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DETERMINATION OF THE HINDERED AMINE ADDITIVE CHIMASSORB 944 IN POLYETHYLENE BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A chromatographic method was developed to determine the polymeric hindered amine additive Chimassorb™ 944 in polyethylene. Chimassorb 944 can be separated from other polyolefin additives, which are commonly used in different additive formulations, using a separation technique described as size-exclusion–non-aqueous reversed-phase chromatography. The stationary phase was Ultragel, a non-polar styrene–divinylbenzene copolymer and the mobile phase employed a step-gradient from toluene to 0.1 *M* piperidine in toluene. The additive was detected using a flame ionization detector. The method can be applied for the determination of Chimassorb 944 in polyethylene at concentrations ranging from 0.05% to 10%. There are no known interferences with this method.

INTRODUCTION

A selective method is needed to determine the UV/light stabilizer Chimassorb™ 944 polyolefins both for quality assurance and lot certification. The structure of Chimassorb 944 is shown in Fig. 1. Previously used methods for determining Chimassorb 944 involved the determination of the nitrogen content in the polymer by combustion or Kjeldahl methods[1], spectrophotometric measurement of the infrared absorbance of the triazine group[2], or measurement of the UV absorbance at 225 nm of the polymer extract[3]. Because the existing methods either lack accuracy or are subject to interferences from other additives, a new method is desired.

During the development of a liquid chromatographic method for Chimassorb 944, it was found that the additive adsorbed on columns containing silica based stationary phases, but that the additive could be eluted from polystyrene–divinylbenzene columns. Other additives were separated from the Chimassorb 944 under size-exclusion chromatography conditions and the Chimassorb 944 could be eluted from the column under non-aqueous reverse phase conditions employing a step gradient.

Since the additive absorbed only in the low UV region with an absorption maximum at 225 nm, UV detection was unsuitable because the mobile phase con-

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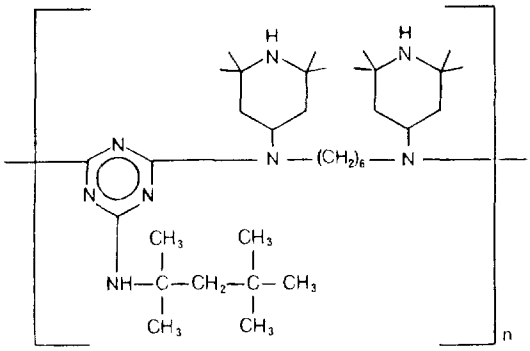

Fig. 1. Chemical Structure of Chimassorb 944.

taining toluene also absorbs in this region. The polyolefin pellets were extracted in hot decalin as reported by Schabron *et al.*[4], and the additive content was determined by high-performance liquid chromatography with flame ionization detection.

EXPERIMENTAL

Apparatus

The chromatograph consisted of two 6000A pumps, a WISP 710B autosampler, and a system controller Model 720 (Waters Assoc., Milford, MA, U.S.A.). The column used was an Ultraguard GPC 10^2–10^3 Å, 5 cm × 7.8 mm I.D. packed with 10-μm styrene–divinyl benzene copolymer (Analytical Sciences, Santa Clara, CA, U.S.A.). Elution was monitored with a Tracor Model 945 flame ionization detector for LC and a Hewlett-Packard Model 3390A recording integrator.

The sample preparation system consisted of a Lab-Line Pyro-Magnestir No. 1268 from VWR Scientific, an IEC centrifuge Model HN-II (International Equipment Company), a Welch Duo-seal Model 1402 vacuum pump (Sargent-Welch), a Buchi Model R rotary evaporator equipped with a water bath (Brinkmann Instruments), and a sample filtering apparatus as described by Schabron *et al.*[4]. For this, a 20–30 μm stainless-steel solvent reservoir filter was connected to a 5-cm length of 3 mm I.D. PTFE tubing. The other end of the PTFE tubing was connected to a 1.5-in, blunt 16-gauge Luer-Lock needle with a 1/16-in. stainless-steel nut and ferrule at the end of the needle. The needle was connected to a Hamilton No. 1010W gastight 10-ml syringe with a PTFE plunger.

Reagents

Toluene and chloroform were Baker AR grade. Piperidine (98% purity) was obtained from Aldrich. Irganox 1010, Irganox 1076, and Chimassorb 944 were obtained from Ciba-Geigy. Ethyl 330 was obtained from Ethyl Corporation. Ultranox 624 was obtained from Borg-Warner. Goodrite 3114 was obtained from Goodrich. Triallylcyanurate and dilauryl-3,3′-thiodipropionate (DLTDP) were obtained from American Cyanamid. Lupersol 130 was obtained from Lubrizol. Butylated hydroxylated toluene (BHT) was obtained from Uniroyal. High purity decalin was obtained

from American Scientific. Mobile phase solvents were filtered through a 0.45-μm PTFE filter prior to use. All additives and reagents were used without further purification.

