

183901

NHTSA-98-3588-181

Project B.10 – Study of Flammability of Materials

Identification of the Base Polymers in Selected Components and Parts from a 1997 Chevrolet Camaro by Pyrolysis / Gas Chromatography / Mass 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. Samples acquired from ninety polymeric components of a 1997 Chevrolet Camaro were analyzed by pyrolysis/gas chromatography/mass spectrometry to identify the base polymer. In a few samples, additives also were identified.

DEPT. OF TRANSPORTATION
100 18th St NW
WASHINGTON, DC 20590
02 AUG 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). This 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 to fabricate 90 non-metal components from 56 parts¹ in a 1997 Chevrolet Camaro (VIN: 2G1FP22K1V2109145) were identified by a chemical analysis technique called pyrolysis/gas chromatography/mass spectrometry.

Pyrolysis is simply the breaking apart of large, complex molecules into smaller molecules by the action of heat. When a polymer undergoes pyrolysis or 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.

In the pyrolysis/GC/MS analyses done in this study, samples of each polymer were subjected to thermal decomposition in an inert atmosphere. The resulting thermal decomposition products were separated by gas chromatography and identified by mass spectroscopy. 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. Chemical additives to the base polymers were identified in some samples.

EXPERIMENTAL

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

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

coil in the pyroprobe, and the pyroprobe 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 maintained for 40s. The sample was purged with Helium at 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 was 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.

RESULTS

Ninety polymeric materials from a 1997 Chevrolet Camaro (VIN: 2G1FP22K1V2109145) were analyzed by pyrolysis/gas chromatography/mass spectrometry. These materials were sampled from the following areas of the test vehicle: body front end; engine cooling and radiator; engine air

intake system; windshield, windshield wiper/washer system; 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. Identification of the base polymer in parts from a 1997 Chevrolet Camaro

	Component / Part	Base Polymer	Additive
1	front bumper fascia	polyurethane ¹	
2	front bumper fascia lower deflector	(propylene/ethylene) copolymer	
3	headlamp support panel	(propylene/ethylene) copolymer	
4	rear bumper fascia	polyurethane ¹	
5	rear bumper fascia energy absorber	polyethylene	
6	rear bumper impact bar	poly(propylene)	
7	front wheelhouse panel liner	(propylene/ethylene) copolymer	
8	hood insulator – backing	poly(ethylene)	
9	hood insulator – fiber	glass fiber / phenolic binder	
10	hood insulator - scrim	Nylon 6	benzoic acid
11	air inlet screen	(propylene/ethylene) copolymer	
12	radiator inlet tank	Nylon 6/6	orgo-Cu compound
13	engine coolant fan shroud	Nylon 6/6	

Table 1, continued. Identification of the base polymer in parts from a 1997 Chevrolet Camaro

	Component / Part	Base Polymer	Additive
14	radiator upper mounting panel	Nylon 6/6	
15	radiator air lower deflector	(propylene/ethylene) copolymer	
16	radiator air lower baffle	(propylene/ethylene) copolymer	
17	radiator air upper baffle	(propylene/ethylene) copolymer	
18	air cleaner housing cover	(propylene/ethylene) copolymer	
19	air cleaner outlet duct	Nylon 6	
20	mass air flow sensor	(propylene/ethylene) copolymer	
21	air cleaner outlet rear duct	(ethylene/propylene/butadiene) copolymer	
22	brake master cylinder reservoir	(propylene/ethylene) copolymer	
23	power steering fluid reservoir	Nylon 6/6	
24	battery storage tank	(propylene/ethylene) copolymer	
25	ABS/TCS relay cover	(propylene/ethylene) copolymer	
26	wire conduit	(propylene/ethylene) copolymer	
27	windshield wiper blade	poly(isoprene)	
28	windshield wiper arm	poly(ethylene terephthalate) polyester	
29	windshield wiper arm finishing cap	styrene / ethylene / butene copolymer	

Table 1, continued. Identification of the base polymer in parts from a 1997 Chevrolet Camaro

