

## The Rapid Identification Method of Additives in Polypropylene by Mass Spectrometry

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### Synopsis

For the rapid identification of additives such as antioxidant, ultraviolet absorber, and slipping agent, polypropylene containing such additives was heated in a tube connected directly to the inlet system of a mass spectrometer. The vapor of the additives evaporating out of the polypropylene was led to the reservoir and then submitted to mass spectrometry to give spectra for identification.

### INTRODUCTION

The identification of additives in polypropylene usually needs their separation by solvent extraction. This procedure demands a large quantity of materials and a long operation time. Mass spectrometry possesses high sensitivity and can distinguish between homologous compounds. Because many additives with homologous structure and common functional groups are generally used for polypropylene, mass spectrometry is particularly suited for their identification.

The authors found that additives in polypropylene could be identified without extraction procedure by carrying out mass spectrometry for the volatile matter of polypropylene heated in a tube connected to the inlet system of the mass spectrometer.

The present paper describes the limits of detection and the application for the routine analytical work of this "direct evaporation method." The fragmentation of various phenolic model antioxidant compounds as base for analysis, is also discussed, inasmuch as only a few papers<sup>1,2</sup> have been published on the phenolic compounds related to antioxidant.

### EXPERIMENTAL

#### Materials

Polypropylene (Ube Industries, MFI = 5) was reprecipitated from benzene-methanol, washed with methanol, dried under vacuum, and used as the base polymer. For the preparation of polypropylene containing known additives, the base polymer was mixed with solutions of additives

TABLE I  
Fragmentation of Methyl- and *tert*-Butylphenols

No.	mp or bp, °C	Position of side chain		P	P-1	P-15	P-18	P-29	P-43	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	Fission <sup>a</sup>
		Methyl-	Butyl-									
1	m 40-43	—	—	100	—	—	—	29	—	—	—	26
2	b 191-192	2	—	100	88	—	25	53	—	46	—	46
3	b 202	3	—	100	95	—	15	35	—	30	—	33
4	b 201.8	4	—	75	100	—	—	25	—	30	—	14
5	b 101-103 <sup>b</sup>	—	2	30	—	100	—	—	60	16	—	26
6	—	—	3	31	—	100	—	—	34	8	—	8
7	m 98	—	4	20	—	100	—	—	27	12	—	20
8	m 54-64	—	2, 4	15	—	100	—	—	10	6	—	—
9	m 36.4	—	2, 6	18	—	100	—	—	—	—	—	25
10	m 70	4	2, 6	23	—	100	—	—	16	6	—	58

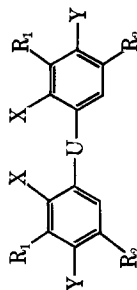
<sup>a</sup> *m/e* 39, due to the fission of benzene ring.

<sup>b</sup> At 13 mm Hg.

TABLE II  
Fragmentation of Diphenols

No.	mp, °C	Structure <sup>a</sup>				Relative intensity of peaks						
		—U—	X	Y	R <sub>1</sub>	R <sub>2</sub>	P	P-15	Fissions <sup>b</sup>	C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	Other peaks	
1	186	none	H	OH	B <sup>a</sup>	B	100	20	—	—	85	
2	151-152		OH	H	B	B	26	27	—	—	100	
3	158	—CH <sub>3</sub> —	H	OH	H	H	53	—	100	20	—	26(P-1), 12(P-18)
4	119.5		OH	H	H	H	72	—	100	33	—	15(P-18)
5	120		OH	H	B	M <sup>c</sup>	35	—	100	63	35	
6	125		OH	H	B	E <sup>o</sup>	47	8	100	75	30	
7	147-148		OH	H	B	B	63	32	87	48	100	
8	154		H	OH	B	B	95	100	35	—	53	
9	—	—CH(CH <sub>3</sub> )—	OH	H	B	M	15	4	100	—	—	
10	150-155	—C(CH <sub>3</sub> ) <sub>2</sub> —	H	OH	H	H	23	100	7	44	10	
11	110-112		H	OH	B	H	25	100	—	—	27	
12	129-131		H	OH	B	M	22	100	—	—	57	3(P-28)
13	—	—CH(C <sub>3</sub> H <sub>7</sub> )—	H	OH	B	M	19	—	50	24	100	
14	150	—S—	M	OH	H	B	100	47	—	—	17	

<sup>a</sup> The general structure of the diphenols is shown below:



<sup>b</sup> Fission between —U— and either one of the phenolic ring of diphenols.

