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Discrimination Power of Automotive Paint Comparisons using a Paint Analytical Scheme

ABSTRACT

Understanding the discrimination power of each analytical step in the testing process of automotive paint samples is necessary when performing comparisons between known and unknown paint samples. To help evaluate the value of automotive paint evidence, and to compare and validate previous studies, 231 automotive paint samples were microscopically examined using stereomicroscopy, compound comparison microscopy, fluorescence microscopy, and instrumentally analyzed using Fourier Transform Infrared (FTIR) spectroscopy, and a Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy (SEM/EDS). Microscopic examination of the number, thickness, and color sequence of paint layers allowed for differentiation of the majority (99.97 %) of the samples. Sample pairs that appeared microscopically similar using reflected and transmitted light were further analyzed using fluorescence microscopy, FTIR spectroscopy, and SEM/EDS. Two sample pairs remained undifferentiated using these further techniques. Both undifferentiated pairs represented paint samples from vehicles of the same make and model, manufactured two years apart, in the same manufacturing plant. These results indicate that the current trace evidence analysis process and methods allow for significant discrimination between automotive paint samples when comparing known samples to unknown samples, and support the discrimination power of previous studies.

Keywords: Forensic Science, Trace Evidence, Automotive Paint, Fourier Transform Infrared Spectroscopy, Comparison Microscope, Paint Analysis

Automotive paint samples from criminal cases represent a common type of evidence submitted for trace evidence analysis and comparison. Automotive paint serves as a robust forensic sample, as it is generally present in multiple layers of differing colors

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and compositions. The electrocoat primer, primer surfacer, color coat, and clearcoat layers are commonly observed in evidence samples. Each subsequent layer offers the ability to differentiate one sample from another on the basis of physical, chemical and elemental characteristics.

A variety of techniques are commonly used for automotive paint analysis (1), including microscopical and instrumental techniques. Stereomicroscopy, often the first microscope used in the analytical scheme, identifies the outermost layers and any possible layer sequence of a paint sample and is used as a screening tool to categorize and separate different types of paint evidence. Comparison microscopy, using a compound microscope, of paint cross-sections can be used to examine the number, color sequence, and thicknesses of layers present in a paint sample, and observe the side-by-side comparison of two paint samples. Fluorescence microscopy can show differences in organic pigments, additives, and film forming components. FTIR spectroscopy can be used to examine the organic components of the binder present in a paint sample, and can be used to classify general binder types. FTIR spectroscopy is capable of distinguishing between paint samples even when the samples are identified as the same color by the manufacturer (2). SEM/EDS is used to examine the elemental composition of a paint sample, layer by layer. This type of spectroscopy is able to distinguish between two paint samples with different elemental compositions.

Previous work, by Gothard, Ryland and Kopec, and Edmondstone, et al., has established the discrimination power of specific combinations of microscopical examination and instrumental analysis methods for automotive paint evidence (3, 4, 5). Gothard examined 500 total automotive paint samples. By using a combination of microscopy techniques, solvent tests, and instrumental techniques including FTIR and PGC, the study was able to show a discrimination power of 99.998%. The next study, performed by Ryland and Kopec, used a total of 200 automotive paint samples. A 100% discrimination power was obtained with the use of microscopy, solvents tests and an extensive combination of instrumental techniques. The most recent study, done in Canada by Edmondstone et al., used microscopy and FTIR techniques on 260 automotive paint samples, obtaining a 99.997% discrimination power. These types of studies bear repeating, to not only support the previous studies' findings, but also determine if a calculated discrimination power varies when different combinations of analytical techniques are used (e.g., fluorescence microscopy which has not been used in previous studies) or different populations of automotive paints are sampled. Paint type frequencies can change with time (6) and this can be determined with a study of more recent automotive paint samples. This study assesses the discrimination power of the combination of non-destructive analytical methods, including microscopical examinations and instrumental analyses.

METHODS

Sample Preparation

Automotive paint samples (231) were randomly collected from tow lots, junk yards, forensic casework examinations, and personally owned damaged vehicles between 1999 and 2010. These paint samples were collected for the purpose of submission to the Paint Data Query (PDQ) database. There was enough remaining paint from these collected paint samples to keep a portion at the lab. The remaining portions were cataloged into the Crime Laboratories' paint reference collection and used as part of this study. Cross-sections of these samples were prepared and mounted on glass slides using Cargille Quickstick Meltmount mouting medium (refractive index 1.662, Cargille Labs).