	Component / Part	Base Polymer	Additive
30	windshield inner-layer	polyvinyl butyral	dihexyl dipate, Tinuvin P
31	windshield washer solvent container	poly(ethylene)	
32	instrument panel compartment – front panel	poly(propylene)	
33	instrument panel compartment – box	(propylene/ethylene) copolymer	
34	instrument cluster – lens	(styrene/acrylonitrile) copolymer	
35	instrument cluster – housing	(acrylonitrile/butadiene/styrene) copolymer	
36	instrument cluster – housing	poly(styrene) / phenolic resin	
37	instrument panel cluster trim plate - bezel	(styrene/acrylonitrile) copolymer	
38	instrument panel - skin	(acrylonitrile/butadiene/styrene) copolymer	bis(2-ethyl-hexyl) phthalate
39	instrument panel - foam	polyurethane	
40	instrument panel - structure	poly(styrene)	
41	Instrument panel upper trim panel	poly(<i>bis</i> -phenol A carbonate)	
42	dash sound barrier – film	poly(ethylene)	
43	dash sound barrier – foam	urethane ²	triphenyl phosphate
44	windshield defroster nozzle and air distributor	poly(propylene)	
45	dash panel insulator – film	poly(ethylene)	

Table 1, continued. Identification of the base polymer in parts from a 1997 Chevrolet Camaro

	Component / Part	Base Polymer	Additive
46	dash panel insulator – foam	urethane ²	
47	instrument panel driver knee bolster	polypropylene	
48	front floor console door	(propylene/ethylene) copolymer	
49	steering wheel inflatable restraint module – cover	poly(vinyl chloride)	
50	steering wheel inflatable restraint module – air bag	Nylon 6/6 w/ Neoprene coating	
51	instrument panel inflatable restraint module – air bag	Nylon 6/6	
52	HVAC module rear case	poly(propylene)	
53	HVAC module auxiliary A/C evaporator and blower lower case	polyester ⁴	diallylphthalate C ₁₆ & C ₁₈ acid derivatives
54	HVAC module vent mode valve - foam	urethane ²	
55	front side door trim panel insert	(propylene/ethylene) copolymer	
56	front side door trim panel map pocket	(propylene/ethylene) copolymer	
57	front side door trim panel armrest - skin	poly(vinyl chloride)	phthalate esters
58	front side door trim panel armrest - foam	urethane ²	
59	front side door trim panel – carpet upper	poly(ethylene terphthalate) polyester	
60	front side door trim panel – carpet lower	Nylon 6	
61	front seat cushion – sew pad	urethane ² / styrene/acrylonitrile	

Table 1, continued. Identification of the base polymer in parts from a 1997 Chevrolet Camaro

	Component / Part	Base Polymer	Additive
62	front seat cushion – pad	urethane ² / styrene/acrylonitrile	
63	front seat cushion – cover seating area	poly(ethylene terphthalate) polyester	
64	front seat cushion bottom cover & rear seatback back cover	poly(propylene)	
65	rear seat cushion – backing	poly(ethylene terphthalate) polyester	glutaric acid di-N-butyl ester
66	rear seat cushion cover – seating area	poly(ethylene terphthalate) polyester	
67	rear seat cushion cover – side panels	poly(propylene)	
68	seat belt	poly(ethylene terphthalate) polyester	
69	rear compartment panel rear sound absorber	[unidentified]	
70	floor carpet – pile	Nylon 6	
71	floor carpet – weave	poly(ethylene terphthalate) polyester	
72	floor carpet – backing	poly(ethylene)	
73	floor pan drain hole plug	ethylene / propylene / butadiene copolymer	benzothiazole 2-(2-butoxy-ethoxy)-ethanol
74	headlining trim finish panel – substrate	glass fiber w/ Novolac binder	
75	headlining trim finish panel – foam	urethane ³	
76	headlining trim finish panel – fabric	Nylon 6	

Table 1, continued. Identification of the base polymer in parts from a 1997 Chevrolet Camaro

