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Determination of Antioxidants in Polypropylene by Liquid Chromatography

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Synopsis

Polyolefins, such as polypropylene, are subject to thermal and oxidative degradation and are not used in practical applications unless protected by several antioxidants. Liquid exclusion (LEC) and liquid adsorption (LAC) chromatography have been used to determine the antioxidants in commercial polypropylenes and molded parts. Although a LEC analysis takes as long as 3 hr, LAC separations can be obtained in less than 15 min. Prior to the chromatographic measurements, the antioxidants were extracted from the talc-filled polypropylene using tetrahydrofuran (THF) and methylene chloride (CH_2Cl_2) for the LEC and LAC separations, respectively. Room-temperature extraction of the additives as a function of time showed that 24 hr was sufficient for THF. A comparison of the LEC chromatogram for a freshly molded part to that for a part which was heat treated showed not only the depletion of certain antloxidants but also showed that the antioxidant distearyl 3,3′-thiodipropionate (DSTDP) thermally decomposed to give stearyl propionate. Mass spectrometry was used to confirm the identity of the additives in the polypropylene without extraction. The "life" af several polypropylenes was also measured by thermogravimetric analysis and compared to the concentration of DSTDP.

INTRODUCTION

Polyolefins are subject to thermal and oxidative degradation and cannot be used in practical applications, such as automobile parts, unless they are protected with efficient antioxidants. Isotactic polypropylene is especially sensitive to oxygen and ozone. As a protection against degradation, mixtures of additives consisting of one or more antioxidants and a synergist are used. The antioxidants act by breaking the oxidation reaction sequence, eq. (1), converting the peroxide formed in oxidation to a hydroperoxide, eq. (2):

$$R\cdot + O_2 \rightarrow RO_2\cdot \quad (1)$$

$$RO_2\cdot + R'H \rightarrow RO_2H + R'\cdot \quad (2)$$

where R· is the polymer chain and R′H is the antioxidant. The synergists react with the hydroperoxide formed to remove oxygen from the polymer, eq. (3):

$$RO_2H + R_2''S \rightarrow RH + \text{other products} \quad (3)$$

where R_2''S is the synergist. The practical applicability of a polymer is determined by the amount and the chemical structure of each component in the stabilizer mixture.

The analytical procedures used in the determination of polymer additives and the problems associated with these analyses have been reviewed by Wheeler[1] and Crompton.[2] The difficulties in identifying and determining antioxidants and synergists arise from three factors:[1] (1) the high reactivity and low stability of antioxidants; (2) the low concentration (0.1% to 1.0%) at which they are present; (3) the relatively insoluble polymer matrix. The second and third factors generally require a separation of the additives from the polymer, while the first and second require careful handling of the extracts if quantitative results are to be obtained. In addition, the wide variety of commercially available antioxidants and synergists further complicate the interpretation of the data.

Howard[3] has shown how useful liquid exclusion chromatography can be for polymer additive systems, particularly when determining the commercial source of polypropylene. Although Coupek et al.[4] have also reported results with this technique, their work was limited to synthetic mixtures of additives. Both Howard and Coupek used nine 4-ft column sets, which were packed with styrene–divinylbenzene gel and tetrahydrofuran (THF) as the eluent. In this paper, the primary results are presented from liquid exclusion and liquid adsorption chromatography of additives in commercial polypropylenes. Results are also presented from mass spectrometry (for qualitative identification) and thermogravimetric analysis (as a performance test).

Since the type of liquid exclusion chromatography used in this study and by previous workers is best known by the name gel permeation chromatography, the acronym GPC is used in the remainder of the paper.

EXPERIMENTAL

Additives and Polypropylene Materials

The additives that were used as qualitative and quantitative standards in this work were purchased from Chem Service Inc., Westchester, Pa., as part of a standard kit of antioxidants and UV stabilizers. Commercial polypropylene samples from four suppliers (labeled 1 through 4) and molded parts were used in this study.

Gel Permeation Chromatography (GPC)

The GPC instrument, Waters Associates Model 200, was equipped with an automatic injector and a differential refractometer detector. The flow rate was set at 1.0 ml/min. Column set C, which consists of four Styragel columns with porosities of 250, 100, 60, and 60 Å, was calibrated by determining the elution volumes for standards of known molecular weight.

Samples were prepared for GPC analysis as follows: To 4 g of 8-mesh polypropylene pellets (approximately 2-mm cubes, weighed to the nearest 0.001 g) contained in a 50-ml screw-capped, darkened glass vial was added 20.0 ml tetrahydrofuran (THF). The liquid level was marked, and the vial was placed on an Eberbach shaker table and shaken for 24 hr at room temperature. The vial was then removed, and the contents were allowed to settle for approxi-

mately 30 min. Evaporation losses were replaced by adding THF to the mark. A known volume (2-ml injection loop) of the supernatant liquid, which contains the extracted antioxidants and synergists, was then injected into the GPC. Six to eight samples could be loaded at one time and run overnight using the automatic sample injector.

