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DETERMINATION OF POLYMERIC HINDERED-AMINE LIGHT STABILISERS IN PLASTICS BY PYROLYSIS-GAS CHROMATOGRAPHY

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SUMMARY

Pyrolysis-gas chromatography was used to determine the polymeric hindered-amine light stabilisers Tinuvin 622 and Chimassorb 944, which are used in various plastics, especially polyolefins. By performing pyrolysis-gas chromatography on two different stationary phases, it was possible to differentiate accurately between five commercial stabilisers of which two are of the polymeric type (mentioned above), and three have well-defined molecular masses (Tinuvin 144, Tinuvin 770 and Hostavin TM N 20). An extraction procedure, which allows a semi-quantitative determination of the polymeric stabilisers, is described.

INTRODUCTION

The use of hindered-amine light stabilisers (HALS) in plastics was first patented by the Sankyo Co. in 1967¹. Further development of these compounds was undertaken by Ciba-Geigy, and mention of the first commercial HALS —the bis(2,2,6,6-tetramethylene-4-piperidiny)sebacate, later known by the trade name Tinuvin 770— may be found in two papers published during 1973^{2,3}. This new class of compounds offered excellent protection for plastics against ultra-violet (UV) radiation⁴.

The mechanism whereby HALS stabilise polymers against the effects of light irradiation has formed the subject of a large number of publications⁵⁻¹³. Review articles, covering the literature on the photostabilisation mechanism with HALS, have also been published¹⁴⁻¹⁶.

A later development was the introduction of the polymeric-type HALS, which improve the long-term weathering characteristics of plastics.

A search for suitable methods for the identification and determination of HALS began shortly after they became commercially available. Nuclear magnetic resonance spectroscopy was used to determine a polymeric HALS, *viz.*, Tinuvin 622, but no attempt was made to differentiate between different types of HALS¹⁷. A thin-layer chromatographic method of identification for HALS with well-defined molecular masses has been published¹⁸. These HALS may be termed "monomeric"

in order to distinguish them from those having high molecular mass. Monomeric HALS have been determined by high-performance liquid chromatography^{18,19}. Recently, the determination of a polymeric HALS, Chimassorb 944, by UV spectroscopy, was described²⁰. However, no differentiation between different polymeric HALS was possible when using the latter method.

In this institute, pyrolysis-gas chromatography (Py-GC) is used for the identification of polymers on a routine basis²¹. Given the polymeric nature of the HALS, Py-GC was an obvious choice for the determination of these stabilisers.

This paper describes a method, based on Py-GC, which permits the identification and determination of the polymeric HALS Tinuvin 622 and Chimassorb 944. The method involves dissolution of the polyolefin, followed by precipitation and extraction with sulphuric acid as described by Freitag²⁰. The last step facilitates the separation of the cycloaliphatic nitrogen-containing HALS from other additives such as antioxidants, lubricants or other types of light stabilisers, some of which may interfere with the Py-GC identification.

During the course of the investigation it became clear that not only the polymeric, but also the monomeric HALS such as Tinuvin 144, Tinuvin 770 and Hostavin TM N 20, give characteristic pyrolysis patterns (pyrograms). By using two different stationary phases for the separation of the pyrolysis products, it is therefore possible to differentiate between all the aforementioned HALS.

EXPERIMENTAL

Materials

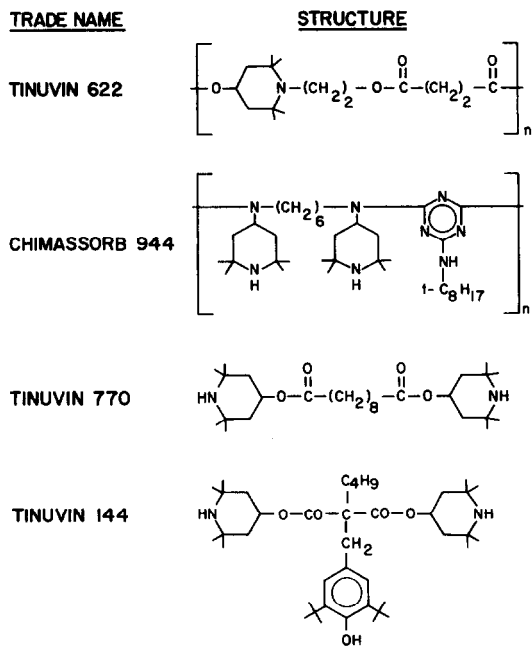
Tinuvin 144, Tinuvin 622, Tinuvin 770 and Chimassorb 944 are Ciba-Geigy products. Hostavin TM N 20 is produced by Hoechst. The chemical structures of the HALS are shown in Fig. 1. The diethyl ether, toluene, xylene, methylene chloride and sulphuric acid were of analytical grade. The polyolefins used were low-density polyethylene (LDPE) and polypropylene (PP), both supplied by BDH. The antioxidants Topanol OC and Irganox 1076 were obtained from I.C.I. and Ciba-Geigy, respectively.

