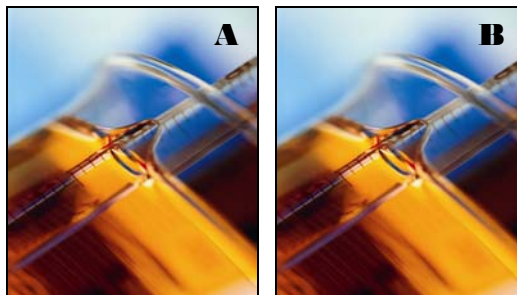


POLYMER SOLUTIONS INCORPORATED

providing quality answers through independent chemical analysis, physical testing, and R&D

A Case Study: Stolen Formulations



A former employee of Company A was discharged, started his own company (Company B), and began producing a specialty coating. Company A, however, suspected that the employee had actually stolen the proprietary formula for this coating. Polymer Solutions Incorporated (PSI) was asked to analyze this coating from Company A and the corresponding coating from Company B to objectively document their similarities and differences.

After extensive analysis, PSI determined that the likelihood of the formula being identical was very high. The corresponding coatings from the two companies showed virtually no difference. The chances of this occurring by coincidence were astronomical.

The Approach

In order to arrive at the conclusion of chemical similarity, Polymer Solutions Incorporated used two major analytical techniques to compare and contrast the coating samples:

- Fourier transform infrared (FTIR) spectrometry
- Capillary gas chromatography (GC)

Approximately 10 mL of each coating sample was placed in a glass test tube and centrifuged until the solids began to settle and the first two or more millimeters from the top of the liquid in the tube was clear of solid particles. This took approximately 15 to 20 minutes. This centrifuging was done in order to separate the liquid fraction of the coating formulations from solid particles. Talc and silica particles present in the formulations could interfere with the Fourier transform infrared spectroscopic analysis.

Two or three drops of the clear liquid from the top of each test tube were placed on a glass microscope slide for the Fourier transform infrared spectroscopic analysis. Approximately 40 to 50 microliters of the clear liquid from the top of each test tube was placed in a 2 mL glass autosampler vial and diluted with approximately 1.8 milliliters of chloroform for the GC analysis.

Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared spectra of the coating formulations were acquired. An infrared spectrum provides a rather unique fingerprint of an organic chemical or mixture of chemicals as a result of absorbance values (peaks) that have specific intensities (the y-axis) at specific wavelengths (the x-axis). Each peak in the



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spectrum represents the absorption of energy by a specific chemical bond or functional group. Every chemical compound or mixture of compounds has its own unique combination of chemical bonds and functional groups and therefore will provide a rather unique infrared spectrum.

Duplicate infrared spectra were acquired from each coating formulation sample. A comparison of the duplicate infrared spectra is shown in Figure 1. As seen in Figure 1, the duplicate spectra for the same sample are nearly identical, as expected.