Liquid Adsorption Chromatography (LAC)

A du Pont liquid chromatograph Model 830 with a 25-cm column packed with Zorbax-SIL was used for separation of the antioxidants. Separations were made using either a constant (isocratic) or varying (gradient elution) solvent composition at a flow rate of 1 ml/min. Isocratic measurements were made using hexane with 0.2% methylene chloride (CH_2Cl_2) and hexane with 25% CH_2Cl_2. For the gradient elution measurements, the eluent was varied from 0.9% to 70% CH_2Cl_2 in hexane at a rate of 10% per minute. Ultraviolet (UV) and refractive index (RI) detectors were used to monitor the separations. Samples were prepared as indicated for GPC except that CH_2Cl_2 was used to extract the additives.

Mass Spectrometry (MS)

The mass spectrometer used was manufactured by Associated Electrical Industries, Model MS-30. The samples of polypropylene, in pellet form as supplied by the manufacturer, were placed directly in the mass spectrometer by means of the solids probe and slowly heated to vaporize selectively the various components.[5] An increase in the ion current indicated when a component was evolved and thus signaled when to scan the mass spectrum. The mass spectra obtained were compared to mass spectra of known additives which were analyzed similarly. Positive identification could thus be obtained.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis tests were made using a Perkin-Elmer Model TGS-1. In this test,[6] the sample is continuously weighed in an oxygen environment at 190°C to determine the time to sudden decomposition. This time is a measure of the life or oxidation resistance of the material.

Separation of Additives from the Polymer

Because of the low concentration of additives, it was necessary to separate them from the polymer to get quantitative results. Wheeler[1] has published a summary of methods for the quantitative extraction of antioxidants from polymers prior to analysis. The British Standard method[7] has been favored for dealing with polyolefin polymers. It involves dissolving the polymer in boiling toluene under reflux, followed by precipitation of the high molecular weight fraction with ethanol. The filtrate contains the additives plus a quantity of low molecular weight polymer wax. We have had some difficulty with this technique, however, because of additive decomposition under the rigorous conditions of extraction. In addition, this method requires constant operator attention.

Spell and Eddy[8] have found that the required extraction time at room temperature varies linearly with polymer density and particle size, and also with

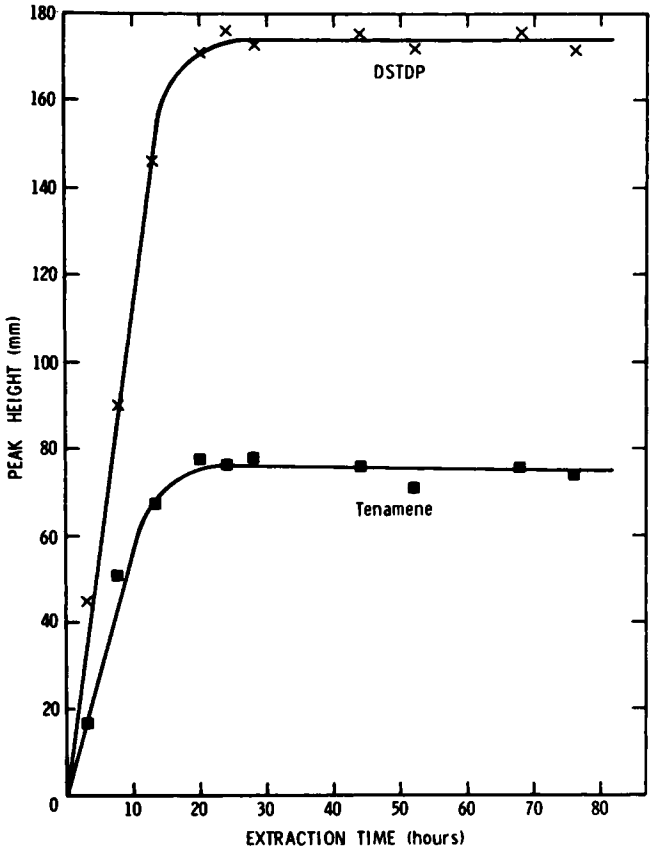

Fig. 1. Extraction of additives from pellets of talc-filled polypropylene with THF.

the nature of the extraction solvent. They concluded that, for polyethylene powdered to 50 mesh, only 3 hr of shaking with chloroform is sufficient to remove 98% of the common additives. Although we have confirmed the feasibility of room temperature extraction for talc-filled polypropylene, we have found that 72 hr is required for the chloroform extraction of the additives from this material. The most efficient extraction solvent found was THF. Figure 1 illustrates the progress of the extraction of two additives, DSTDP and Tenamene, from 8-mesh pellets of talc-filled polypropylene using THF. From this figure, it appears that 24 hr is sufficient to extract either additive completely. THF was particularly convenient since it is the eluent we used in the GPC instrument.

