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Analysis of Photostabilizer in High Density Polyethylene by Reverse- and Normal-Phase HPLC

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ABSTRACT

Photostabilizer-type HALS were analyzed by reverse- and normal-phase liquid chromatography (HPLC) using C-18, cyano, silica, and amino columns with different solvent mixtures as the mobile phase. The stabilizers analyzed were Tinuvin 770 and Chimassorb 944. The best separation was attained using a NH_2-column and acetonitrile/water as the mobile phase. Also, three types of extraction procedures were performed to isolate these additives from the polymeric matrix. The most efficient extraction method was achieved by refluxing the sample with toluene. Recoveries of 95% were found for additives using this method.

Key Words. Photostabilizer; HPLC; Extraction of photostabilizer; High density polyethylene

INTRODUCTION

Polymers are exposed to high temperatures during manufacturing procedures and the result is thermal degradation. Also, as manufactured products, polymers are exposed to long periods of sunlight, and photodegradation occurs (1–3). This effect can be delay by polymer modification or by the addition of photostabilizers (more often used). During the last 20 years, 2,2,6-tetramethyl-piperidine and its derivatives (hindered amine light stabilizers or HALS) have been used as photostabilizers. Recently, stabilization mechanism studies have been developed for these compounds (4, 5), as have some chromatographic studies (2, 6–12). The application of these methods depends on the analyzed compounds (simple or oligomeric) and the chromatographic group in the molecule. The following chromatographic procedures have been developed to analyze these compounds: reverse-phase high performance liquid chromatography (HPLC) using a C-18 column (9, 13, 14), normal-phase HPLC an using amino column (10, 15) or a silica column (16), and HPLC using gel columns (11). UV detection was used for these analyses. The wavelength used depends on the chromophore present.

The analysis of these compounds has usually been done in monomeric or oligomeric form. On the other hand, Soxhlet and reflux extraction procedures have been used to isolate the polymeric matrix by using toluene, decaline, or chloroform as the extraction solvent.

In this paper we describe a rapid and reproducible extraction method and a HPLC separation procedure for the analysis of the Tinuvin 770 and Chimassorb 944 in high density polyethylene.

EXPERIMENTAL

Extraction of Photostabilizers

Three types of extraction procedures were performed. 1) Diffusion extraction at room temperature. About 10 g of high density polymer (HDPE) pellets were used with 100 mL of chloroform. Exposure time was between 1 and 4 weeks. 2) Ultrasonication extraction. The same procedure described previously was followed using a 1200 Branson bath and two solvent mixtures reported by Nielsen (17): cyclohexane/methylene chloride 50/50 and cyclohexane/isopropanol 50/50. Extraction time was between 1 and 5 hours. 3) Hot extraction was performed in three different ways. (a) By refluxing at 160°C between 2 and 4 hours, using 10 g of sample and toluene as the extraction solvent. (b) About 10 g of HDPE pellets was dissolved in 100 mL of *o*-dichlorobencene (*o*-DCB) at 160°C for about 1 hour (this mixture was heated to 160°C on a hot plate with gentle stirring).

The polymer was precipitated with isopropanol and then filtered to obtain the extract and the additives. (c) By using a Soxtec extraction apparatus model HT2. About 5 g of HDPE pellets was employed with 80 mL of methylene chloride as solvent.

In all cases the extract was evaporated to dryness using a Rotavapor under vacuum. The residue was then redissolved in hexane and filtered using a 0.2-μm filter. The solution was evaporated to 10 mL, and then 10 μL of this solution was analyzed by HPLC.

The amount of HALS was determined from each sample injection by comparing peak areas for samples and standards. Calibration plots were performed using standards between 25 and 500 ppm dissolved in hexane.

UV Scan

UV scan was carried out using a Perkin-Elmer spectrophotometer model 1700 from 190 to 300 nm. Standard solutions of 0.1% w/v of each compound in hexane were prepared for this analysis. The scan rate was of 20 nm/min.

HPLC Studies

HPLC separation was performed in a Waters liquid chromatograph (Waters Associates, Milford, MA) equipped with a 600 E pump, a U6K injector, and a 991 photodiode array detector coupled to a NEC computer.