Microscopical Examination

Automotive paint samples were examined using a Leica GZ 7 stereomicroscope to document the topcoat color and the presence or absence of effect pigments. Samples were sorted into groups according to the observed topcoat color, excluding the presence or absence of effect pigments. Cross-sections of each sample were then examined microscopically using a Leica DMR comparison microscope, with transmitted and reflected light at 200x magnification. Each cross-section was microscopically compared side-by-side to every other sample within their already pre-sorted color group.

Fluorescence Microscopy

After cross-sections were compared and further sorted into indistinguishable groups based on the samples' layer system: number, color sequence and thickness of layers, an Olympus BX-FLA reflected light fluorescence microscope was used on the remaining indistinguishable pairs. These cross-sections were observed under four excitation filters (WB: blue, 450-480 nm, WG: green, 510-550 nm, WBV: blue violet 400-440 nm, WU: ultraviolet, 330-385 nm) and the results were documented.

FTIR Spectroscopy

All pairs which remained indistinguishable after comparison microscopy were also analyzed using a Thermo Nicolet 6700 Fourier Transform infrared (FTIR) spectrometer with a Thermo Nicolet Continuum microscope attachment with a Mercury Cadmium Telluride-Narrowband detector, and a diamond compression cell as the sampling vessel. Three spectra were collected in different areas of each paint layer by transmission, with 200 scans, to obtain the best overall averaged spectrum for comparison.

SEM/EDS Spectroscopy

Cross-sections of the remaining indistinguishable pairs after FTIR microscopy were analyzed using a JEOL IT300LV Scanning Electron Microscope with an Oxford X-Max^N 50 Energy Dispersive X-ray detector (SEM/EDS). The cross-sections were placed on a carbon adhesive tape and carbon coated with a Denton Vacuum Etch/Sputter coater with a Carbon accessory. Six spectra were collected of each layer of the paint cross-sections and the spectra were examined for the best overall spectra for comparison purposes.

RESULTS AND DISCUSSION

Automotive paint samples were classified by make and year of manufacture, using the documented VIN during the collection phase. The years of manufacture of the vehicles sampled ranged from 1977 to 2009, with the highest number of vehicles (15) coming from 1992. Between 1992 and 2009 the majority of the vehicles were observed, 162 out of a total of 219 (Table 1). There were several vehicles of which the VIN was incorrect or missing, therefore, the year and sometimes the make was undetermined.

Table 1: *Number and percentage of automotive paint samples by year of manufacture*

Manufacture Year*	**Vehicles, *n***	**% of Vehicles**
1977	1	0.4
1981	1	0.4
1982	2	0.9
1983	1	0.4
1984	1	0.4
1985	7	3.2
1986	5	2.3
1987	8	3.6
1988	5	2.3
1989	10	4.6
1990	8	3.6
1991	8	3.6
1992	15	6.9
1993	13	6.0
1994	14	6.4
1995	12	5.5
1996	10	4.6
1997	7	3.2
1998	9	4.1
1999	10	4.6
2000	7	3.5
2001	12	5.5
2002	8	3.6
2003	3	1.4
2004	12	5.5
2005	8	3.6
2006	11	5.0
2007	6	2.7
2008	4	1.8
2009	1	0.4
Totals	**219**	**100**

* VIN was incorrect/missing for 12 vehicles, therefore, the year was undetermined.

There were a total of 19 different manufacturers (Table 2), with the majority coming from General Motors (45 samples).

Table 2: *Number and percentage of automotive paint samples by vehicle make.*

Make	**Vehicles, *n***	**% of Vehicles**
General Motors (GM) (including Buick, Cadillac, Chevrolet, GMC, Oldsmobile, Pontiac)	45	19.8
Chrysler (including Dodge, Eagle, Jeep, Plymouth)	37	16.3
Ford	36	15.9
Honda (including Acura)	22	9.7
Toyota	21	9.3
Nissan	15	6.6
Mazda	10	4.4
Volkswagen	9	4.0
Lincoln	6	2.6
Hyundai	5	2.2
Mitsubishi	4	1.8
Subaru	4	1.8
Audi	3	1.3
Mercury	3	1.3
Jaguar	2	0.9
Volvo	2	0.9
Infiniti	1	0.4
KIA	1	0.4
Mercedes	1	0.4
Total	**227***	**100**

*Four vehicles were two-tone in color and were not counted twice in this chart.

Examination of the topcoat color of paint samples using reflected light on a stereo-microscope allowed for the classification of the samples into nine color groups (Table 3). The most common colors observed were grey/silver, red/purple, and blue (18.2, 17.7, and 17.3% of the total sample set, respectively). Comparing these colors to the previous studies which reported the observed topcoat colors, Ryland/Kopec and Edmondstone, a blue topcoat color was observed within the top three samples for these two studies as well.