The same procedure was used for CH_2Cl_2 which is used for the extractions for LAC. With CH_2Cl_2, however, only 50% of the additives were extracted in 24 hr which was sufficient for the LAC analyses.

RESULTS AND DISCUSSION

GPC Analysis

Once the extraction was accomplished, the samples were ready for GPC analysis. Column set C, which was used in this work, has been designed for samples with molecular weights of less than 1000. In addition to the usual

TABLE I
GPC Elution Volumes of Selected Additives for Isotactic Polypropylene

Trade name	Chemical name	MW	V_e[a]
Irganox 1010	tetrakis[methylene-3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate]methane	1168	18.88
Ionox 330	1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene	775	19.50
Topanol CA	1,1,3-tris(5-*t*-butyl-4-hydroxy-2-methylphenyl)-butane	544	20.65
Santowhite Powder	4,4′-butylidenebis(3-methyl-6-*t*-butylphenol)	382	21.75
AO 2246	2,2′-methylenebis(4-methyl-6-*t*-butylphenol)	340	23.00
Santovar A	2,5-di-*t*-amylhydroquinone	250	23.75
Tenamene	2,6-di-*t*-butyl-4-methylphenol	220	24.87
Agerlite Alba	hydroquinone monobenzyl ether	200	25.19
	4-butylcatechol	166	26.60
Ansul HA	hydroquinone monomethyl ether	124	27.06
DSTDP	distearyl 3,3′-thiodipropionate	682	19.83
DLTDP	dilauryl 3,3′-thiodipropionate	514	20.69

[a] V_e is the peak elution volume in counts. One count = 5 ml.

calibration curve (see experimental section), a special calibration curve was prepared using common antioxidants and synergists of known molecular weight as standards. Table I contains the chemical names and commercial trade names of these materials along with their molecular weights and peak elution volumes.

Analysis of Commercial Materials

The column set used is quite suitable for the analysis of mixtures of low molecular weight. Figure 2 shows the GPC chromatograms obtained on the additives extracted with THF from six samples of polypropylene from four different suppliers. There are significant differences in the additives systems that can be used as a "fingerprint" for identification of the source of supply. In addition, the components can be at least tentatively identified by comparing their retention volumes to a calibration curve. For example, both samples obtained from source 1 (A and B in Fig. 2) have the same three additives, identified by GPC and later confirmed by mass spectroscopy (MS) as DSTDP, Topanol CA, and Tenamene. However, the chromatograms show that these additives are present in different relative amounts. The two samples obtained from source 3 (D and E in Fig. 2) were significantly different in their overall GPC fingerprints. The type 1 sample contained an additive at 19.8 counts (DSTDP) which was not detected in the type 2 sample. In addition, there were slight differences in the ratio of the amounts of the additives which elute between 24 and 26 counts.

The identification of the additives in source 1 polypropylene, which was determined by MS, is shown in Table II. A GPC chromatogram of the THF extract from this sample is shown in Figure 3 along with a reference chromatogram containing the same additives in the indicated amounts. Again, the peak elution volumes (indicated by the vertical lines on the figure) can be used as a qualitative identification of the antioxidants. However, MS gives a positive identification and should be used on samples in which the antioxidants are com-