Instrumentation

The Curie-point Py-GC instrumentation has been described previously²¹. Iron wire, which gives a temperature of 770°C in the radio-frequency coil of the pyrolyser, was used throughout this work. The solid light stabilisers were placed in the hook made from the flattened end of the iron wire, and the hook was then securely pinched together. The wire was weighed before and after the addition of the light stabilisers by using a microbalance readable to $\pm 1 \mu\text{g}$. The mass of solids pyrolysed varied between 200 and 500 μg . The recorder speed was 10 mm/min. The operating conditions of the gas chromatograph are given in Table I.

Preparation of LDPE and PP formulations

LDPE and PP were freed from any additives by Soxhlet extraction, first with diethyl ether (6 h) and then with methylene chloride (6 h). The polymers were solvent blended in the following manner: 16 g of LDPE or 6 g of PP were mixed with the HALS and the antioxidants, and then dissolved in 400 ml of boiling toluene. The



HOSTAVIN TM N 20

UNKNOWN

Fig. 1. The structures of the HALS determined in this study.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

	<i>Column packing</i>	
	<i>Porapak QS</i>	<i>10% Carbowax 20M on Chromosorb W (80-100 mesh)</i>
Column	Glass 1.6 m × 0.4 mm I.D.	Glass 2.1 m × 0.4 mm I.D.
Injector temp. (°C)	125	125
Detector temp. (°C)	250	200
Nitrogen carrier-gas flow-rate (ml/min)	60	30
Temperature programme	120-250°C at 12°C/min, hold at 250°C	70°C for 10 min, 70-180°C at 16°C/min, hold at 180°C

antioxidants used were Topanol OC and Irganox 1076. Finally, the toluene was evaporated and the polymer was dried in a vacuum oven at 55°C.

Method of extraction

To 150 ml of xylene contained in a 250-ml round-bottomed flask, 1.5 g of the

formulated polyolefin was added and dissolved by heating to reflux. The contents of the flask were poured into a beaker and allowed to cool. The beaker was placed in a ultrasonic bath for 10 min, and the contents then poured into a separating funnel to which 200 ml of 1 *N* sulphuric acid was added for extraction. The phases had separated well after standing for 1 h. The separated aqueous phase was filtered through a Whatman No. 1 filter, neutralised with 4 *N* sodium hydroxide and extracted three times with a total of 150 ml of methylene chloride. The solvent was evaporated, and the residue of HALS was weighed and identified by Py-GC.

RESULTS AND DISCUSSION

Identification of polymeric HALS

The characteristic pyrolysis peaks recorded on two different column packings, which permit the identification of HALS, are given in Table II.

TABLE II

RETENTION DATA FOR THE CHARACTERISTIC PYROLYSIS PEAKS USED FOR THE IDENTIFICATION OF HALS

The gas chromatographic conditions are given in Table I.

HALS	Retention time (min)	
	Porapak QS	Carbowax 20M
Tinuvin 622	9.04	1.65, 2.42, 28.5
Chimassorb 944	11.60	2.10
Tinuvin 144	26.55	14.32, 26.06
Tinuvin 770	—	12.37, 13.90
Hostavin TM N 20	—	18.92

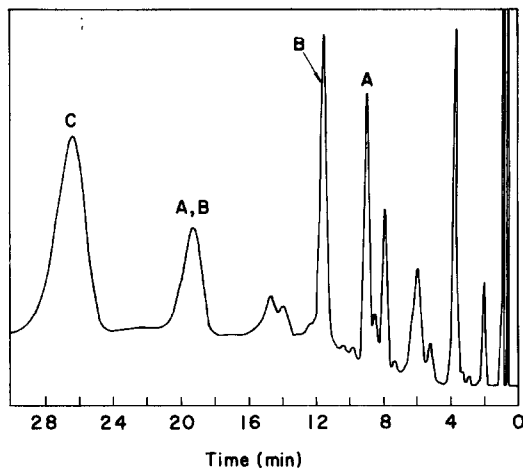


Fig. 2. Pyrogram of a mixture of equivalent quantities of three HALS on a Porapak QS column. The characteristic peaks are: A = Tinuvin 622, B = Chimassorb 944; C = Tinuvin 144.

The pyrogram recorded on a Porapak QS column of a mixture of Tinuvin 622, Chimassorb 944 and Tinuvin 144 is shown in Fig. 2. These three HALS may be differentiated easily by the characteristic peaks which they produce.