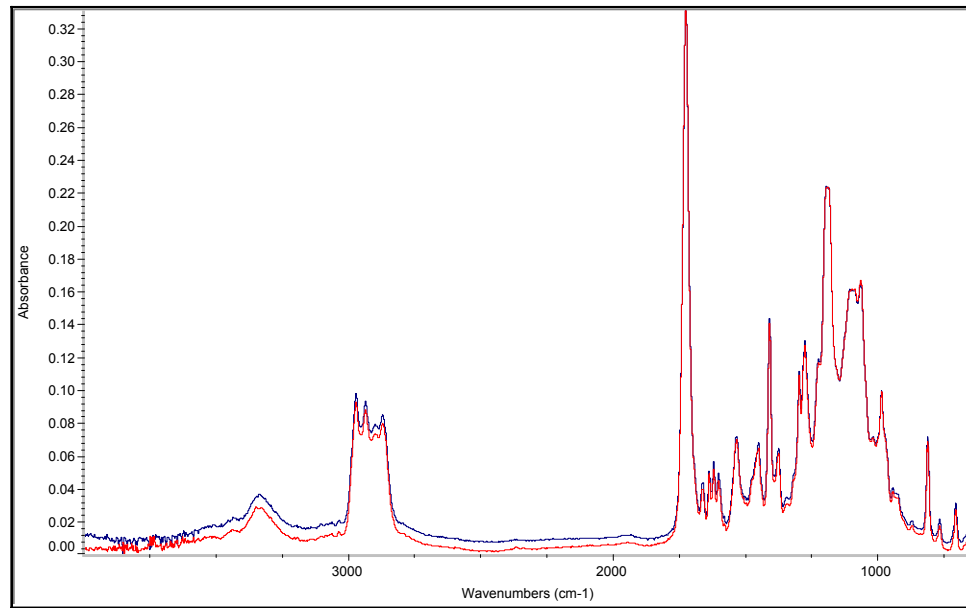


Figure 1. Comparison of duplicate infrared spectra acquired from the Sample A1.

A comparison of the spectra from samples A1 and B1 is shown in Figure 2. As seen in this overlay plot, the two spectra are nearly identical in terms of the locations (x-axis) and intensities (y-axis) of spectral peaks. This is strong evidence that these two coating formulations contain the same components because the positions of the peaks along the x-axis are identical. The nearly identical peak intensity for corresponding peaks indicates that the concentration of each component is very similar in the two coating formulations. If the concentrations of the various components were significantly different between the two formulations, then there would be noticeable differences in peak intensities (y-axis values) between the two spectra in Figure 2. Slight variations in peak intensities could be the result of 1) slight variations in chemical composition between the two coating samples or 2) the inherent variability of the infrared spectroscopic technique.

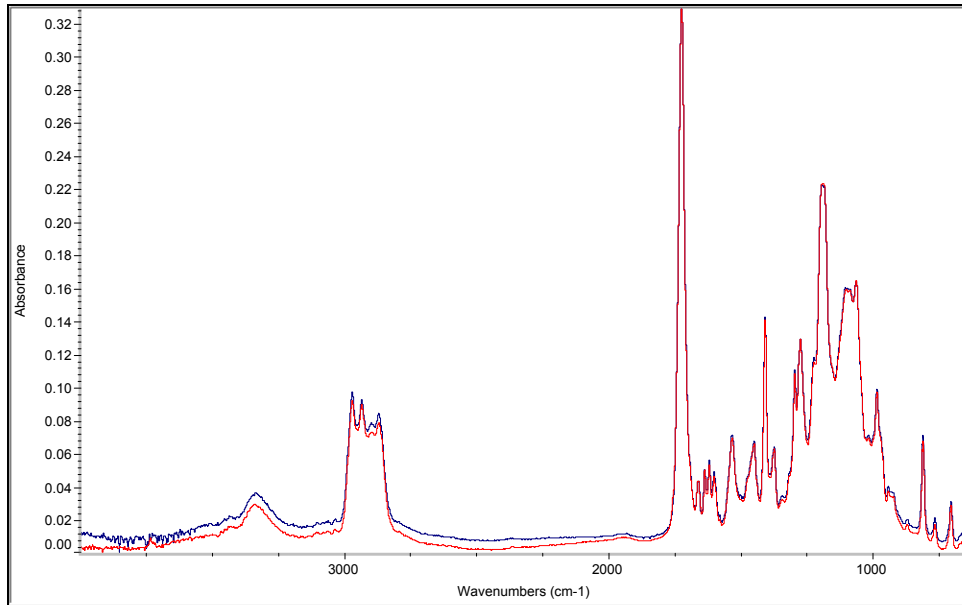


Figure 2. Comparison of the infrared spectra acquired from Sample A1 (blue) and Sample B1 (red).