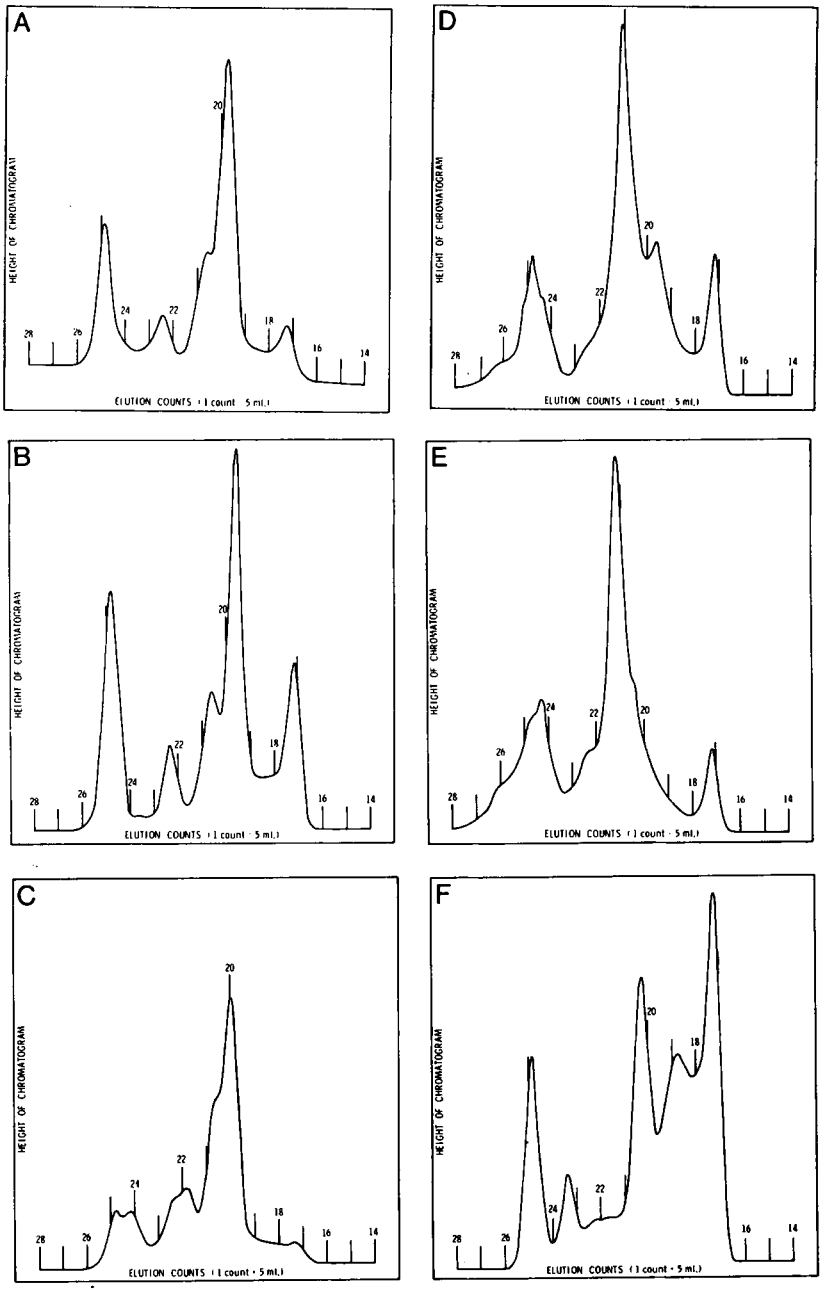

Fig. 2. GPC chromatogram of additives from commercial polypropylene.

	Source	Identification	Attenuation
A	1	lot 1	1×
B	1	lot 32	1×
C	2	—	2×
D	3	type 1	1×
E	3	type 2	2×
F	4	—	1×

pletely unknown. The GPC chromatogram is useful in the routine screening of samples to determine whether the supplier has changed his formulation, and in the determination of the concentration of the antioxidants. Quantitative results were obtained from linear calibration curves of peak height versus weight