	Component / Part	Base Polymer	Additive
77	quarter inner trim finishing panel	(propylene/ethylene) copolymer	
78	fuel tank filler pocket	(propylene/ethylene) copolymer	
79	rear compartment carpet – backing	poly(ethylene terphthalate) polyester / poly(propylene)	
80	rear compartment carpet – pile	poly(ethylene terphthalate) polyester	
81	rear speaker – seal	urethane ²	
82	rear speaker – screen	poly(ethylene terphthalate) polyester / poly(propylene)	
83	rear speaker – grille	propylene / ethylene copolymer	
84	rear end spoiler	polyester ⁴	
85	rear compartment lift window panel	polyester ⁴	
86	rear compartment lift window inner panel cover	(propylene/ethylene) copolymer	
87	rear compartment lift window weatherstrip	(propylene/ethylene) copolymer	diphenyl ether
88	rear compartment lift window closeout panel assembly - backing	poly(ethylene terphthalate) polyester	
89	rear compartment lift window closeout panel assembly - binder	poly(propylene)	
90	rear compartment lift window closeout panel assembly - felt	Nylon 6	

¹ Reaction injection molded urethane – methylene diisocyanate / poly(2-propylene glycol) based urethane.

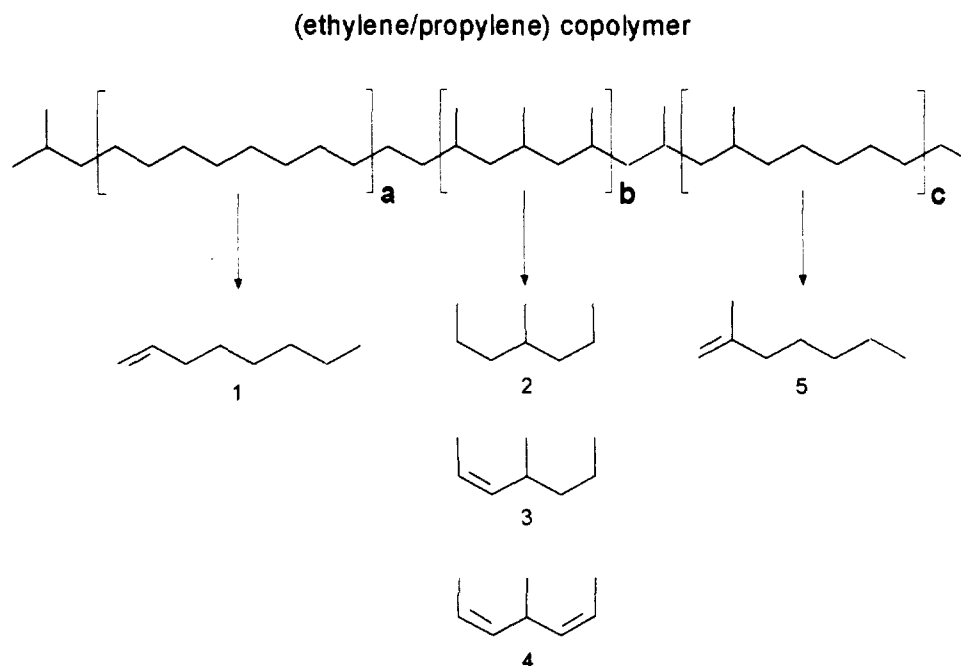
² Flexible foam – toluene diisocyanate / poly(2-propylene glycol) based urethane.

³ Rigid urethane foam – toluene diisocyanate / poly(2-propylene glycol) based urethane.

⁴ Styrene cross-linked maleic anhydride / poly(2-propylene glycol) polyester.

(ethylene/propylene) copolymer. The brackets labeled **a** indicate a C₈ segment containing only ethylene monomer. The brackets labeled **b** indicate a C₈ containing only propylene monomer. The brackets labeled **c** indicate a C₈ segment containing ethylene and propylene monomer.