Table 3: *Number and percentage of automotive paint samples by the observed reflected light color. Paints were additionally classified based on the presence or absence of effect pigments.*

	Effect Samples		**Non-effect Samples**		**Combined**	
Color Group	***n***	**% of Total**	***n***	**% of Total**	***n***	**% of Total**
Grey/Silver	42	27.6	0	0.0	42	18.2
Red/Purple*	25	16.4	16	20.3	41	17.7
Blue	38	25.0	2	2.5	40	17.3
Black	6	4.0	32	40.5	38	16.4
White	2	1.3	29	36.7	31	13.4
Green	23	15.1	0	0.0	23	9.9
Yellow	7	4.6	0	0.0	7	3
Tan	5	3.3	0	0.0	5	2.2
Champagne	4	2.6	0	0.0	4	1.7
Totals	**152**	**65.8**	**79**	**34.2**	**231**	**100**

*Four purple effect samples were grouped in with the red samples

The presence or absence of effect pigment was also noted for all but seven samples. The majority of the paint samples (65.8%) exhibited having an effect pigment rather than having no effect pigment (32.7%). This is extremely comparable to the numbers which Edmondstone reported, with effect pigments observed in 64.6% of the overall paint samples and 35.4% having no effect pigments reported. These very similar results are understandable since the Edmondstone study examined vehicles around the same time period as this study. However, there is a difference in the effect pigments observed in the Ryland/Kopec study, being performed around 1977, with 57.5 % having metallic pigments and 42.5 % with no metallic pigments. This also is very understandable since manufacturers began to add effect pigment through the years.

The color classifications created using stereomicroscopy were used to group the paint samples for comparison microscopy. Cross-sections of each sample were compared to cross-sections of every other paint sample within the assigned color group. The number of layers (Table 4), color sequence, and thickness of the layers present were considered when comparing two samples. After comparison microscopy, 217 samples (94% of the total number of samples) were individualized; significant differences were observed when these samples were paired with any other sample in their designated color category. Seven pairs of samples (14 total paint samples) appeared similar to one another through comparison microscopy of the cross-sections. These samples were subjected to further analysis to try and differentiate each sample from its pair.

Table 4: *Number and percentage of automotive paint samples by number of layers observed in cross-sections using a comparison microscope.*

# of Layers	Vehicles, *n*	% of Vehicles
2	11	4.8
3	57	24.7
4	86	37.2
5	32	13.9
6	21	9.1
7	6	2.6
8	10	4.3
9	2	0.9
10	4	1.7
11	1	0.4
13	1	0.4
Totals	**231**	**100**

A common initial step in automotive paint analysis is the microscopical examination of the layer structure of the sample. Here, 217 of 231 samples (94%) were individualized using this technique alone. The discriminating power of microscopical comparison is highest for paint samples having a greater numbers of layers. In this study, no paint sample with more than four layers required analysis beyond microscopical comparison for individualization. This concurs with the Ryland/Kopec study where it was observed that it is extremely rare to examine two paint chips with numerous layers, six or more, and find them to be dissimilar.

Sample pairs appearing similar to one another by comparison microscopy were observed using fluorescence microscopy. Of the seven pairs examined, three pairs were differentiated with fluorescence microscopy, while four sample pairs still appeared similar, all having a total of four layers.

The seven pairs of samples appearing similar by comparison microscopy were also fully analyzed using a FTIR microscope. Five pairs showed significant differences in the spectra obtained from one or more layers of the paint. Similar spectra for all layers were observed for only two of the pairs, four total samples (Figures 1 and 2). Both of these pairs represented samples of the same make and model, produced in different years, however, manufactured at the same plants. One pair consisted of paint from a white 2005 Mazda 6 and a white 2006 Mazda 6, and the second pair consisted of paint from a blue 2004 Jeep Liberty and a blue 2006 Jeep Liberty. The addition of SEM/EDS did not allow discrimination of these two indistinguishable paint sample pairs. This is an expected result based on the fact of these two paint samples pairs came from the same make, model, and manufacturing plant. Even though the SEM/EDS instrument showed no further discrimination in this study, this instrument is still considered a useful tool with the addition of elemental composition results for the comparison of paints which are found to be similar.

All of the paint sample pairs which were differentiated through fluorescence microscopy were also differentiated with the FTIR microscope. Therefore, inclusion of fluorescence microscopy may provide relatively quick paint sample discrimination and can decrease the need to analyze samples by FTIR.