Six columns were used: 1) a μ-Bondapack C-18 column, stainless steel, 250 mm × 4.6 mm, 10 μm particle size, manufactured by Waters; 2) a Zorbax-CN column, stainless steel, 250 mm × 4.6 mm, 10 μm particle size, manufactured by Dupont USA; 3) a Silica 60 column, stainless steel, 250 mm × 4.6 mm, 10 μm particle size, manufactured by Hibar-Merck; 4) a NH_2 Econosphere column, stainless steel, 250 mm × 4.6 mm. 10 μm particle size, manufactured by Alltech; 5) a NH_2 μ-Bondapack column, stainless steel, 250 mm × 4.6 mm, 10 μm particle size, manufactured by Waters; 6) a NH_2 Adsorbosphere column, stainless steel, 250 mm × 4.6 mm, 10 μm particle size, manufactured by Alltech. The mobile phases were filtered with a Millipore 0.2 μm filter before use. Then the mobile phases were degassed by ultrasonication and by continuous stripping with helium gas.

All solvents used for chromatographic and extraction analysis were HPLC grade from Merck, J. T. Baker, and Mallinckrodt. High purity samples of Tinuvin 770 and Chimassorb 944 were from Ciba-Geigy. HDPE pellets with a stabilizer content of 500 ppm were supplied by INDESCA, Complejo Petroquímico El Tablazo-Venezuela.

RESULTS AND DISCUSSION

UV Scan

Figure 1 shows the UV spectrum of Tinuvin 770 (Fig. 1A) and Chimassorb 944 (Fig. 1B). The λ_{max} of Tinuvin 770 and Chimassorb 944 were 222 and 238 nm, respectively. This figure also shows a clean absorption region after 260 nm. Therefore, the wavelength was set at 230 nm for quantitative analysis.

Chromatographic Separation

Reverse- and normal-phase chromatography were used to separate a mixture of Tinuvin 770 and Chimasorb 944 (photostabilizer type HALS).

Initially, reverse-phase chromatographic analyses were performed using a C-18 column with different polar mobile phases, such as water,

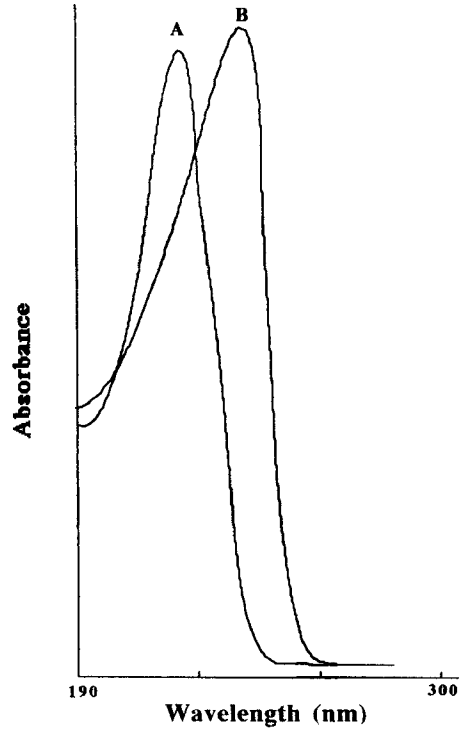

FIG. 1 UV spectrum of Tinuvin 770 (A) and Chimassorb 944 (B).

methanol, and acetonitrile, without any good separation found. Best results were achieved using methylene chloride as the mobile phase. Figure 2 shows this chromatographic separation. However, poor resolution was attained using this chromatographic condition, and it was not practical for quantitative analysis at very low concentrations. Furthermore, reverse-phase chromatographic separation was carried out using a CN column. However, no good separation was achieved using this column with any mobile phases employed.

Normal-phase chromatographic studies were performed using a silica column. A little improvement was attained by using a very low polar solvent as the mobile phase, i.e., hexane, as shown in Fig. 3. This separation in the normal phase is better than that obtained by reverse-phase HPLC. However, the separation attained was not satisfactory for the purpose of this study.