Procedure

Standard solutions of Chimassorb 944 at 0.2, 0.4, 0.6, 0.8, and 1.0 mg/ml concentration in toluene were prepared. These solutions were used for calibration and to establish linearity.

A 0.5–2.0 g portion of polyethylene was weighed into a 200-ml tall Berzelius beaker. A stirring bar was added and 50 ml of decalin was pipetted into the beaker. The beaker was covered with a watch glass and the mixture was heated, with stirring, to 120°C on a hot plate for about 30 min or until dissolution was complete. The beaker was then transferred to a cold stirrer and cooled, with continual stirring, to room temperature to precipitate the polyethylene.

Depending on the estimated Chimassorb 944 concentration in polyethylene, the decalin solution was prepared for analysis by two different methods. (i) For polyethylene master blends that contained more than 0.5% Chimassorb 944 the solution was filtered using the porous metal filter described above. About 4 ml were collected and dispensed into an autosampler vial. (ii) For polyethylene commercial blends that contained less than 0.5% Chimassorb 944 it was necessary to concentrate the extract. About 35 ml of the decalin solution were decanted into a 50-ml centrifuge tube. The solution was centrifuged for 10 min, then a 25-ml aliquot was transferred to a 50-ml round bottomed flask and the solution was evaporated to dryness at 50°C under vacuum using a rotary evaporator. The residue was dissolved in 5 ml of toluene, then the solution was filtered through a 0.45-μm disposable PTFE syringe filter into an autosampler vial.

The flame ionization detector fuel gases were set at the following rates. Detector: hydrogen at 140 ml/min; air at 0.4 ml/min. Cleaning flame: hydrogen at 500 ml/min; oxygen at 200 ml/min. The block temperature controller was set to produce the following thermocouple readings: No. 1, 117°C; No. 2, 130°C; No. 3, 140°C; and No. 4, 124°C. (For location of the thermocouples, see ref. 5.) At these settings, a steady baseline was obtained.

The mobile phase consisted of solvent A (toluene) and solvent B (0.1 *M* piperidine in toluene). The flow-rate was set at 1 ml/min and the gradient table was as follows: 100% solvent A for 2 min, 100% solvent B for 8 min, and 100% solvent A for 5 min. The total run time was 15 min and the mobile phase step gradient was started at the time of injection. Triplicate injections (25–50 μl) of each of the standards and the sample solutions were made. The retention volume for Chimassorb 944 was about 7.0 ml. A typical chromatogram is shown in Fig. 2. The Chimassorb 944 content for each sample was calculated from the peak areas for standards and sample.

RESULTS AND DISCUSSION

Preliminary studies

Chimassorb 944 is a polymeric hindered amine with a molecular weight greater than 2500. The structure of Chimassorb 944 is shown in Fig. 1. Attempts to separate

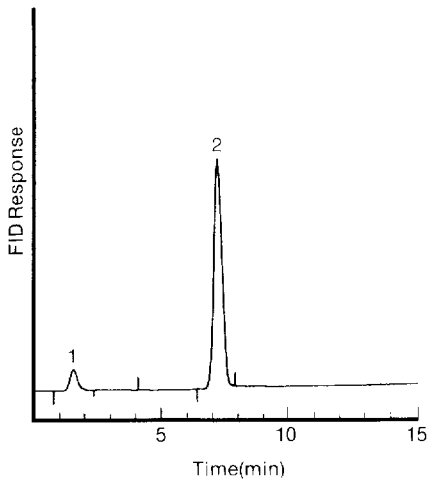

Fig. 2. Chromatogram of polyethylene extract. 1 = Polyethylene oligomers plus additives; 2 = Chimassorb 944 (22 μg). Injection volume 25 μl, integrator–recorder attenuation 2[6]. Other conditions reported in the Experimental section.

and determine this additive using a variety of columns packed with a silica based stationary phase produced unsatisfactory results. Chimassorb 944 adsorbs strongly to silica and to bonded silica packings due to the interaction between the silanol groups present on the packing and the multiple amine functional groups in the Chimassorb 944 structure. The addition of ammonia or triethylamine to the mobile phase did not sseem to help in eluting the additive from the columns.