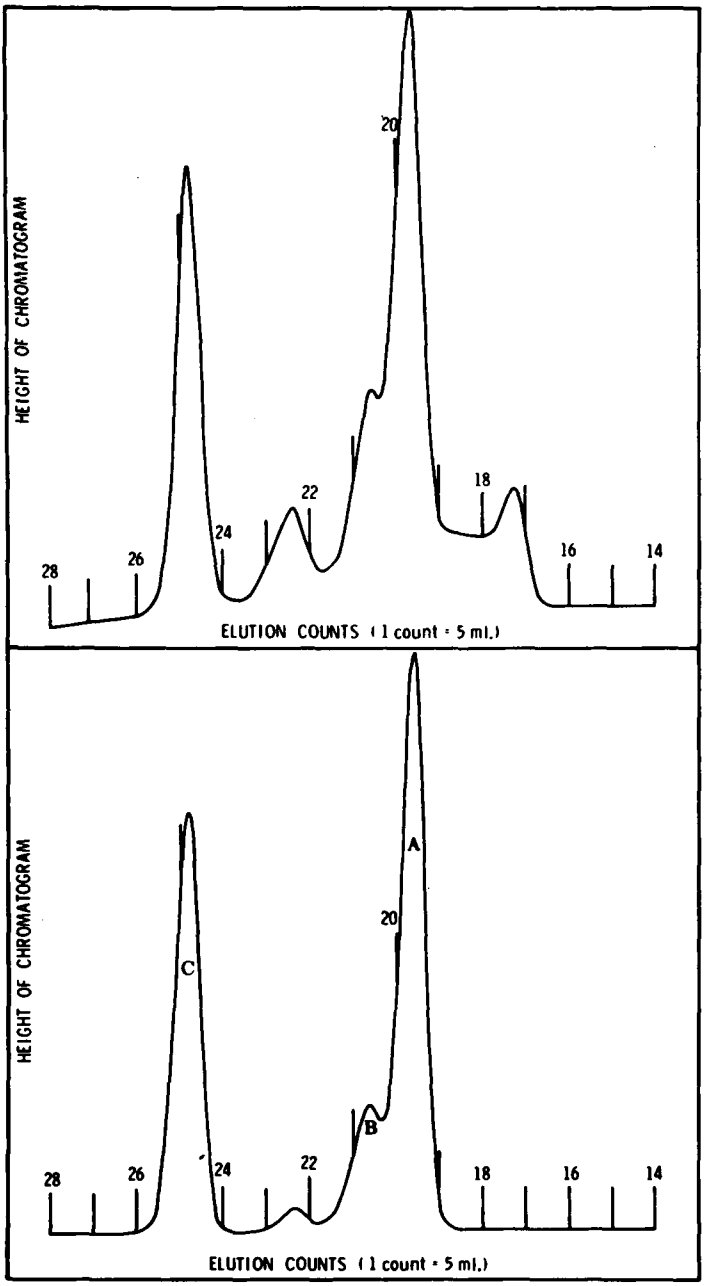

Fig. 3. Comparison of GPC chromatograms of additives in source 1 polypropylene to standard additive mixture. Upper curve: THF extract from source 1 polypropylene; lower curve: standard additive mixture containing 10.72 mg DSTDP (A), 1.48 mg Topanol CA (B), and 4.45 mg Tenamene (C).

TABLE II
Results of Mass-Spectrometric Identification of Additives in Talc-Filled Polypropylene

Source	Additives[a]
1 (lot 1)	Tenamene, Topanol CA, DSTDP[b]
3	Tenamene, DSTDP
2	Santowhite Powder, unknown (MW-612)
4	Tenamene, possibly two others

[a] Chemical names of the additives are given in Table I.
[b] DSTDP contained 66% stearyl groups, 34% cetyl groups.

of antioxidant. The calibration curves were obtained by injecting the same volume (2-ml injection loop) of the standard solutions of antioxidants and synergists into the GPC instrument under the same conditions as those used for the extracts. Excellent quantitative results were obtained even though some interference is encountered from the extracted low molecular weight polypropylene which elutes between counts 17 and 18.

Analysis of Molded Parts

Figure 4 shows a comparison of the GPC chromatograms obtained on the additives extracted with THF from a new molded part and from one which has been subjected to an environment simulating that under the hood in an automobile. Since the additives are consumed in the prevention of polymer degradation, the concentrations of the additives are much lower in the "used" sample. In fact, the antioxidants Topanol CA and Tenamene were not detectable in the GPC chromatogram. From this chromatogram, one can also calculate a detection limit for DSTDP of 0.02%. (This detection limit could be improved by using a sample larger than 4 g.)

The presence of the large peak at 22.7 counts (MW $\cong$ 330) in the lower chromatogram of Figure 4 is also significant. The products of the reaction of synergists with hydroperoxide to remove oxygen from the polymer, eq. (3), have never been completely characterized. The photochemical decomposition of DLTDP has been shown to produce the corresponding ester, lauryl propionate, along with lesser amounts of long-chain hydrocarbons.[9] The corresponding ester of DSTP is stearyl propionate which has a molecular weight of 326. Therefore, from the GPC chromatograms, it appears that the reaction product stearyl propionate is the same in both the synergistic reaction and the photochemical decomposition. Thus, eq. (3) can be rewritten as

$$RO_2H + (C_{18}H_{37}\text{—}O\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_2\text{—}CH_2)_2S \rightarrow RH + SO_2 + 2C_{18}H_{37}\text{—}O\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_2\text{—}CH_3. \quad (4)$$

Table III gives the results obtained from seven lots taken from one batch of source 1 polypropylene and also for two molded parts which had been made from this batch and subjected to ozone and heated environments. Repeat analyses on the same sample extract yielded a relative standard deviation of 5%. These results are excellent considering that the total additives comprise only 0.4% of the total sample weight (including filler), which is about 35%.

The large variation in the concentration of additives was confirmed by the TGA performance tests. These results are also included in Table III.

An interesting correlation can be made between TGA and chemical analysis data. Figure 5 is a plot of the life of the sample, measured as TGA time in