Infrared spectra can be compared to libraries of other infrared spectra for similarities. Various comparison algorithms have been developed for the purpose of quantitatively rating the similarity between two infrared spectra. Comparison algorithms generate a numerical score based on the similarities of the intensities of the various peaks in the two infrared spectra. Comparison algorithms are typically used to search libraries of infrared spectra in order to find one or more spectra that most closely match the sample spectrum. A match score is generated that quantifies the degree of similarity between each library spectrum and the sample spectrum. The higher the score, the better the match. A score of 100 indicates a perfect match.

The infrared spectra acquired from the four coating samples, which included two duplicate spectra from each coating sample for a total of eight spectra, were placed in a spectral search library. A comparison algorithm was used to rate the degree of similarity between each spectrum and the eight spectra in the search library. The match scores are shown in Table 1. The lower the score, the less similar the two spectra are. Generally, a score of 90 or higher is considered to be a good match.

Table 1. Spectral Match Scores for Duplicate Infrared Spectra Acquired from the Four Coating Samples

	A1(1)	A1(2)	A2(1)	A2(2)	B1(1)	B1(2)	B2(1)	B2(2)
A1(1)	100.00	98.01	97.73	96.97	99.02	98.85	97.79	97.69
A1(2)		100.00	97.65	97.90	99.23	99.30	97.85	97.95
A2(1)			100.00	99.61	98.37	98.33	99.73	99.74
A2(2)				100.00	98.26	98.36	99.58	99.69
B1(1)					100.00	99.68	98.53	98.57
B1(2)						100.00	98.52	98.56
B2(1)							100.00	99.78
B2(2)								100.00

All of the match scores ranged between 96.97 and 100.00. The scores of 100.00, indicating perfect matches, occurred only when spectra were compared to themselves. The highest match scores between different spectra occurred most of the time between the two duplicate spectra acquired from the same sample. This was the case for the A2, B1, and B2 samples. For the A1 Sample, the B1 spectrum actually provided a higher match score than the duplicate A1 spectrum. In other words, the difference between duplicate spectra of the A1 sample was greater than the difference between the A1 sample spectrum and the B1 spectrum. The match scores between the A1 and B1 spectra ranged between 98.85 and 99.30. These are considered to be very high match scores. This indicates a very high degree of similarity between the A1 and B1 coating formulations.

Gas Chromatography (GC)

The four coating samples were analyzed by gas chromatography (GC) on a capillary column, as shown to the right. Gas chromatography separates volatile chemical compounds based on their differing rates of travel through a column through which a gas stream is flowing. A capillary GC column is a very long and narrow column that provides a high degree of resolution of the different chemical compounds in a mixture. The term



resolution refers to the ability to separate and distinguish one compound from another. Two compounds that are retained in the GC column for the same amount of time are said to not be resolved, while compounds that exit the column at different times are said to be resolved. A concentration-sensitive detector positioned at the outlet of the GC column measures the amount of each compound in a mixture as it exits the column. Specific compounds will yield peaks on the x-axis (retention time) having intensities (y-axis) or peak areas that are proportional to their concentrations in the sample. Non-volatile components will not yield peaks and different chemical compounds can yield peaks having identical or nearly identical retention times.

The parameters for the gas chromatographic analysis are presented in the following table:

Parameter	Value
Instrument	Shimadzu GC-17A with flame ionization detector (FID)
Column	Restek Rtx-5 capillary GC column 15 m length x 0.25 mm diameter x 0.25 µm film thickness
Temperature Program	1) Hold at 75°C for 1 minute 2) Heat to 300°C at 15°C per minute 3) Hold at 300°C for 9 minutes
Injection Technique	Split injection, 100:1 split ratio
Injected Volume	1 µL

Samples of the individual components used in the Company A coating formulations were provided to Polymer Solutions Incorporated. The samples listed in the table below were diluted with chloroform and analyzed by gas chromatography in order to establish retention times for each of the volatile components in the coating formulations. It should be noted that the AO acrylate oligomer and the VM viscosity modifier were not volatile enough to be analyzed by gas chromatography; however these two samples contained minor volatile compounds that were detectable by GC. Not listed in the table below were a wax-coated silica powder and a talc powder that were used in the A2 coating formulation. The wax-coated silica and talc additives were not analyzed by GC because they were not soluble in any solvent and thus could not be injected into the GC instrument.