Two hundred and thirty-one automotive paint samples were examined in this study. Mathematically this results in the potential of having 26,565 pair comparisons. Four of these pairs were not differentiated using stereomicroscopy, comparison microscopy, and fluorescence microscopy. This means the combination of these analytical techniques alone have a discrimination power of 99.985%. By adding the FTIR microscope to the analytical scheme, an even better discrimination power was obtained. With this instrumental analysis technique added to the combination of microscopical techniques, only two pairs of 26,565 possible pair combinations could not be differentiated, which corresponds to a discrimination power of 99.992%. This is fairly consistent with previous reports of 99.998% (3), 100% (4) and 99.997% (5), using a different combination of microscopical and instrumental techniques. This study validated the high discrimination power of trace evidence analysis of automotive paint samples using a current analytical scheme.

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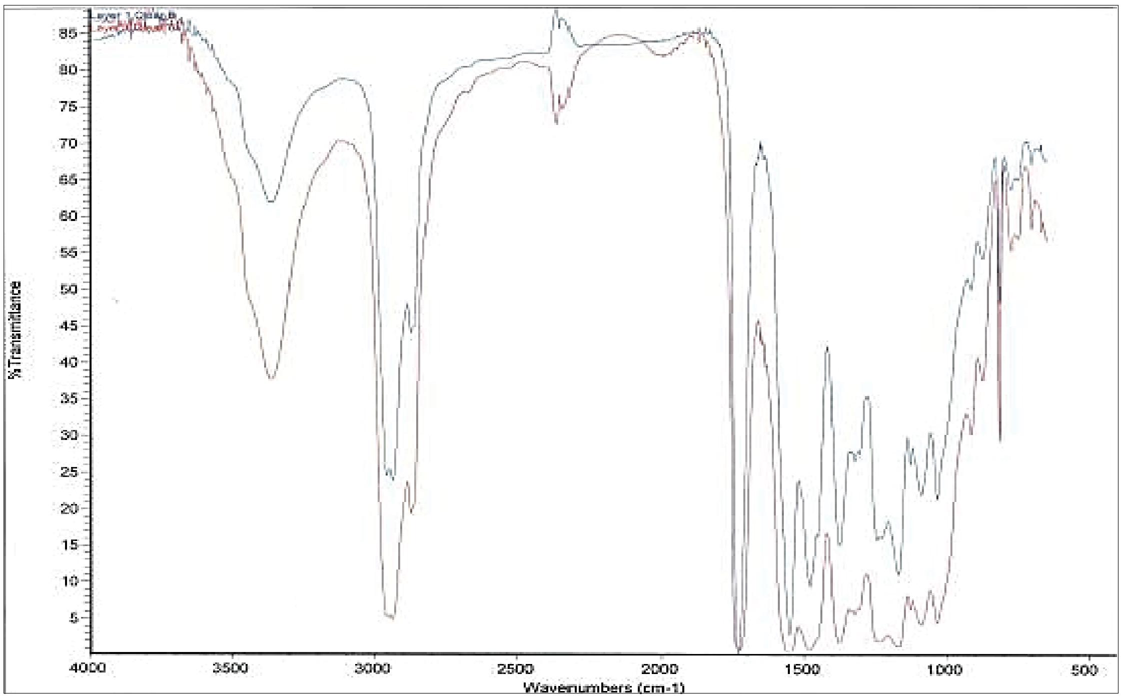