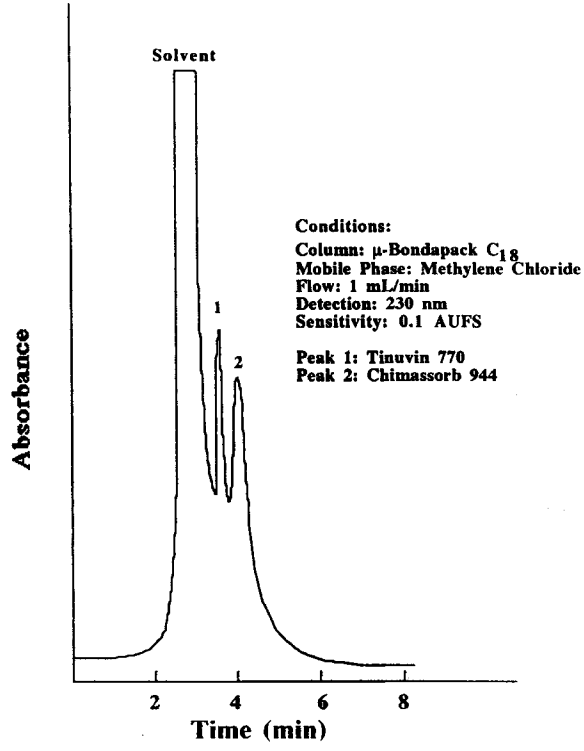

FIG. 2 HPLC separation of Tinuvin 770 (peak 1) and Chimassorb (peak 2) on a C-18 column.

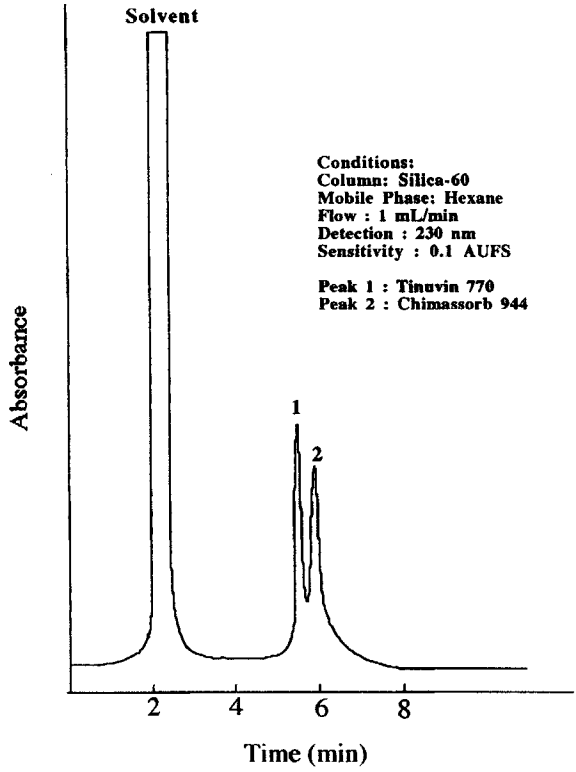

FIG. 3 HPLC separation of Tinuvin 770 (peak 1) and Chimassorb 944 (peak 2) on a Silica 60 column.

Finally, amino columns were employed for this separation. First, a NH_2 Adsorbosphere column was used with 100% acetonitrile as the mobile phase to separate this mixture. Good resolution, good symmetric peaks, and good reproducibility was obtained under these chromatographic conditions as shown in Fig. 4(A). Excellent separation of these additives with those described previously was obtained by adding a polar modificator to the mobile phase, i.e., water. Figure 4(B) shows this chromatographic separation using a NH_2 Econosphere column with acetonitrile/water 98:2 as the mobile phase. Furthermore, the tridimensional chromatogram of this run (Fig. 5) shows no signal after 240 nm, which agrees with the results obtained in the previous wavelength scan analysis (Fig. 1).

To compare the chromatographic efficiencies of different columns, a μ-Bondapack NH_2 column was used with acetonitrile/water 98:2 as the