Abbreviation	Chemical compound
AM1	Acrylate Monomer 1
AM2	Acrylate Monomer 2
AM3	Acrylate Monomer 3
AM4	Acrylate Monomer 4
AO	Acrylate Oligomer
PI1	Photoinitiator 1
PI2	Photoinitiator 2
VM	Viscosity Modifier

The gas chromatograms of a pair of coating samples are shown in Figures 3 and 4. The first five minutes of the chromatograms are not shown, because the only major peaks occurring in this region were associated with the chloroform used to dilute the coating samples. Likewise, the last 5 minutes of the chromatograms were not shown because no significant peaks eluted during this time. The peaks associated with the major volatile components are labeled in each chromatogram.

The chromatograms for the pair of coating samples are very similar in terms of the retention times and heights of the peaks that are present. This indicates that the chemical compositions are very similar for the coating samples. Approximately 31 different peaks were detected in the GC chromatograms of the coating samples. These peaks include the major volatile components listed in the above table, as well as minor components present in each of the major coating formulation components. These minor compounds represent impurities present in individual components of the coating formulations.

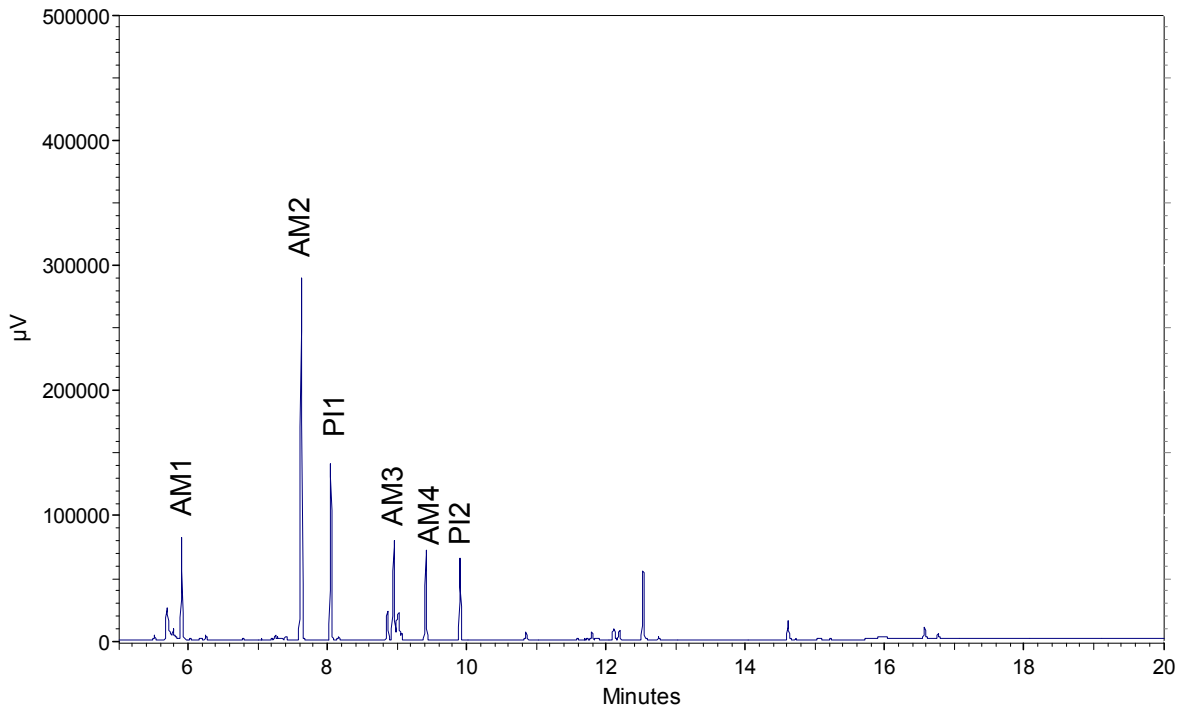


Figure 3. Gas chromatogram of the A1 coating sample.

