*Journal of Chromatography*, 260 (1983) 507–512
Elsevier Science Publishers B.V., Amsterdam — Printed in the Netherlands

CHROM. 15,675

## Note

# Chromatographic determination of some hindered amine light stabilizers in polyolefins

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(First received December 13th, 1982; revised manuscript received January 7th, 1983)

Thin-layer (TLC) and high-performance liquid chromatographic (HPLC) methods are widely used in the identification and determination of various types of additives in plastics and rubbers. The recent introduction of a new class of polyolefin photostabilizers, known as hindered amine light stabilizers (HALS), and the increasing number of studies on their stabilization mechanism[1–6], require the development of suitable procedures for their identification and determination in polymers. Accordingly, a method for the extraction from polypropylene and the HPLC determination of one of these additives, Tinuvin 144, has been proposed[7].

This paper describes a TLC procedure for the identification of the photostabilizers Tinuvin 770, Hostavin TMN 20 and Tinuvin 144 in polyolefins. An HPLC method is also reported for the determination of Tinuvin 770 and Hostavin TMN 20, which have been proved of great interest in commercial polypropylene ligth stabilization.

The structures of two of the additives are shown in Fig. 1 (that of Hostavin TMN 20 is unknown).

## EXPERIMENTAL

### *HPLC apparatus*

A Varian Model 5000 liquid chromatograph, equipped with a 10-$\mu$l loop injection valve, a Varichrom variable-wavelength UV detector and a Varian Model 9176 recorder, was employed.

The analytical column was Hibar 250-4 (25 × 0.4 cm I.D.) packed with LiChrosorb-$NH_2$ (10 $\mu$m) (Merck, Darmstadt, G.F.R.); this stationary phase is known as an "amino" bonded phase on silica gel. A precolumn (2.0 × 0.4 cm I.D.) packed with LiChroprep-$NH_2$ (25–40 $\mu$m), Merck), was connected to the analytical column.

### *TLC apparatus*

Pre-coated TLC plates (20 × 20 cm) with a layer thickness of 0.25 mm of alumina $F_{254}$ type E (Merck) were used.

### *Reagents*

Tinuvin 770 and Tinuvin 144 were commercial products supplied by Ciba-

0021-9673/83/$03.00 

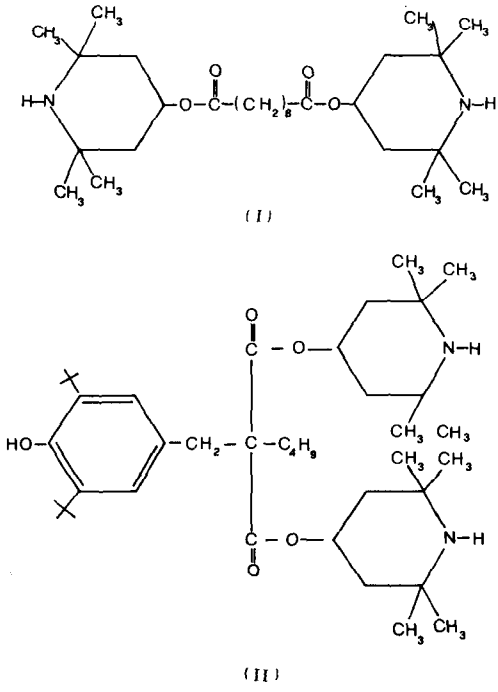

Fig. 1. Structures of (I) Tinuvin 770 and (II) Tinuvin 144.

Geigy (Basle, Switzerland); Hostavin TMN 20 was a commercial product supplied by Hoechst (Frankfurt, G.F.R.).

Chloroform, acetone, *n*-hexane, potassium iodide and soluble starch were analytical-reagent grade materials from Carlo Erba (Milan, Italy). Acetonitrile and water for HPLC and *tert.*-butyl hypochlorite were Baker products supplied by BHS Schilling (Milan, Italy).

*Extraction procedure*

A weighed polymer sample (10 g), in pellet or powder form, is extracted with chloroform in a Kumagawa-type extractor for 16 h. The extract is concentrated to about 20 ml under a flow of nitrogen, then 80 ml of acetone are added with stirring, to precipitate oligomers. These are filtered and carefully washed with hot acetone. The whole washing liquor is concentrated again to a few millilitres under a flow of nitrogen and finally brought to a volume of 10 ml with chloroform. This solution is ready for TLC and HPLC analysis.

*TLC analysis*

A portion (10 $\mu$l) of the above sample and equivalent amounts of standard solutions of the pure additives are spotted on the TLC plates, which are eluted in the ascending mode with *n*-hexane–isopropanol (88:12). After drying, the chromatograms are developed by chlorination with chlorine gas or *tert.*-butyl hypochlorite, then sprayed with potassium iodide–starch solution[8,9]. Yellow to orange spots appear

on a violet background, with average $R_F$ values of Hostavin TMN 20 0.45, Tinuvin 770 0.65 and Tinuvin 144 0.75, so that the identification of an unknown additive can be achieved.