Scheme VI



Thermolytic cleavage of the C-C bonds intersected by the brackets designating segment **a** yields 1-octene (1). Thermolytic cleavage of the C-C bonds intersected by the brackets designating segment **b** yields 4-methylheptane (2), 4-methyl-2-heptene (3), or 4-methyl-2,5-heptadiene (4). Thermolytic cleavage of the C-C bonds intersected by the brackets designating segment **c** yields 2-methyl-1-heptene (5). Note that small amounts of other products may be formed by thermal decomposition of propylene/ethylene copolymer. For example, 4-methyl-1-heptene, 4-methyl-2,6-heptadiene, and 4-methyl-1,6-heptadiene can be produced from segment **b**. Formation of these products requires cleavage of the C-C bonds intersected by the brackets, followed by carbon-carbon double bond formation involving a branching methyl group, which is less probable than double bond formation involving carbons on the polymer backbone as shown in scheme VI. 4-Methyl-1-heptene would have coeluted with 4-methyl-2-heptene, and 4-methyl-2,6-heptadiene, and 4-methyl-1,6-heptadiene would have coeluted with 4-methyl-2,5-heptadiene in the chromatographic analysis used here.

Figure 4 shows sections of chromatograms ($3.8 < t_R < 5.2$ minutes) showing the C_8 pyrolysis products from a poly(ethylene) standard, a poly(propylene) standard, and a propylene/ethylene copolymer standard. The peaks in these chromatograms were identified from their mass spectra and retention times. Pyrolysis of a poly(ethylene) standard yielded 1-octene. Pyrolysis of a poly(propylene) standard yielded 4-methylheptane, 4-methyl-2-heptene, and 4-methyl-2,5-heptadiene. Pyrolysis of a propylene/ethylene copolymer standard yielded 4-methylheptane, 4-methyl-2-heptene, 4-methyl-2,5-heptadiene, 2-methyl-1-heptene, and 1-octene.