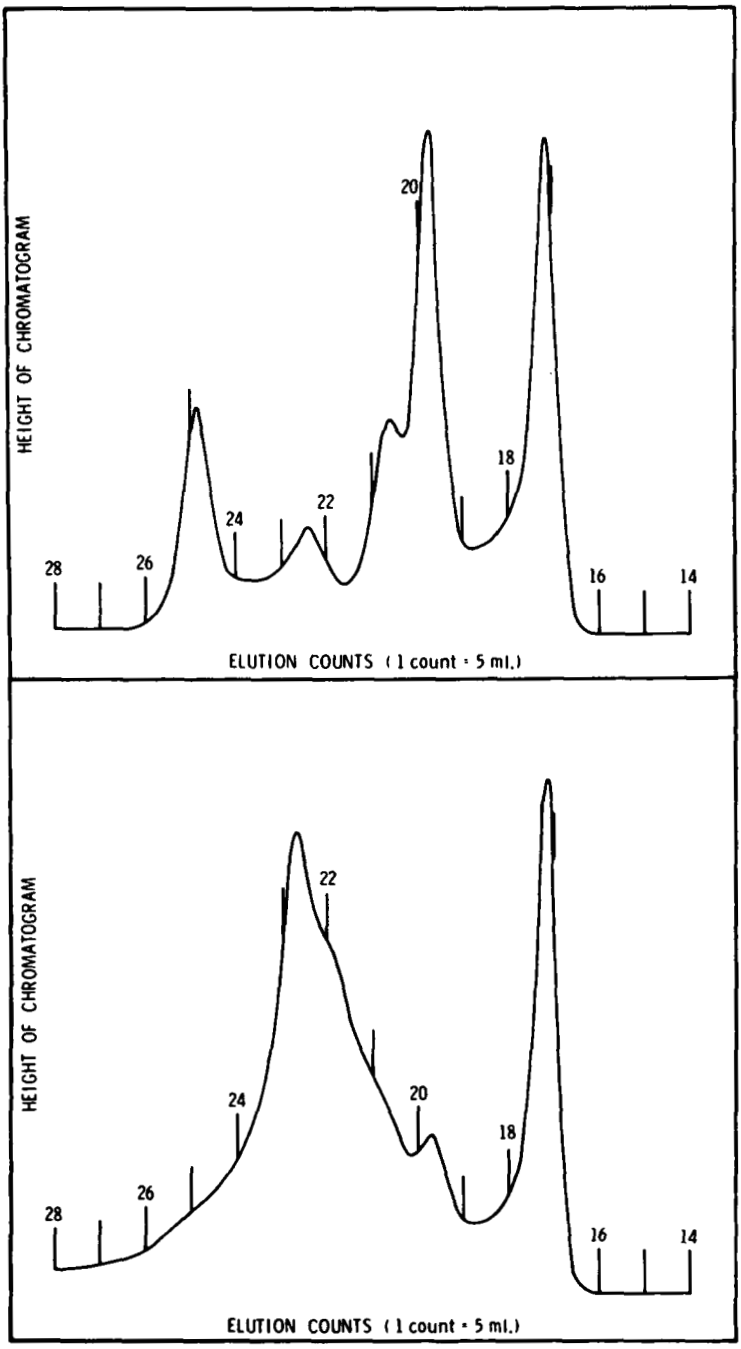

Fig. 4. GPC chromatogram of additives in molded parts. Upper curve: THF extract from new molded part; lower curve: THF extract from molded part which was heated for 500 hr at 120°C.

TABLE III
Results of GPC Determination of Additives in Polypropylene and Correlation with Performance Test Method

Sample[a]	Additive, %			Performance Test, TGA, min[b]
	DSTDP	Topanol CA	Tenamene	
Lot 1	0.471	0.130	0.128	866
Lot 19	0.400	0.072	0.162	440
Lot 32	0.396	0.076	0.162	223
Prototype	0.322	0.064	0.158	195
Lot 2	0.134	0.027	0.055	77
Lot 7	0.106	0.024	0.047	32
Lot 23	0.055	0.017	0.062	14
Molded part, new	0.277	0.061	0.075	...
Molded part, ozone treated[c]	0.213	0.044	0.032	...
Molded part, heat treated[d]	0.044	N.D.[e]	N.D.	

[a] All samples taken from one batch of source 1 polypropylene.
[b] The performance test measures the life of the sample when heated in air.
[c] Sample subjected to 270 parts per hundred million of ozone at 120°C for 24 hr.
[d] Sample subjected to 120°C for 500 hr.
[e] N.D. = Not detected.

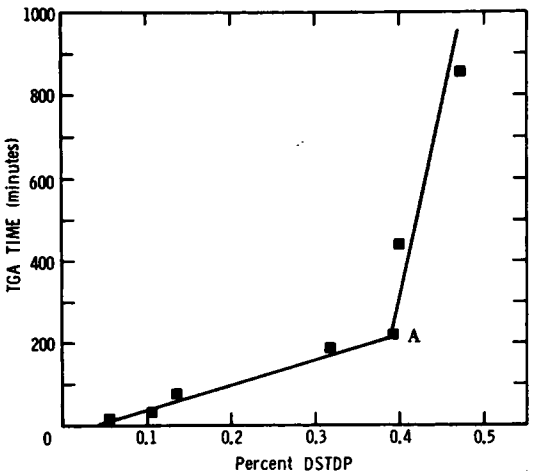

Fig. 5. Correlation of data obtained from performance test and chemical analysis (TGA in an oxygen atmosphere at 190°C).

minutes, versus the concentration of DSTDP in the sample. The dramatic change in slope which occurs at point A in this figure indicates that small increases in DSTDP concentration above 0.4% increase the life of the molded part to a much greater degree than do increases in the region below 0.4%.

