[13].

Another parameter of initial emission that is specific to CL measurements, TLI_{600}, provides information about the capacity of hydroperoxide annihilation at high temperature. It leads to basically similar result as I_0. Thus, Sanduvor PR 31 is the most effective, while a very high luminescence value is observed with LDPE (no hydroperoxide annihilation); Uvasil 299 exhibits an intermediate value between LDPE free of additives and LDPE stabilized with Sanduvor PR 31. However, Tinuvin 123 exhibits a higher luminescence value, suggesting a lower effectiveness. Similar high luminescence results from Tinuvin 123-containing samples was also observed in another work, and it has been assigned to specific interaction of this compound with polymer hydroperoxides[18]. Thus, the effectiveness in inhibiting the hydroperoxides at ambient temperatures

TABLE III CL parameters from unstabilized LDPE films as a function of exposure time

Exposure time (days)	t_i (min)	$t_{1/2}$ (min)	t_{max} (min)	V_{ox} (%/min)	I_{max} (r.u./g)
0	19	105	225	0.57	71965
30	18	72	173	0.65	92931
60	14	76	168	0.82	100867
90	5	71	165	0.76	88439
120	0	55	123	1.02	59249
150	0	42	120	1.01	58000
180	0	45	120	0.9	59312

TABLE IV Initial CL emission from 90-day weathered samples

Sample	I_0 (r.u./g)	TLI_{600}
LDPE free of additives	33 333	443 846
LDPE+0.3% (w/w) Sanduvor PR 31	7 542	93 855
LDPE+0.3% (w/w) Tinuvin 123	6 135	164 110
LDPE+0.3% (w/w) Uvasil 299	16 667	105 758

(as described by I_0) and the capacity of hydroperoxide annihilation at 190°C (as described by TLI_{600}) appear to be different, perhaps because of the high temperature that changes the mechanism of HALS action.

FTIR Analysis

The formation rate of carbonyl groups of the HALS-stabilized samples is plotted in Figure 6 as a function of exposure time and compared to the unstabilized samples. Figure 6 shows that the PR 31-stabilized

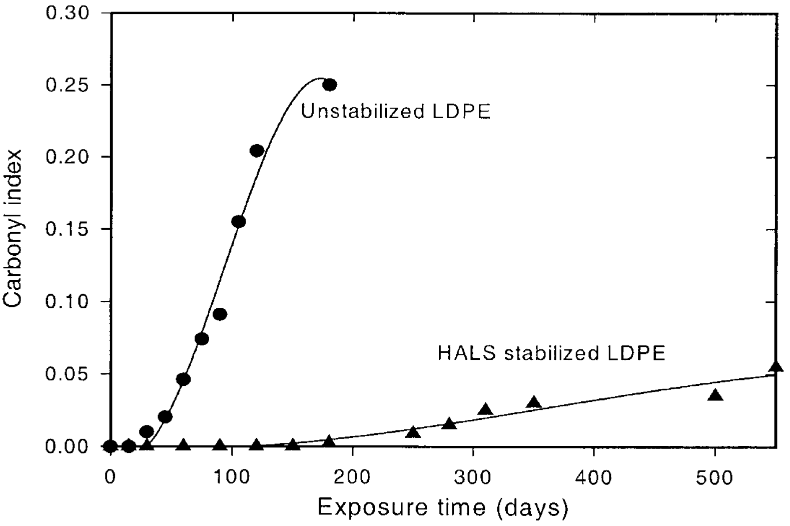


FIGURE 6 Carbonyl index as a function of exposure time for unstabilized and Sanduvor PR 31-stabilized LDPE films during natural weathering.

samples exhibit an initial auto-retarding effect corresponding to an oxidation induction period of almost 250 days, whereas the unstabilized samples, as expected, show a very short induction period and the highest carbonyl levels up to 180 days of exposure. These results are in good agreement with those obtained from the CL tests.

CONCLUSIONS

The oxidative stability under natural weathering conditions of both unstabilized and HALS-stabilized LDPE films has been investigated by means of CL analysis and FTIR spectroscopy. CL has been shown to provide useful data to assess the light efficiency of the HALS stabilizer. For the same period of exposure, higher stability was found for the stabilized samples, which exhibit longer oxidation induction time when compared to unstabilized samples. This is in agreement with the carbonyl index evolution determined by FTIR spectroscopy, where an auto-retarding effect was observed during the first 250 days. Finally, the reported results obtained with grafted HALS showed better stabilization performance in LDPE films.

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