

183908

NHTSA-98-3588-182

Project B.10 – Study of Flammability of Materials

Identification of the Base Polymers in Selected Components and Parts from a 1997 Ford Explorer by Pyrolysis / Gas Chromatography / Mass Spectroscopy and Attenuated Total Reflectance / Fourier Transform Infrared Spectroscopy

Jeffrey Santrock
General Motors Corporation

ABSTRACT

This report describes laboratory tests conducted pursuant to an agreement between General Motors and the United States Department of Transportation. The base polymers from fifty-eight polymeric components or parts from a 1997 Ford Explorer were identified by pyrolysis/gas chromatography/mass spectrometry analysis and attenuated total reflectance/Fourier transform infrared spectroscopy analysis. Additives in the base polymers also were identified in some of the samples using these chemical analysis techniques.

DEPT. OF TRANSPORTATION
RECEIVED
02 JUN 12 PM 4:12

INTRODUCTION

The work described in this report was conducted by General Motors (GM) pursuant to an agreement between GM and the United States Department of Transportation as part of Project B.10 (Study of Flammability of Materials). The vehicle from which parts were sampled for this study was one of the test vehicles used in Project B.3 (Fire Initiation and Propagation Tests). The base polymers used in 58 non-metal components or parts¹ from a 1997 Ford Explorer (VIN: 1FMDU34X4VUB02606) were identified by chemical analysis techniques called pyrolysis/gas chromatography/mass spectroscopy (pyrolysis/GC/MS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR).

Pyrolysis is simply the breaking apart of large, complex molecules into smaller molecules by the action of heat. When a polymer undergoes thermal degradation, the volatile products created in this process usually retain some of the molecular structure of the original polymer. Analysis of the mixture of polymer thermal decomposition fragments by gas chromatography/mass spectroscopy thus provided a means to elucidate the molecular structure of the original polymer. For the pyrolysis/GC/MS analyses, samples of each material were subjected to thermal decomposition in an inert atmosphere. The resulting thermal decomposition products were separated by gas chromatography and identified by mass spectroscopy.

When exposed to infrared radiation, polymeric materials absorb some of the incident radiation. The molecular structure of the polymer determines the fraction of the incident radiation at a given frequency that is absorbed. Analysis of the absorption infrared spectrum of a material thus provides a means to elucidate the molecular structures of the constituent polymers in that material. For FTIR analysis, an attenuated total reflectance accessory was used to obtain an infrared spectrum of the surface of a sample.

In this study, some of the samples were analyzed by pyrolysis/gas chromatography/mass spectrometry, some of the samples were analyzed by attenuated total reflectance/Fourier transform infrared spectroscopy, and some of the samples were analyzed by both chemical analysis techniques. The base polymer or polymers in each sample were identified by comparison to results from the analysis of polymer standards. When a standard was not available, the base polymer was identified by reconstructing the structure of the polymer from the structures of its thermal decomposition fragments identified in the mass chromatogram and by interpretation of the infrared spectrum. Chemical additives were identified in some samples.

¹ Some parts were assemblies containing components made from different base polymers. In these cases, samples of each component were analyzed.

EXPERIMENTAL

Pyrolysis/Gas Chromatography/Mass Spectroscopy

The analytical instrumentation consisted of a Pyroprobe 2000 sample pyrolyzer (CDS Analytical, Inc, Oxford, PA), a Model 6000 Purge and Trap Sample Concentrator (CDS Analytical, Inc.), a Model 5890 Series II Gas Chromatograph (Hewlett Packard Co., Palo Alto, CA), and a Model 5989B Mass Spectrometer (Hewlett Packard Co.).

Pyrolysis. The sample (< 1 mg) was loaded into an open-ended quartz tube. The sample was held in place by two plugs of quartz wool. The quartz tube was inserted into the platinum heating coil in the pyroprobe, and the pyroprobe is installed in the pyrolysis interface chamber in the purge and trap concentrator. The sample was purged with Helium at flow rate of 30 mL/min for 2 minutes before being heated.