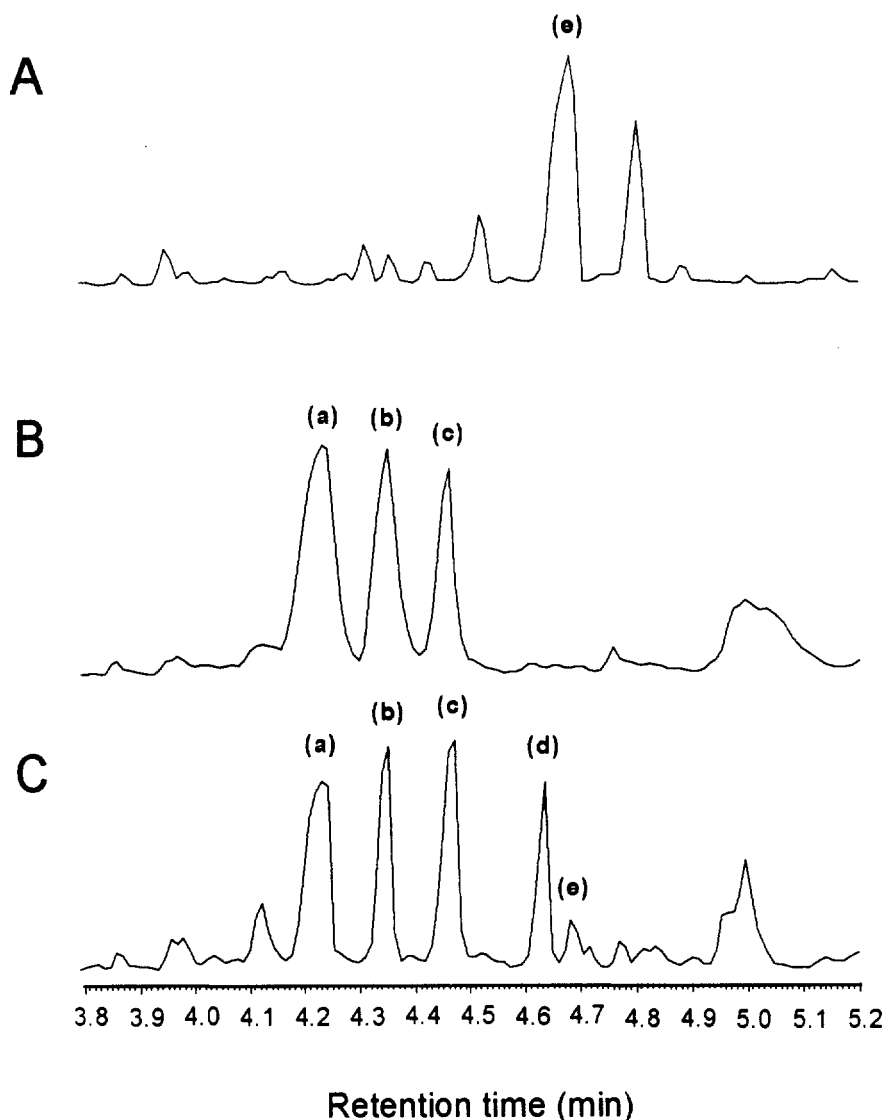


Figure 4. Chromatograms of thermal decomposition products from a poly(ethylene) standard (A), a poly(propylene) standard (B), and a propylene/ethylene copolymer standard (C). The peaks in these chromatograms were identified from their mass spectra and retention times as follows: (a) 4-methyl-2-heptene, (b) 4-methylheptane, (c) 4-dimethyl-2,5-heptadiene, (d) 2-methyl-1-heptene, and (e) 1-octene.

The chromatograms shown in Figure 4 indicate that 2-methyl-1-heptene was formed only by pyrolysis of the propylene/ethylene copolymer standard. The composition of the polymer (mol-% ethylene and propylene) determined the relative amount of 2-methyl-1-heptene in the pyrolysate of the propylene/ethylene copolymer standards. The amount of 2-methyl-1-heptene in the pyrolysate increased was directly proportional to the mol-% ethylene in the polymer increased. Figure 5 shows plots of [2-methyl-1-heptene]/[4-methyl-2-heptene], [2-methyl-1-heptene]/[4-methylheptane], and [2-methyl-1-heptene]/[2,4-dimethyl-1,5-hexadiene] as functions of the mol-% ethylene in the propylene/ethylene copolymer standards, where the brackets indicate the area of the chromatographic peak. The data plotted in this figure represents means of 3 replicate analyses of each standard. The error bar parallel to the abscissa indicates the range in mol-% ethylene supplied with each standard. The error bar parallel to the ordinate is the standard deviation of the 3 replicate analyses.