<sup>c</sup> B = *tert*-butyl, E = ethyl, M = methyl.

in carbon tetrachloride and the mixtures were dried under vacuum. The mixtures thus obtained were compression molded at 190°C for 1 min into a film with a thickness of 1.0 mm to be used for mass spectrometry. Various grades of polypropylene pellets commercially available were used as purchased.

The model antioxidant compounds were distilled or recrystallized before use to give the melting or boiling points as given in Tables I and II.

### Mass Spectra

The mass spectra were obtained with a Hitachi RMU-6 single-focus mass spectrometer under the following conditions: ion source temperature, 250°C; ionization voltage, 80 V; accelerating voltage, 1.2 kV; ionizing current, 80 microamperes. The temperature of the sample inlet system (Hitachi MG-141) was kept between 250° and 350°C according to the volatility of the additives.

An additive (ca. 20 mg) or polypropylene (0.2 g) was placed in a glass tube which was connected to the heated sample inlet system. By heating the tube with an electric furnace to the same temperature as the inlet system, the additive sublimed and was led into the reservoir (1000 ml) of the inlet system. For all samples the evaporation was found to be complete within 30 min. The vapor of the additives stored in the reservoir was then submitted to mass spectrometry.

## RESULTS AND DISCUSSION

### Mass Spectrum of Phenolic Model Compounds and Commercially Available Additives

**Alkylphenols.** Table I shows the numerous peaks for phenol, methylphenols, and *tert*-butylphenols. All methylphenols show P, P-1, P-29,  $C_6H_5^+$ , and a peak at  $m/e$  39 due to benzene ring fission. *Ortho*- and *meta*-cresols, but not *para*-cresol, show P-18 due to the elimination of  $H_2O$ . Phenols with a *tert*-butyl group or groups have peaks at P and P-15, the latter being always the base peak. Except for 2,6-di-*tert*-butylphenol, they show P-43, (P- $CH_3$ -CO), and  $C_6H_5^+$ . Those with two *tert*-butyl groups show  $C_4H_9^+$ .

**Diphenols.** Table II shows the abundant peaks for various diphenols. Their base peaks are either P, P-15,  $C_4H_9^+$ , or a peak corresponding to the fission between two phenolic nuclei. Diphenols, isopropylidenediphenols, and thiobisphenol show no fission between the phenolic nuclei. Diphenols with *tert*-butyl groups show P-15, except for compounds no. 5 and 13, and  $C_4H_9^+$ , except for no. 9. As for methylenediphenols without substituents, it is interesting that the 4,4'-isomer possesses the P-1 peak, whereas the 2,2'-isomer shows no P-1 peak.

**Commercially Available Additives.** Table III shows the main fragmentation peaks for the important commercially available antioxidants,

TABLE III  
Mass Number and Relative Intensity<sup>a</sup> of Main Mass Peaks of Commercially Available Additives