LAC Analysis

Although GPC is a good method for separating antioxidants by molecular weight, a complete separation takes over 3 hr per sample. Therefore, we decided to explore liquid adsorption chromatography to reduce the separation

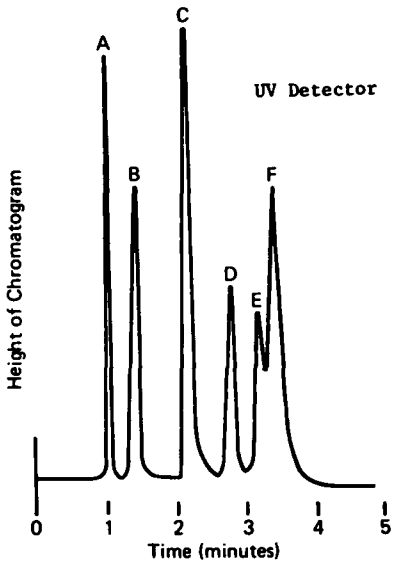

Fig. 6. LAC chromatogram of some low-polarity antioxidants obtained using a UV detector (mobile phase, 99.8% hexane/0.2% methanol): (A) BHT, 2,6-di-*t*-butyl-*p*-cresol; (B) Ionox 220, 4,4′-methylenebis(2,6-di-*t*-butylphenol); (C) Ionox 330; (D) Irganox 1076, octadecyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate; (E) AO 425, 2,2′-methylenebis(4-ethyl-6-*t*-butylphenol); (F) AO 2246.

time from hours to minutes. Figure 6 shows the LAC chromatograms obtained for several commonly used antioxidants using 99.8% hexane/0.2% CH_2CL_2 as the mobile phase. Under these conditions, excellent resolution is obtained among these lower polarity antioxidants, but other antioxidants of interest, particularly DSTDP and Topanol CA, elute only at long times. In order to elute more strongly retained materials, the mobile phase was changed to 75% hexane/25% CH_2Cl_2. Under these conditions (Fig. 7), the more strongly retained antioxidants Santanox R and Santowhite and the synergist DSTDP are eluted in a reasonable time. These results also demonstrate that the RI detector must be used to detect DSTDP (peakC). (With our instrumentation, the RI and UV chromatograms are obtained simultaneously.)

In order to separate antioxidants of widely varying polarity, a gradient elution technique must be used.

The LAC chromatogram for a synthetic mixture of antioxidants is shown in Figure 8. Although the gradient elution technique gives very good results for a wide range of antioxidants, this technique can only be used with a UV detector. With a RI detector, a continuous baseline shift occurs because of the changing solvent composition. Thus, for DSTDP, one still has to rely on the isocratic measurements with the RI detector.

Samples from sources 3 (lot 1) and 4 were extracted into CH_2Cl_2 using the procedure described for GPC. The chromatograms for these samples are also shown in Figure 8 for easy comparison to the synthetic mixture. The identification of these antioxidants by LAC agrees with the results by GPC. To make the method quantitative, a calibration curve can be established using either the peak heights or the peak areas. The main advantage to the LAC method is that separation can be obtained in less than 15 min instead of about 3 hr. How-