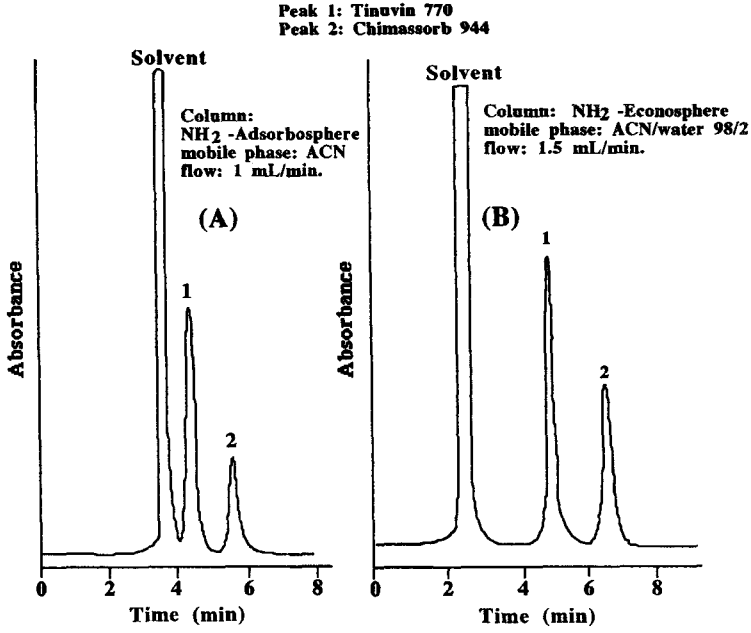

FIG. 4 HPLC separation of Tinuvin 770 (peak 1) and Chimassorb 944 (peak 2) on a NH_2 column. (A) NH_2 Adsorbosphere, mobile phase 100% ACN, flow 1.0 mL/min. (B) NH_2 Econosphere, mobile phase ACN/water 98/2, flow 1.5 mL/min.

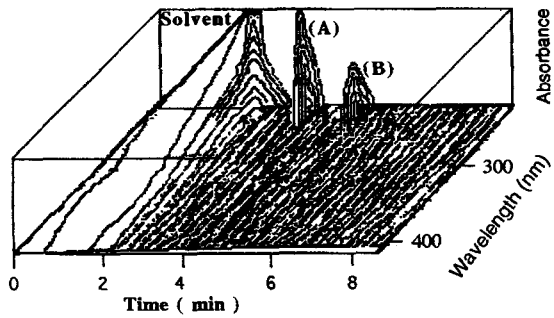

FIG. 5 Three-dimensional chromatogram for the separation of Tinuvin 770 (peak A) and Chimassorb 944 (peak B).

mobile phase. Good separation was achieved for both compounds using these chromatographic conditions, as shown in Fig. 6(A). However, there is some strong retention for these compounds, especially for Chimassorb 944 whose base peak became very broad, probably due to a greater degree of amino groups bonding to this stationary phase. In order to avoid this

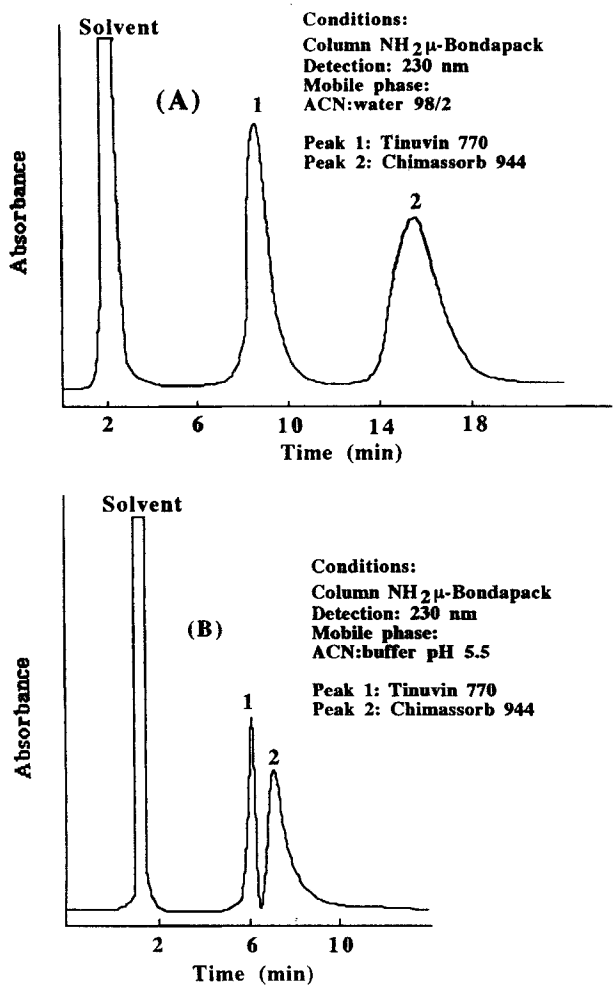

FIG. 6 HPLC separation of Tinuvin 770 (peak 1) and Chimassorb 944 (peak 2) on a NH_2 μ-Bondapack column. (A) Mobile phase ACN/water 98/2, flow 1.0 mL/min. (B) Mobile phase ACN/buffer acetate 99/1, pH 5.5, flow 1.5 mL/min.