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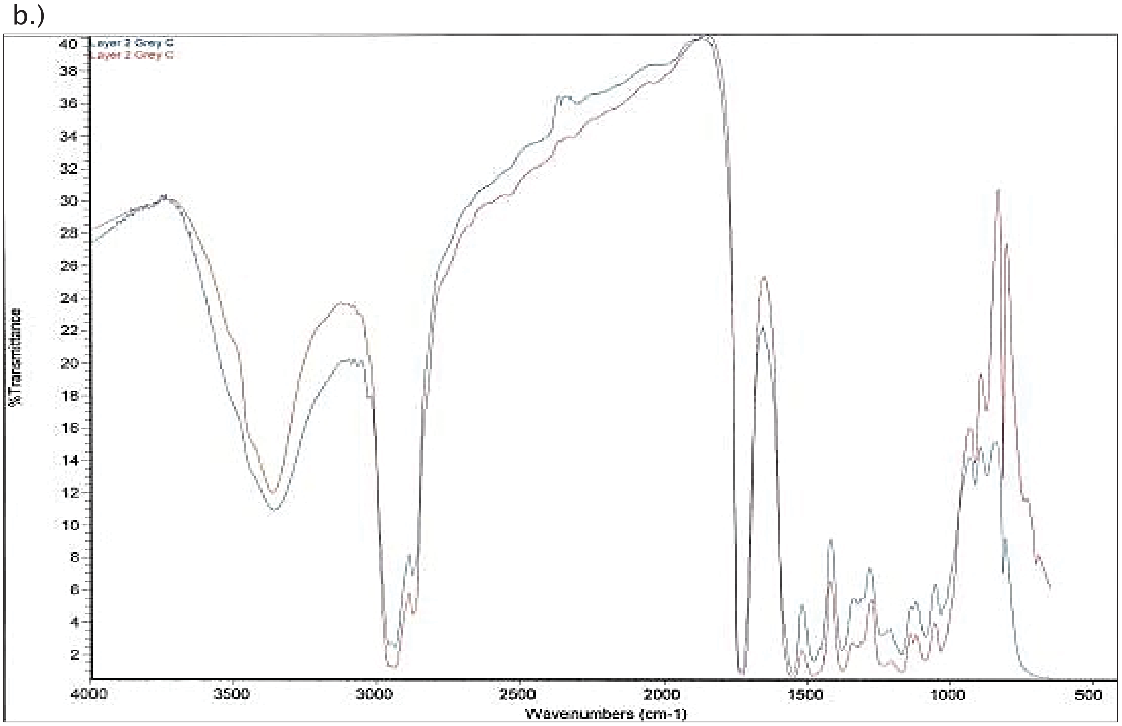

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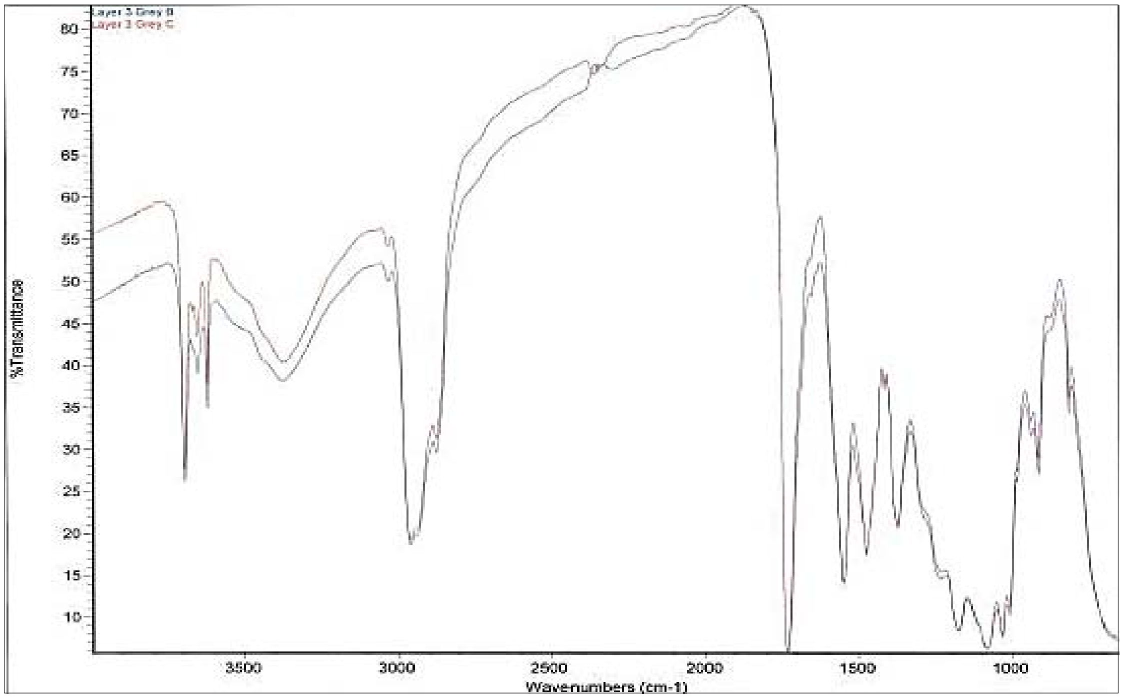