Attention was focused on the neutral polymeric packing polystyrene–divinylbenzene to perform the separation. A Waters 100 A μStyragel GPC column (30 cm $\times$ 7.8 mm) was tested with three mobile phase solvents. Methylene chloride and toluene did not elute Chimassorb 944 from the μStyragel column. Tetrahydrofuran (THF) seemed to elute Chimassorb 944, but the peak was broad and tailed excessively and the peak area increased during successive injections. The elution behaviour of Chimassorb 944 from μStyragel with THF can be attributed to hydrogen bonding between the analyte and the mobile phase. Piperidine was added to the mobile phase to compete with Chimassorb 944 and to minimize adsorption. A solution of 0.05 *M* piperidine in THF was used as the mobile phase at a flow-rate of 1 ml/min. A 10-μl sample of 1 mg/ml Chimassorb 944 was injected and a regularly shaped peak eluted at 5.6 min with minimal tailing. To investigate the effect of piperidine further, a solution of 0.05 *M* piperidine in toluene was used as the mobile phase and again a well-shaped peak at 5.6 min eluted. Since toluene does not elute Chimassorb 944 from a μStyragel column and elution occurred only when piperidine was added, toluene was chosen rather than THF for the gradient elution to minimize peak broadening and to have better control of the retention time for other additives. Methylene chloride was not investigated further because we previously experienced corrosion of the heating block of the flame ionization detector[6].

The effect of the concentration of piperidine in toluene on the elution of Chi-

TABLE I

EFFECT OF PIPERIDINE CONCENTRATION IN TOLUENE ON THE ELUTION OF CHIMASSORB 944 AT A FLOW-RATE OF 1 ml/min

Piperidine concn. (moles/l)	*μStyragel 100 Å**			*Ultragel 100–1000 Å***		
	Retention time (min)	*Normalized area****	*Peak width (min)*	*Retention time (min)*	*Normalized area****	*Peak width (min)*
0.0	No elution	0	–	No elution	0	–
0.005	No elution	0	–	1.3	0.86	0.38
0.010	No elution	0	–	1.3	0.95	0.33
0.025	6.8	0.23	2.7	1.2	0.97	0.32
0.050	5.6	0.79	0.79	1.2	1.02	0.32
0.100	5.3	1.00	0.55	1.2	1.00	0.32

* Column dimensions 30 cm × 7.8 mm I.D.
** Column dimensions 5 cm × 7.8 mm I.D.
*** Normalization based on the area obtained at 0.1 *M* piperidine in toluene.

massorb 944 was studied. μStyragel 100 Å (30 cm × 7.8 mm) and Ultragel 100–1000 Å (5 cm × 7.8 mm) columns were evaluated. Concentrations of piperidine at 0.005, 0.010, 0.025, 0.05, and 0.10 *M* were prepared in toluene. Each of these solutions was tested as a mobile phase at an isocratic flow-rate of 1 ml/min with 50 μl of 1 mg/ml of Chimassorb 944 injected on each column. The data obtained are listed in Table I. The concentration of piperidine required to elute Chimassorb 944 appears to be related to the size of the column. For the 30-cm column packed with μStyragel, the peak area and the peak width started to level off at 0.10 *M* piperidine, while for the 5-cm column packed with Ultragel, the peak area and the peak width started to level off at 0.025 *M* piperidine. To minimize the adsorption effect and to shorten the analysis time, the 5-cm column was selected and the mobile phase was a step gradient from toluene to 0.1 *M* piperidine in toluene. First, toluene was used to elute polyethylene oligomers and any other additives that might be present, then piperidine–toluene was used to elute Chimassorb 944.

TABLE II

RESULTS OF DUPLICATE ANALYSES OF FIVE POLYETHYLENE SAMPLES

Sample	*Sample weight (g)*	*Chimassorb 944 (wt. %)*
Orange	1.0060	5.81
Orange	1.0175	5.89
White	1.0063	4.43
White	1.0194	4.39
Green	0.5033	8.73
Green	0.5168	8.73
Blue	0.5033	8.01
Blue	0.5142	8.18
Yellow	1.0176	5.22
Yellow	1.0288	5.45

TABLE III

RECOVERIES OF CHIMASSORB 944 FROM 2.0-g PORTIONS OF ADDITIVE-FREE POLYMER

Amount added (mg)	*Amount found (mg)*	*Percent recovered*
50.0	51.3	103
50.0	49.6	99
25.0	25.5	102
25.0	25.6	102
10.0	10.2	102
10.0	10.0	100
1.00	0.97	97*
1.00	0.97	97*

* Extract was centrifuged, evaporated, and residue redissolved in toluene as described in Experimental section.