No.	Trade name	MW	Peaks in order of intensity										Limit of detection, phr			
			1	2	3	4	5	6	7	8	9	10		m.s. <sup>a</sup>		
1	BHT	220	205 (100)	220 (25)	206 (15)	—	—	—	—	—	—	—	—	—	—	0.02
2	DL <sup>b</sup>	514	346 (100)	329 (95)	514 (62)	273 (40)	347 (37)	330 (35)	241 (30)	300 (28)	515 (27)	441 (3)	—	—	—	0.06
3	Irganox 1010	1176	309 (100)	323 (95)	342 (66)	219 (50)	410 (44)	425 (44)	227 (33)	355 (33)	292 (25)	351 (25)	—	—	—	0.1
4	Irganox 1076	530	530 (100)	219 (89)	515 (39)	225 (8)	277 (6)	203 (3)	210 (1)	217 (1)	262 (1)	307 (1)	505	—	—	0.1
5	Topanol CA	544	339 (100)	340 (25)	205 (24)	544 (3)	353 (2)	323 (2)	206 (2)	309 (1)	365 (1)	545 (1)	—	—	—	0.1
6	Antioxidant 2246	340	340 (100)	284 (51)	341 (30)	283 (26)	269 (8)	228 (6)	227 (3)	255 (1)	265 (1)	325 (1)	—	—	—	0.02
7	Santowhite	382	339 (100)	340 (25)	382 (75)	341 (5)	323 (3)	383 (2)	367 (2)	309 (1)	203 (1)	219 (1)	—	—	—	0.02
8	Tinuvin 327	357	342 (100)	344 (33)	357 (28)	343 (25)	359 (10)	358 (5)	287 (4)	309 (3)	315 (3)	301 (2)	329	—	—	0.1
9	Ercamide	337	337 (100)	320 (40)	338 (30)	294 (16)	240 (16)	212 (15)	226 (13)	521 (9)	254 (9)	210 (8)	—	—	—	0.06
10	Oleinamide	281	281 (100)	225 (37)	264 (33)	238 (25)	212 (25)	226 (25)	253 (22)	210 (10)	220 (10)	222 (10)	—	—	—	0.02

<sup>a</sup> Metastable ions.

<sup>b</sup> Dilauryl thiodipropionate.

<sup>c</sup> Figure in parentheses.

TABLE IV  
Published Chemical Structure of Additives

No. (Table III)	Chemical structure
1	2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol
2	Pentaerythritol tetraester of 2-(4-hydroxy-3,5-di- <i>tert</i> -butylphenyl)propionic acid
4	Octadecyl-3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate
5	1,1,3-Tris(2-methyl-4-hydroxy-5- <i>tert</i> -butylphenyl)butane
6	2,2'-Methylenebis(4-methyl-6- <i>tert</i> -butylphenol)
7	4,4'-Butylidenebis(3-methyl-6- <i>tert</i> -butylphenol)
8	2-(2-Hydroxy-3,5-di- <i>tert</i> -butylphenyl)-5-chlorobenzotriazole

ultraviolet absorber (Tinuvin 327), and slipping agents (amides). The published structures for BHT and Antioxidant 2246 (Table IV) are identical to compound no. 1 of Table I and no. 5 of Table II, respectively.

The most intensive peaks with  $m/e$  larger than 200 for each additive are given in the order of relative intensity. A peak or a set of peaks at these mass numbers characterizes the additives in the polymer. Even for antioxidants with high molecular weight and without parent peak such as Irganox 1010, the fragmentation peaks are usable for their identification.

Figure 1 shows, as an example, our interpretation of the mass spectrum of Topanol CA based on the result of the mass spectra of the model compounds.

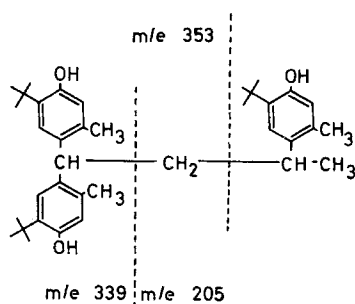


Fig. 1. The fragmentation of Topanol CA.

### Detection of Additives in Polypropylene by the Direct Evaporation Method

**Limit of Detection.** The last column in Table III shows the limit of detection of additives in the prepared polypropylene film using 0.20 g polypropylene film for each measurement. The limit of detection is defined to be the lowest concentration in phr (part per hundred parts resin) of additives where the most intensive peak of the additive can be distinguished from the background peak. It was revealed that even high molecular weight antioxidant in an amount as low as 0.1 phr could be detected.