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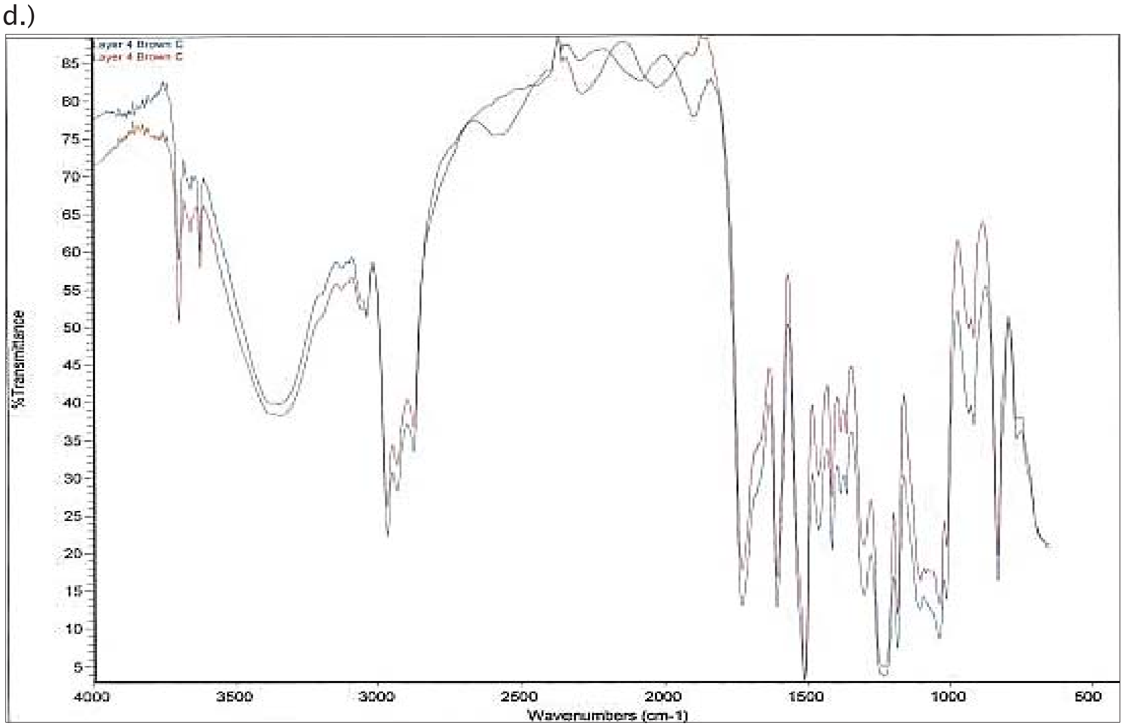
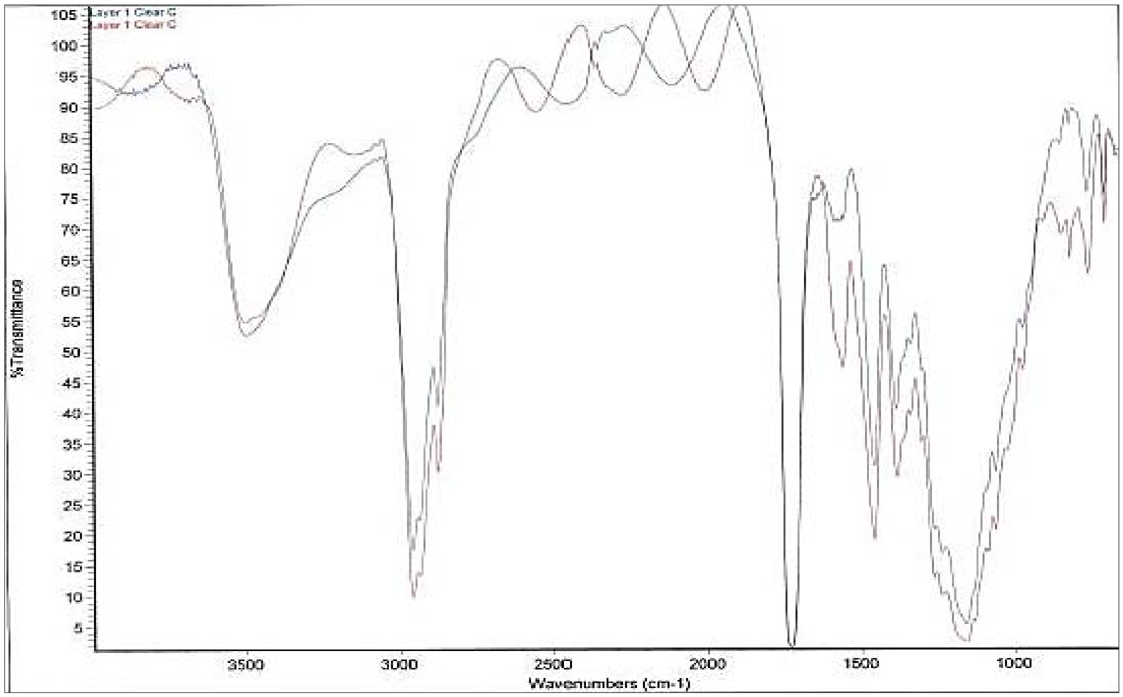