retention effect, a new mobile phase composed of the mixture acetonitrile/water 98:2 at pH 5 with the buffer acetic acid–sodium acetate was prepared. Figure 6(B) shows the chromatogram obtained under these chromatographic conditions. It is worth noting in this figure that acidification of the mobile phase decreases the interaction of the analyte with the stationary phase, especially for Chimassorb 944, which is shifted from 15 minutes (Fig. 6A) to 8.5 minutes (Fig. 6B) retention time. It is suspected that protonation of the amino group of the stationary phase occurs.

Table 1 shows the separation parameters obtained for the analysis of HALS using the evaluated amino columns. The results correspond to the optimum mobile phase. As shown in this table, the best data for the capacity factor (k'), separation factor (α), and resolution (R) were obtained using the NH_2 Econosphere column with acetonitrile/water as the mobile phase. Furthermore, the results suggest that a unique separation parameter (k', α, or R) does not determine the chromatographic behavior of the components. The different k' data for the NH_2 Econosphere and NH_2 Adsorbosphere suggest that two separation mechanisms take place. If the mobile phase contains a polar modificator such as water, the retention mechanism for the NH_2 Econosphere column is probably due to hydrophilic interaction. On the other hand, the separation obtained using acetonitrile with the NH_2 Adsorbosphere column with a low retention time probably suggests hydrophobic interaction.

A calibration curve using peak height was good enough for the Tinuvin 770, attaining a good straight line with good linearity (Fig. 7A). However, Chimassorb 944 shows a little asymmetric peak and less sensitivity. Therefore, the slope of the calibration curve is smaller. Improving Chimassorb sensitivity was achieved when working with the peak area without losing sensitivity for Tinuvin 770; these results are shown in Fig. 7(B). On the other hand, the error that can be introduced by industrial samples is negligible because of the high additive content (more than 200 ppm). The detection limit obtained was 5 ppm with good linearity in the entire range studied (from 25 to 500 ppm).

TABLE 1
Separation Parameters of Different NH_2 Columns

Column	k' Tinuvin	k' Chimassorb	α	R
NH_2 μ-Bondapack	1.42	1.82	1.28	1.79
NH_2 Econosphere	1.23	1.95	1.59	3.76
NH_2 Adsorbosphere	0.28	0.64	2.29	2.05

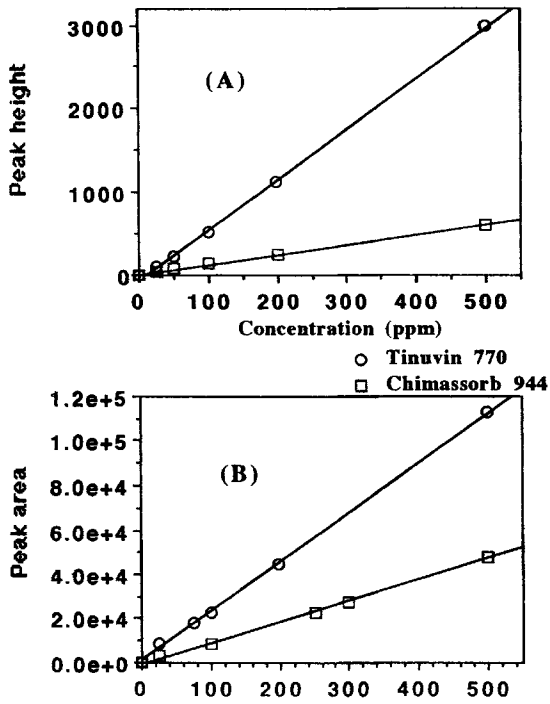

FIG. 7 Calibration curves of Tinuvin 770 and Chimassorb 944. (A) Peak height. (B) Peak area.

Extraction Procedure

The diffusion extraction method was not successful due to the great affinity of these additives for the polymeric matrix. The results attained using this method were very low in comparison with the other methods as shown in Table 2. Similar results were obtained when using the ultrasonication extraction method. Although a long exposition time (5 hours) were tried, no appreciable extraction was achieved (less than 20%) as shown in Table 2. On the other hand, by using a Soxtec extraction apparatus with methylene chloride, only 50% of the additives were extracted with 4 hours of extraction time as shown in Table 2. Nevertheless, these results are better than the results reported until now (18) using the Soxhlet extraction method with the same extraction solvent (methylene chloride) in 16 hours.