A two-step temperature program was used for pyrolysis: from ambient temperature to a final temperature of 750°C at 20°C/ms; and hold at 750°C was kept for 40s. The sample was purged with Helium at a flow rate of 30 mL/min during the pyrolysis. The effluent from the pyrolysis chamber passed through a trap packed with Tenax absorbent maintained at ambient temperature, which retained the thermal decomposition products from the sample. The desorber, valve oven, and transfer line were maintained at a temperature of 300 °C. The trap rest and trap initial temperature were(?)

40°C. The trap final temperature was 300 °C.

After pyrolysis of the sample, the Tenax trap was heated to 300°C to desorb the trapped pyrolysate, which was cyro-focused onto the head of the GC column. The cyrogenic trap at the head of the GC column was cooled with liquid nitrogen. The rest temperature was 275 °C, the trapping temperature was -60 °C, and the desorption temperature was 300 °C. The desorber purge time was 6 minutes.

Gas Chromatography. The chromatography column was a crosslinked methyl silicone capillary column (HP-1, 50 length, 0.2 mm i.d. of 0.33 µm film thickness). After sample transfer from the Tenax trap to the GC column was complete (5 min), the cyro-focus trap was heated from -60 to 300°C at a rate of approximately 12°C/min. The temperature of the chromatographic column was held at 40°C for 2 min, then programmed from 40 to 315°C at a rate of 12°C/min, and held at 315°C for 10 min. The carrier gas was Helium, and the GC was operated in the constant flow

mode at a flow rate of 0.8 mL/min. Both the injector temperature and mass spectrometer interface temperatures were 275°C.

Mass Spectrometry. The ionization source temperature was 200°C and the analyzer temperature was 100°C. The mass spectrometer was operated in positive ion mode. The mass spectrometer was scanned continuously from 40 to 600 amu at a rate of 1.2 scans/s.

Attenuated Total Reflectance/Fourier Transform Infrared Spectroscopy

The analytical instrumentation consisted of a Spectrum 2000 Fourier transform infrared spectrometer (Perkin Elmer, Norwalk CT) and an attenuated total reflectance accessory with silicon windows (Harrick).

Fourier Transform Infrared Spectrometry. The Fourier transform infrared spectrometer was equipped with a mid-range glow-bar infrared source, a mid-range TGS detector, and an optical beam splitter with KBr windows. The spectrometer was operated in single beam mode at an optical resolution of 4.00 cm^{-1} and a spectral range of 15600 cm^{-1} . The optical bench was filled with clean, dry argon and sealed.

Attenuated Total Reflectance Accessory. A circular sample with a diameter of approximately 8 mm was obtained using a laboratory cork bore. The sample was placed on the ATR accessory and centered on the silicon window. The retaining arm was adjusted to apply approximately 2 kg of force to the sample, and locked in place. The ATR accessory was purged continuously with clean, dry argon.

RESULTS

Fifty-eight polymeric materials from a 1997 Ford Explorer (VIN: 1FMDU34X4VUB02606) were analyzed in this study. These materials were sampled from the following areas of the test vehicle: body front end; engine cooling and radiator; engine air intake system; windshield, instrument panel, gauges and console; HVAC module; doors; seats, carpet; roof; rear quarters; and rear bumper. Table 1 summarizes the results of these analyses.

Table 1. Base polymer in selected components and parts from a 1997 Ford Explorer

	Component / Part	Base Polymer	Additive
1	front bumper fascia	poly(propylene)	
2	front bumper valance panel	poly(propylene)	
3	radiator grille – A	(acrylonitrile/butadiene/styrene) copolymer	
4	radiator grille – B	poly(propylene)	
5	radiator – upper sight shield	poly(propylene)	
6	radiator – fan shroud	poly(styrene)	
7	radiator – air deflector	(propylene/ethylene) copolymer	
8	radiator – coolant recovery reservoir	poly(propylene)	
9	radiator – fan blades	poly(propylene)	
10	windshield washer fluid reservoir	poly(ethylene)	
11	windshield inner-layer	poly(vinyl butyral)	
12	rocker panel trim molding	(propylene/ethylene) copolymer	
13	front door rocker step pad	(propylene/ethylene) copolymer	
14	rear bumper stone deflector	(propylene/ethylene) copolymer	
15	lift gate scuff plate	(propylene/ethylene) copolymer	