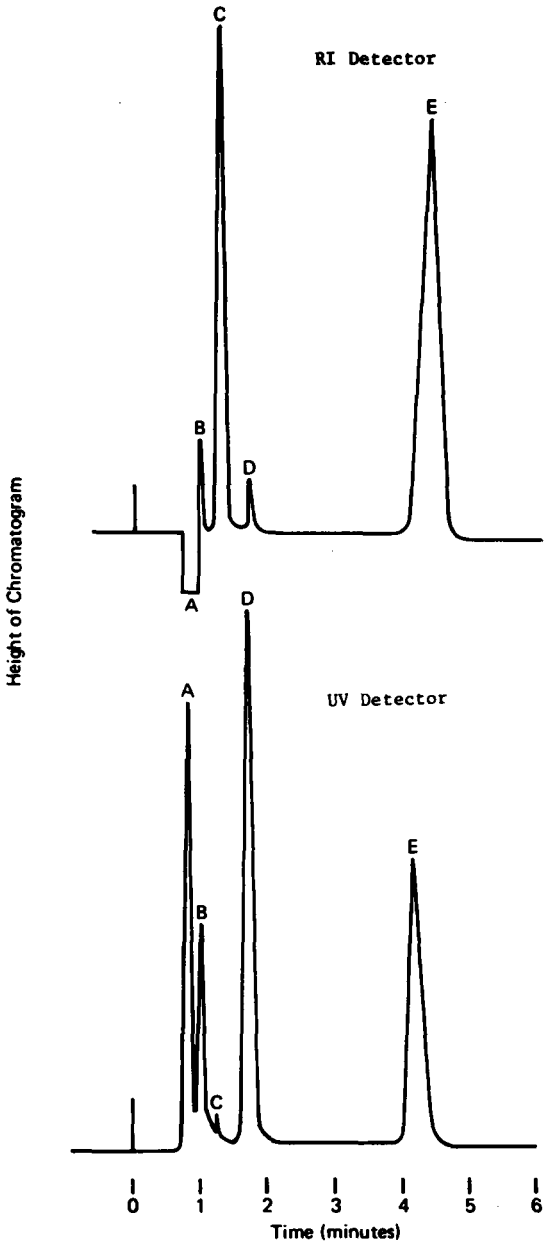

Fig. 7. Comparison of LAC chromatograms of some high-polarity antioxidants obtained using a UV detector and a RI detector (mobile phase, 75% hexane/25% CH_2Cl_2): (A) BHT; (B) A0425; (C) DSTDP; (D) Santanox R, 4,4′-thidois(3-methyl-6-*t*-butylphenol); (E) Santowhite.

ever, both methods require a long, unattended extraction if quantitative results are required.

CONCLUSIONS

Methods have been evaluated for the quantitative analysis of antioxidants in polypropylene for use in quality control. The following conclusions were drawn from this study:

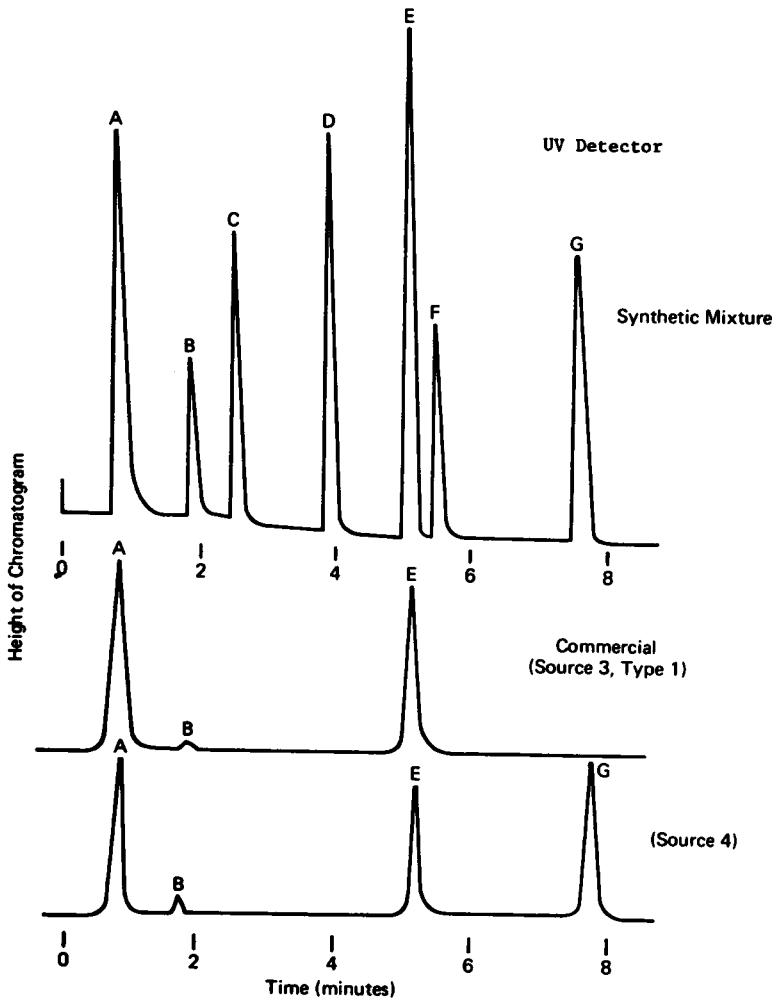

Fig. 8. Comparison of LAC chromatograms from two commercial sources with a chromatogram from a synthetic mixture. These chromatograms were obtained by gradient elution (0.9% CH_2Cl_2 in hexane to 70% CH_2Cl_2 at 10% per minute) using a UV detector: (A) BHT; (B) Ionox 330; (C) A0425; (D) Santanox R; (E) Irganox 1010; (F) Santowhite; (G) Topanol CA.

1. Both GPC and LAC are very good routine monitoring techniques providing qualitative and quantitative analyses for quality control.
2. LAC can be used when a faster analysis of the antioxidants is required, but both GPC and LAC analysis times are controlled by the time to extract the additives ($\geqslant$24 hr when total extraction is required). Although the extraction time can be reduced by heating, more low molecular weight polymer is extracted as well.
3. MS is especially useful for identification of additives in unknown samples.
4. Additives in commercial polypropylenes have been identified and the quantities related to life (oxidation resistance) of molded parts.

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