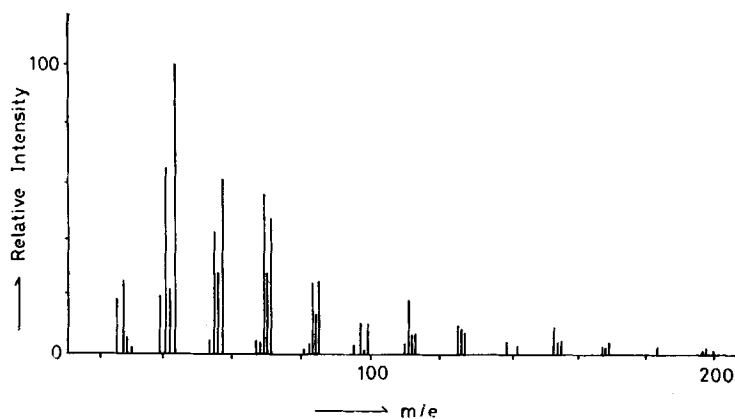


Fig. 2. The mass spectrum of the volatile matter of polypropylene base polymer heated at 280°C.

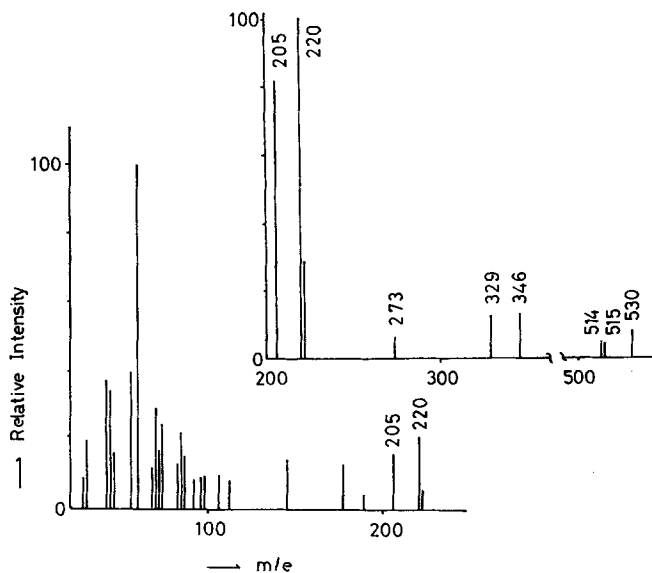


Fig. 3. The mass spectrum of the volatile matter of a polypropylene pellet sample heated at 280°C.

**Application for Polypropylene Pellets.** As the blank test, Figure 2 shows the mass spectrum of volatile matter of polypropylene base polymer when the sample tube and the inlet system were heated at 280°C. The peaks are thought to be originated by the volatile fraction or the pyrolytic product of the base polymer. Owing to these peaks, the peaks with  $m/e$  less than 200 are not recommendable for the analysis of the additives.

Figure 3 is an example of the mass spectrum of the volatile matter of commercially available polypropylene pellets, showing the presence of

BHT (220(P) and 205), dilauryl thiodipropionate (514(P), 346, 329, and 273), and Irganox 1076 (530(P) and 515).

By this procedure, the most generally used additives in various kinds of polypropylene pellets commercially available were revealed, as shown in Table V, to be (a) BHT, (b) dilauryl thiodipropionate, (c) high molecular weight phenolic antioxidant, and (d) slipping agents.

TABLE V  
Additives Detected by the Direct Evaporation Method in Various  
Polypropylene Pellets

Polypropylene sample no.	Additives detected <sup>a</sup>	Polypropylene sample no.	Additives detected
1	2, 4	15	1, 2, 5
2	2, 4	16	1, 2, 5, 9
3	2, 4	17	1, 2, 5, 9
4	1, 2, 10	18	1, 2, 9
5	1, 2	19	1, 2, 7
6	1, 2, 3	20	1
7	1, 2, 6	21	none
8	1, 10	22	1, 2, 7, 9
9	1, 4	23	1
10	2, 7	24	1, 4
11	1, 4	25	1, 2, 10
12	1, 4	26	1, 4
13	1, 2, 8	27	1, 4
14	1, 5, 10		

<sup>a</sup> Numbers correspond to those in Table III.

### References

1. T. Aczel and H. H. Lumpkin, *Anal. Chem.*, **32**, 1818 (1960).
2. A. Cornu and R. Massot, Eds., *Compilation of Mass Spectral Data*, Heydon & Sons Ltd., London, 1966.

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