*HPLC analysis*

A 10-$\mu$l volume of the sample solution and equivalent volumes of suitable standard solutions are injected into the chromatograph by means of the loop injection valve. The mobile phase is acetonitrile–water (99.5:0.5) with isocratic elution at a

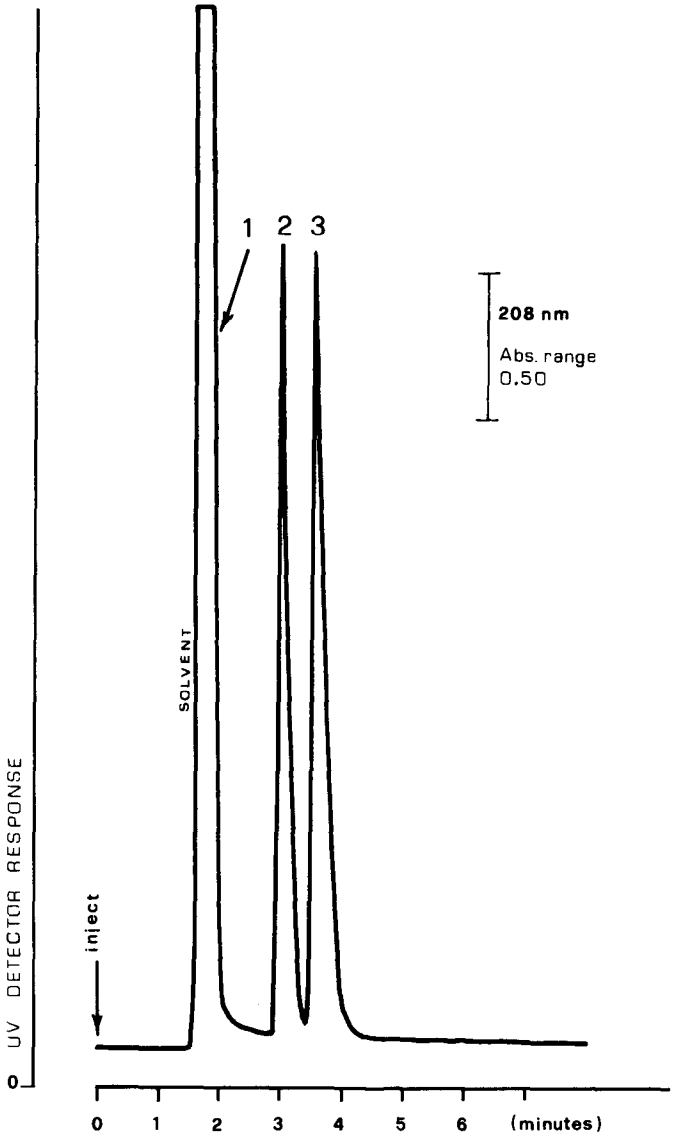


Fig. 2. HPLC trace of a mixture of HALS in chloroform (0.2 g per 100 ml of each additive). Peaks: 1 = solvent; 2 = Tinuvin 770; 3 = Hostavin TMN 20; Tinuvin 144 is eluted with the solvent.

flow-rate of 2 ml/min. The Varichrom UV detector is set at 208 nm, with an absorbance sensitivity range at 0,5. The signal from detector is recorded by a strip-chart recorder at a chart speed of 1 cm/min, for a preliminary qualitative test, and then at 10 cm/min for the quantitative determination.

The retention times of Tinuvin 770 and Hostavin TMN 20 are 3.0 and 3.6 min, respectively (Fig. 2).

The complete elution of both additives is achieved in only 5 min. Quantitative evaluation of each additive is effected by the external standard method, *i.e.*, by comparison of peak areas obtained with the sample and the standard solutions, using average results from duplicate injections.

## RESULTS AND DISCUSSION

Under the above conditions, the HPLC peaks of Tinuvin 770 and Hostavin TMN 20 are symmetrical and well resolved; further, their retention times are reproducible, thus allowing qualitative information to be obtained from the chromatogram. Tinuvin 144, on the other hand, is eluted with the solvent front and therefore cannot be evaluated by this method.

The composition of the mobile phase (volume ratio acetonitrile:water = 99.5:0.5) was found to be important as shown in Fig. 3B. When the proportion of water is slightly increased (to give a ratio of 98:2, Fig. 3C), the peaks become very symmetrical, but the retention times are considerably reduced and approach each other as well as the solvent front, with possible interferences. On the other hand, when the proportion of water is decreased to give a ratio of 99.9:0.1, (Fig. 3A), the retention times increase and a strong tailing effect is produced, affecting the resolution and quantitative evaluations.