Table 1, continued. Identification of the base polymer in selected parts from a 1997 Ford Explorer

	Component / Part	Base Polymer	Additive
16	rear lamp assembly – lens	poly(methyl methacrylate)	
17	battery cover	(propylene/ethylene) copolymer	
18	engine compartment wire conduit	Nylon 6 / poly(ethylene)	
19	power distribution box – cover	poly(butylene terphthalate)	
20	power distribution box – housing	phenol/formaldehyde copolymer	
21	engine air cleaner housing	(propylene/ethylene) copolymer	
22	instrument panel – cover	PVC	phthalate esters
23	instrument panel – foam padding	urethane ¹	
24	HVAC module	poly(propylene)	
25	HVAC – vents	(propylene/ethylene) copolymer	
26	HVAC – ducts	PP or PP/PE	
27	roof trim panel – cover	Nylon 6	
28	roof trim panel – foam	urethane ¹	
29	roof trim panel – substrate	glass fiber w/phenolic binder	
30	front seat cushion – sew pad	urethane ¹ / styrene/acrylonitrile	phenolics ²

Table 1, continued. Identification of the base polymer in selected parts from a 1997 Ford Explorer

	Component / Part	Base Polymer	Additive
31	front seat cushion – pad	urethane ¹ / styrene/acrylonitrile	phenolics ²
32	front seat cushion – cover seating area	poly(ethylene terphthalate)	triphenyl phosphate
33	front seat back – cover seating area	poly(ethylene terphthalate)	triphenyl phosphate
34	front seat back – sew pad	urethane ¹ / styrene/acrylonitrile	phenolics ²
35	front seat back – pad	urethane ¹ / styrene/acrylonitrile	phenolics ²
36	front seat back – cover rear – surface	poly(vinyl chloride)	diisononyl phthalate
37	front seat back – cover rear – backing	poly(ethylene terphthalate)	
38	front seat back – cover rear – pad	urethane ¹ / styrene/acrylonitrile	phenolics ²
39	front seat – track trim cover	(propylene/ethylene) copolymer	
40	seat belt	poly(ethylene terphthalate)	
41	floor carpet – pile	(propylene/ethylene) copolymer	
42	floor carpet – weave	(propylene/ethylene) copolymer	
43	floor carpet – backing	poly(ethylene)	
44	floor panel drain hole plug	(ethylene/propylene/butadiene) copolymer	
45	flood console	(acrylonitrile/butadiene/styrene) copolymer	

Table 1, continued. Identification of the base polymer in selected parts from a 1997 Ford Explorer

	Component/ Part	Base Polymer	Additive
46	floor console – internal support	poly(styrene)	
47	floor console – distribution duct	(propylene/ethylene) copolymer	
48	floor console – blower housing	poly(propylene)	
49	floor console – vent duct	poly(propylene)	
50	floor console – rear bezel	poly(<i>bis</i> -phenol A carbonate)	
51	rear door trim panel – A	poly(vinyl chloride)	phthalate esters
52	rear door trim panel – B	poly(vinyl chloride)	phthalate esters
53	rear door trim panel – C	(acrylonitrile/butadiene/styrene) copolmer	
54	rear door trim panel – D	poly(propylene)	
55	rear door trim panel – E	poly(<i>bis</i> -phenol A carbonate)	
56	rear door trim panel – F	poly(vinyl chloride)	phthalate esters
57	rear washer fluid reservoir	poly(ethylene)	
58	quarter inner trim finishing panel	(propylene/ethylene) copolymer	

¹ Flexible urethane foam - toluene diisocyanate / poly(2-propylene glycol based urethane).

² A mixture of phenolic antioxidants including 2,6-*bis*(1,1-dimethylethyl)-4-methylphenol (BHT), *bis*(3,5-di-tertbutyl-4-hydroxyphenyl)methane, and 1,2-*bis*(3,5-di-tert-butyl-4-hydroxyphenyl)ethane.