Figure 1: Infrared spectra from the (a) clear top layer, (b) white layer, (c) grey layer and (d) brown bottom layer of the 2005 Mazda 6 (blue spectra) and the 2006 Mazda 6 (red spectra).

a.)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Layer 1 Clear C
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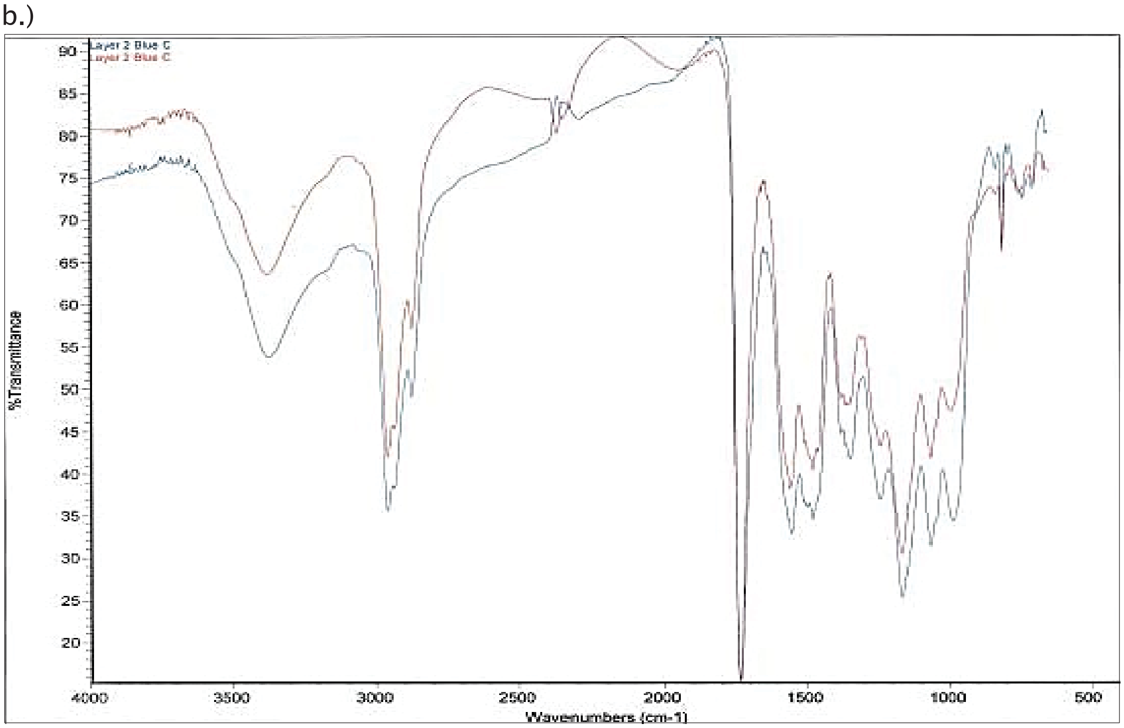
Wavenumbers (cm-1)

b.)


Layer 2 Blue C
Layer 2 Blue C
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Wavenumbers (cm-1)