Precision and accuracy

The average peak area for eleven replicate injections of a standard solution containing Chimassorb 944 at a concentration of 0.2 mg/ml was 2 552 600 counts with a relative standard deviation of 1.36%.

Several polyethylene samples containing varying amounts of Chimassorb 944 were analyzed in duplicate. The results are listed in Table II, demonstrating good precision with real samples. Six replicate analyses of a polyethylene sample containing 0.125% Chimassorb 944 were performed. The average experimental value was 0.123% and the results showed a relative standard deviation of 3.02%.

Spiking experiments were performed with a polyethylene sample initially containing no Chimassorb 944. The experiments were performed by dissolving 2 g of polyethylene in decalin containing known amounts of the additive. The results of duplicate spiking experiments are listed in Table III. The results demonstrate good recoveries at levels corresponding to 0.05, 0.5, 1.25, and 2.5% Chimassorb 944 in polyethylene indicating Chimassorb 944 does not adsorb to the precipitated polyethylene.

Linearity and detection limit

The linearity of the response for Chimassorb 944 was checked over the range 0–1.0 mg/ml. The correlation coefficient was 0.9994. The limit of detection for the method as described, with a signal-to-noise ratio of 2, is 0.02 mg/ml. This corresponds to 0.05% Chimassorb 944 in polyethylene. The sensitivity can be enhanced ten times using the centrifugation and concentration technique described in the Experimental Section.

Filtration techniques

Different filters were evaluated to separate the polyethylene precipitate from the extract. The porous stainless-steel filter described proved practical for filtration of small volumes (5 ml) but plugging occurred with larger volumes (35 ml). A glass microfiber filter, Whatman GF/D was tried, and the filtration proceeded smoothly, but Chimassorb 944 was partially adsorbed. The adsorption effect was confirmed by

TABLE IV

ADDITIVES SOLUTION

Additive	*Concentration (mg/ml)*
DLTDP	0.534
Irganox 1010	0.567
Irganox 1076	0.586
BHT	0.522
Triallylcyanurate	0.522
Goodrite 3114	0.513
Lupersol 130	0.512
Ultranox 624	0.503
Ethyl 330	0.502
Chimassorb 944	0.502

filtering about 75 ml of decalin containing 0.02 mg/ml of the additive. Analysis of the filtrate indicated only a 78–81% recovery. Attempts to use Whatman No. 1 filter paper were abandoned due to slow filtration and low recovery (85–90%). When a 0.45-μm PTFE filter was used, quantitative recovery was obtained but the filtration was too slow, especially if gel type polyethylene precipitate was present. Finally, it was decided to centrifuge the decalin solution to separate the bulk of the polyethylene precipitate and the extract was evaporated and treated as described in the Experimental section. The procedure was convenient and no loss of additive was observed.

Separation technique

Traditionally, neutral polystyrene–divinylbenzene gels are used for size exclusion chromatography and methylene chloride, tetrahydrofuran, and toluene are used as mobile phases[7,8]. These mobile phases are often chosen to reduce or eliminate the interaction of the solute with the stationary phase. The elution of the additives listed in Table IV, except for Chimassorb 944, was of a size exclusion type. The additives

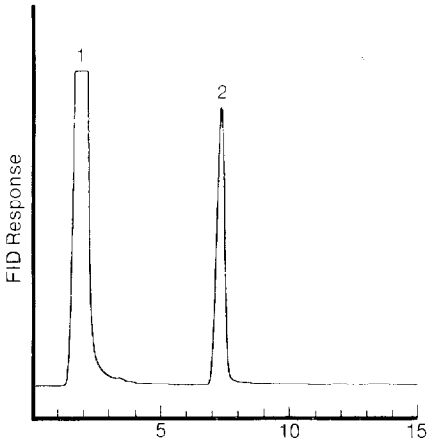

Fig. 3. Chromatogram of a solution containing ten additives (see Table IV). 1 = Additives, 2 = Chimassorb 944 (25 μg). Injection volume 50 μl, integrator–recorder attenuation 2°. Other conditions reported in the Experimental section.

were eluted with toluene and the retention volumes were within the total permeation volume, 1.8 ml. The polymeric hindered amine, Chimassorb 944, was adsorbed by the polystyrene–divinylbenzene packing and was eluted from the column following addition of piperidine to the mobile phase. The separation is illustrated in Fig. 3.

CONCLUSION

We have developed a chromatographic method for the determination of Chimassorb 944 in polyethylene with a typical relative standard deviation of 3% in the range of 0.1%. Also, we demonstrated that Chimassorb 944 can be separated from several polyolefin additives, which are commonly used in different additive formulations, using a combination of size-exclusion and non-aqueous reversed-phase chromatography.

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