Recoveries of 70% were attained using the hot extraction method with *o*-DBC as the extraction solvent. However, solubility problems was found

TABLE 2
Different Extraction Methods[a]

Extraction method	Extraction solvent	Recovery (%)	
		Tinuvin 770	Chimassorb 944
Diffusion extraction	Chloroform	ND	ND
Ultrasonication	Cyclohexane/chloroform	ND	ND
	Cyclohexane/isopropanol	ND	ND
Disolution at 160°C and precipitation with MeOH	*o*-Dichlorobenzene	70 ± 3	65 ± 4
Refluxing with Soxtec	Methylene chloride	50 ± 1	50 ± 2
Reflux	Toluene	95 ± 3	95 ± 3

[a] ND = None detected.

for low molecular weight polymers (waxes). These waxes were filtered before chromatographic analysis. This solubility problem was overcome by using toluene as the extracting solvent. Furthermore, efficient extraction was achieved by refluxing the sample for 2 hours: 95% of the additives were extracted from the polymeric matrix, and the results are shown in Table 2.

CONCLUSION

An analytical procedure using normal-phase HPLC is particularly suited for analysis of HALS-type samples (Tinuvin 770 and Chimassorb 944)) using an amino column with acetonitrile/water as the mobile phase. Excellent separation was attained using this chromatographic condition.

Reverse-phase HPLC using C-18 or cyano columns was not effective for these separations.

The refluxing method using toluene as the extracting solvent was the most efficient extraction method to isolate these additives from the polymeric matrix.

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REFERENCES

1. S. G. Gharfeh, *J. Chromatogr.*, *389*, 211–218 (1987).
2. P. Perlstein, *Anal. Chim. Acta*, *149*, 21–27 (1883).
3. S. Chmela and P. Hrdlovic, *Polym. Degrad. Stab.*, *26*, 159–167 (1990).
4. D. R. Bauer, J. L. Gerlock, and D. F. Mielewski, *Ibid.*, *26*, 115–129 (1990).
5. G. Geuskens and G. Nedelkos, *Ibid.*, *19*, 365–375 (1987).
6. P. P. Klemchuk and M. E. Gande, *Ibid.*, *22*, 241–274 (1988).
7. American Cyanamid Company, Polymer and Chemicals Department (Ed.), *Determination of Cyasorb UV-3346 in Extracts of Polyolefins by High Performance Liquid Chromatography*, 1975.
8. American Cyanamid Company, Polymer and Chemicals Department (Ed.), *Quantitative Determination of Cyanox 1790 in Polypropylene and High Density Polyethylene*, 1975.
9. W. Freitag and Z. Frasenius, *Anal. Chem.*, *316*, 495–496 (1983).
10. W. Freitag, *J. Chromatogr.*, *450*, 430–432 (1988).
11. W. Freitag, R. Wurster, and N. Mady, *Ibid.*, *450*, 219–225 (1988).
12. J. López, R. Vallejo, and M. Zábala, *Cuantificación de Aditivos en Polietileno de Alta Densidad*, Jornadas Técnicas de Pequiven y Las Empresas Mixtas, Maracaibo, November 23–27, 1992.
13. V. Mika, L. Preisler, and J. Sodomka, *Polym. Degrad. Stab.*, *27*, 215–225 (1990).
14. F. Sevini and B. Marcato, *J. Chromatogr.*, *260*, 507–512 (1983).
15. A. J. Chirinos-Padrón, *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.*, *C30*(1), 107–154 (1990).
16. P. T. Rajmankina, *Estudio de la Interacción entre Aminas Impedidas HALS) y Antioxidantes Fenólicos en Polietileno de Alta Densidad.*, Tesis de Maestría, Universidad Central de Venezuela, Caracas, 1994.
17. J. Sedlár and J. Marchal, *Polym. Degrad. Stab.*, *19*, 251–262 (1987).
18. R. Nielsen, *Extraction and Quantitation of Polyolefin Additives*, Waters Chromatography Division, Millipore Corporation, 34 Maple Street, Milford, MA 01757, 1991.

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