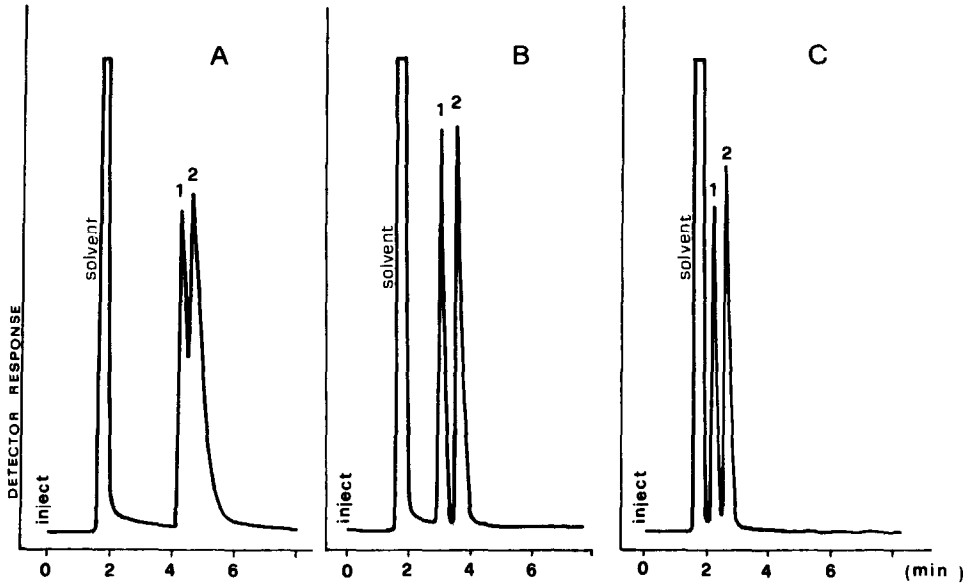


Fig. 3. HPLC trace of a mixture of (1) Tinuvin 770 and (2) Hostavin TMN 20 in chloroform, showing the effect of different mobile phase composition. Acetonitrile–water: A, 99.9:0.1; B, 99.5:0.5; C, 98:2.

TABLE I

RECOVERY TESTS ON POLYPROPYLENE PELLETS BY THE HPLC METHOD

| *Sample* | *Additive* | *Additive in the sample by N analysis (%, w/w)* | *Additive in the extracted sample by N analysis (%, w/w)* | *Additive found in the sample by HPLC method (%, w/w)* | *Recovery (%)* |
|---|---|---|---|---|---|
| A | Tinuvin 770 | 0.210 | <0.043 | 0.202 | 96.2 |
| B | Hostavin TMN 20 | 0.228 | <0.035 | 0.218 | 95.6 |

*Accuracy*

The accuracy of the HPLC method is satisfactory, as shown by determinations of nitrogen content[10,11] either on pure additives (Tinuvin 770 and Hostavin TMN 20), and on polypropylene samples containing only one of them, at a concentration of 0.2%. Table I shows that the amounts of additive determined by the HPLC method are in good agreement with those evaluated by nitrogen analysis of polymer pellets.

Moreover, nitrogen analyses carried out on the extracted polymer showed that the extraction procedure is efficient (residual additives after extraction were not detected).

The oligomer precipitation during the extraction procedure causes no losses of additives, as we found that duplicate HPLC analyses of, *e.g.*, Tinuvin 770, performed without oligomer separation, gave results identical with those obtained by the standard procedure. Oligomer removal, however, is suggested as a useful step in order to lengthen the life of the column.

*Interferences*

Under the proposed HPLC conditions, the following commercial additives, some of which can be determined by other known chromatographic methods[12–15], do not interfere with Tinuvin 770 and Hostavin TMN 20 determinations: BHT, Irganox 1076, Irganox 1010, Irgafos 168, Ionox 330, Cyasorb UV 531, Tinuvin 120, Tinuvin 326, Tinuvin 327, fatty acids, fatty acid salts and fatty acid amides; all of these are eluted at or near to the solvent front.

Tinuvin 144 is eluted with the solvent front and therefore it cannot be evaluated by this HPLC method, even if detected and identified by the previously described TLC method.

*Sensitivity*

By setting the Varichrom UV detector absorbance range at 0.05, instead at the usual 0.5, a sensitivity of 20 ppm of each additive on a polypropylene sample is attained.

*Precision*

The repeatability of the HPLC method was evaluated on the basis of ten runs on the same polypropylene sample, containing Tinuvin 770 at a concentration of 0.2%. Satisfactory results were obtained, as shown by the following data:

Average value (%, w/w): $\bar{X} = 0.198$
Standard deviation (%, w/w): $s = 0.0019$
Relative standard deviation (%): $s/\bar{X} \cdot 100 = 0.97$
Confidence limits (95% probability) for a single analysis (%, w/w): $\pm$ 0.0043

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