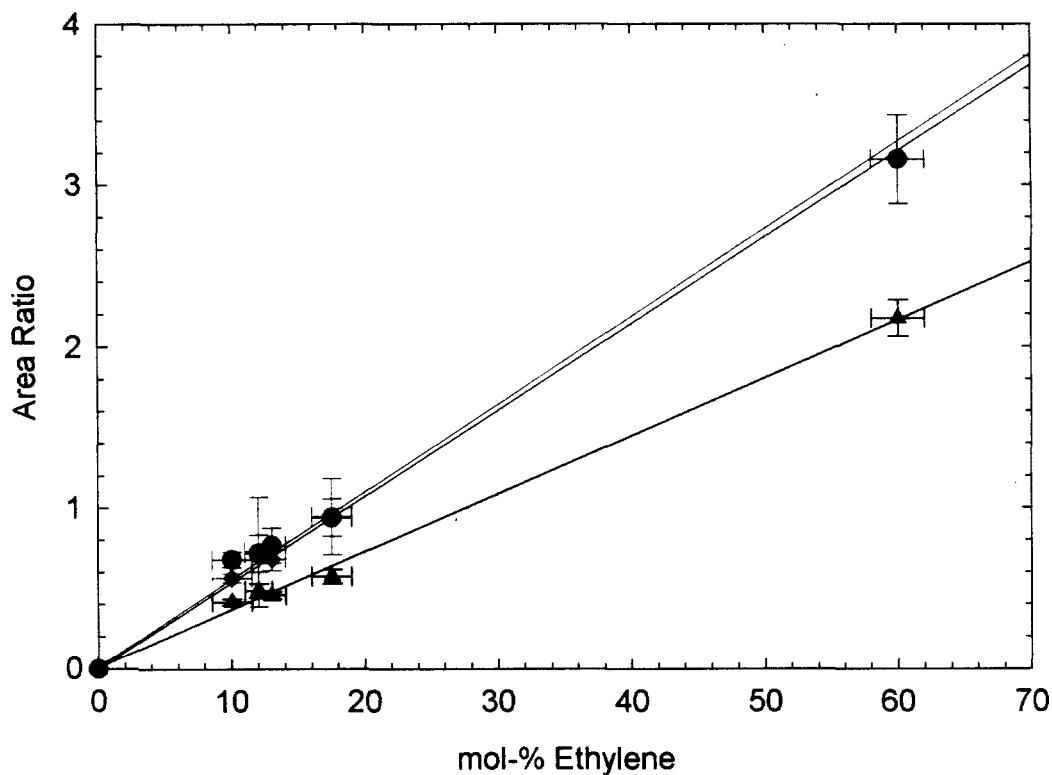


Figure 5. Plots of [2-methyl-1-heptene]/[4-methyl-1-heptene] (\circ), [2-methyl-1-heptene]/[4-methylheptane] (\triangle), and [2-methyl-1-heptene]/[4-methyl-1,5-heptadiene] (\square) as functions of the mol-% ethylene in the propylene/ethylene copolymer standards.

In another study involving identification of the base polymer in 90 components or parts from a 1997 Chevrolet Camaro, 21 of the components or parts analyzed was identified as propylene / ethylene copolymer [5]. The data plotted in Figure 4 was used to determine the mol-% ethylene in these materials. The results of this analysis are listed at Table 2.

Table 2. Mole Percent of ethylene in propylene / ethylene copolymer samples.

Component / Part	Mole % Ethylene
front bumper fascia lower deflector	7.0 - 7.2
headlamp support panel	10.0 - 15.3
front wheelhouse panel liner	5.9 - 8.3
air inlet screen, plastic panel	10.3 - 11.7
radiator air lower deflector	9.2 - 12.0
radiator air lower baffle	22.2 - 27.3
radiator air upper baffle	15.2 - 24.7
air cleaner housing cover	0 - 2.7
mass air flow sensor	6.6 - 7.4
brake master cylinder reservoir	6.8 - 12.7
Battery storage tank	7.2
ABS/TCS relay cover	5.3 - 10.1
wire conduit	4.9 - 9.3
instrument panel compartment – box	0 - 4.0
front floor console door	3.1 - 6.2
front side door trim panel insert	9.7 - 10.4
front side door trim panel map pocket	9.5 - 11.7
quarter inner trim finishing panel	10.5 - 19.0
fuel tank filler pocket	6.5 - 13.6
rear speaker – grille	8.0 - 8.3
rear compartment lift window inner panel cover	13.6 - 19.0

REFERENCES

1. S.L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley-Interscience, New York, 1964, p. 93.
2. Y. Tsuchiya and K. Sumi, *J. Polym. Sci. Part A-1* **7**, 1599 (1966).
3. W. L. Hawkins, *Polymer Stabilization*, John Wiley & Sons, Inc., New York, 1971.
4. C.H. Bamford and C. F. H. Tipper, eds., *Comprehensive Chemical Kinetics*, Elsevier, New York, 1975, p. 59.
5. Jeffrey Santrock; Identification of the Base Polymers in Selected Components and Parts from a 1997 Chevrolet Camaro by Pyrolysis / Gas Chromatography / Mass Spectroscopy. Submitted to the National Highway Transportation Safety Administration pursuant to the Settlement Agreement between General Motors and the Department of Transportation. Submitted XXXX XX, 2002.