The pyrogram, also obtained with use of a Porapak QS column, of a mixture of HALS Tinuvin 144, Tinuvin 622 and Tinuvin 770 with Chimassorb 944 in equal quantities, is shown in Fig. 3. Tinuvin 770 on pyrolysis gives a strong peak at 19.25 min, but at the same retention time, the two polymeric HALS, Tinuvin 622 and Chimassorb 944 also give sizeable peaks (see Fig. 2). Although the presence of Tinuvin 770 in the mixture gives rise to a much enhanced peak at 19.25 min, if only small quantities of it are present, it is difficult to differentiate it from the two polymeric HALS.

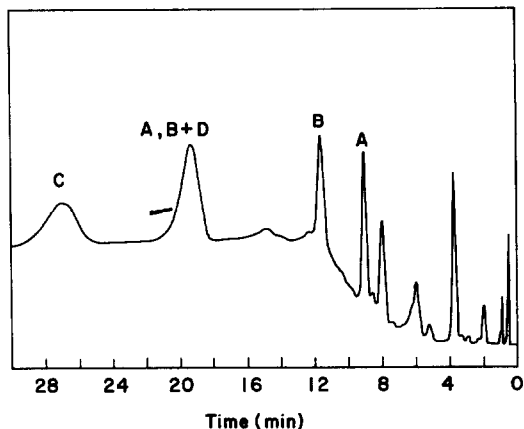


Fig. 3. Pyrogram of a mixture of equivalent quantities of each of four HALS on a Porapak QS column. The notations of characteristic peaks are: A, B and C as in Fig. 2; D originates from the pyrolysis of Tinuvin 770.

Hostavin TM N 20 gives no pyrolysis products detectable on the Porapak QS column.

By recording the pyrolysis products of the HALS mixture on a Carbowax 20M stationary phase, it was possible to differentiate between the five light stabilisers.

The pyrogram on Carbowax 20M of a mixture of five HALS is reproduced in Fig. 4. In this case Tinuvin 770 is very clearly identifiable by its characteristic pyrolysis peaks at 12.37 and 13.90 min, which are well separated from the peak at 14.32 min, derived from Tinuvin 144.

Hostavin TM N 20 gives a distinct pyrolysis peak at 18.92 min on the Carbowax 20M column. Under the pyrolysis conditions used in this study, Hostavin TM N 20 gives a low pyrolysis yield, hence it is more difficult to detect than the other HALS.

Determination of HALS in polyolefins

As the extraction of monomeric HALS has been described previously^{18,19}, the emphasis in this study is on the polymeric HALS. The method used involved the

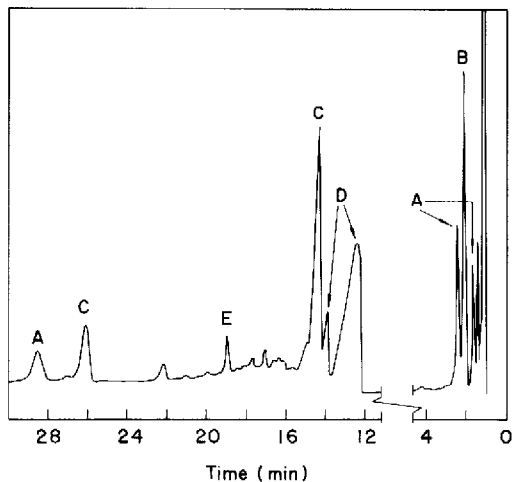


Fig. 4. Pyrogram of a mixture of five HALS on a Carbowax 20M stationary phase. The characteristic peaks are: A = Tinuvin 622; B = Chimassorb 944, C = Tinuvin 144, D = Tinuvin 770 and E = Hostavin TM N 20.

dissolution of the polymer, treatment with sulphuric acid, neutralisation, extraction of the HALS with methylene chloride, evaporation to dryness, weighing and pyrolysing for identification. This method was tested for the different polyolefins and different solvents used for the initial dissolution of the resin.

The polymers were solvent blended with the polymeric HALS (one HALS at a time) and two antioxidants, Topanol OC and Irganox 1076 (0.4% of each). The antioxidants were not present in the final residue after the evaporation of the methylene chloride. The results summarised in Table III are averages of at least seven determinations.

The recoveries are higher for the PP than for the LDPE blends, and better results were obtained when extracting Chimassorb 944 than in the trials with Tinuvin 622. Xylene was found to be a better solvent for this purpose than was toluene. The extraction procedure described may be considered semi-quantitative.

TABLE III

RECOVERY OF POLYMERIC HALS FROM POLYOLEFINS

<i>Polyolefin blended with HALS</i>	<i>Recovery (%)</i>	
	<i>Xylene</i>	<i>Toluene</i>
<i>LDPE</i>		
0.5% Chimassorb 944	94	72
0.5% Tinuvin 622	84	70
<i>PP</i>		
0.5% Chimassorb 944	92	88
0.5% Tinuvin 622	73	85

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