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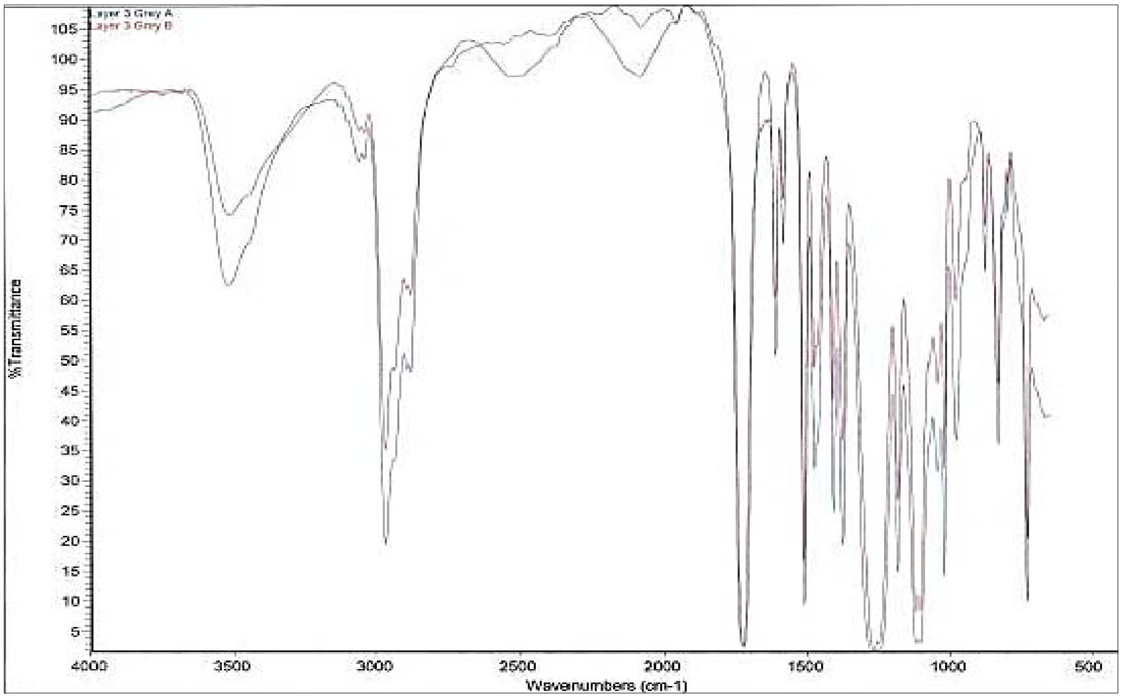

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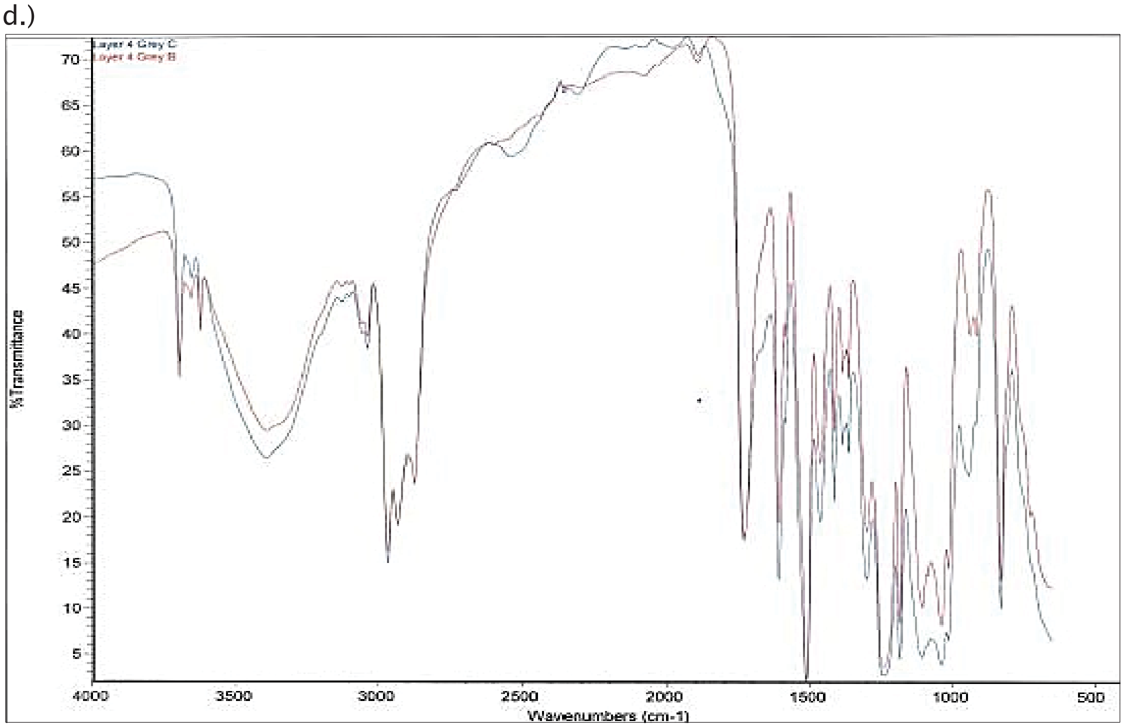

Figure 2: Infrared spectra from the (a) clear top layer, (b) blue layer, (c) grey layer, (d) grey bottom layer of the 2004 Blue Jeep Liberty (blue spectra) and the 2006 Blue Jeep Liberty (red spectra).

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