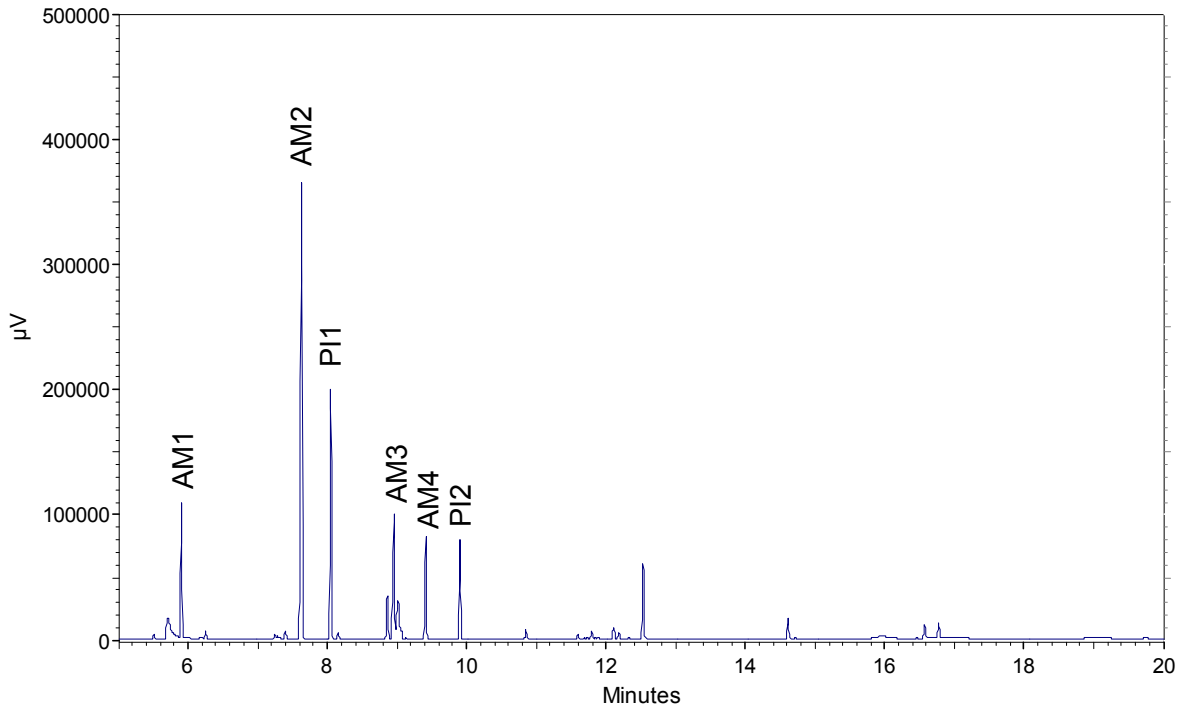


Figure 4. Gas chromatogram of the B1 coating sample.

Table 2. Comparison of the concentrations of volatile compounds in the A1 and B1 coating formulations as a percentage of the total peak area as determined by gas chromatography

Peak No.	Peak ID or Origin*	Retention Time (minutes)	Area Percent	
			A1	B1
1	(AM1)	5.52	0.37	0.34
2	(AO)	5.70	6.05	5.64
3		5.79	0.41	0.00
4	AM1	5.91	7.04	7.15
5		6.20	0.15	0.00
6	(AM1)	6.26	0.31	0.63
7		6.78	0.00	0.00
8	(AM3)	7.25	0.47	0.31
9		7.29	0.36	0.30
10		7.40	0.45	0.63
11	AM2	7.63	29.00	30.50
12	PI1	8.05	13.15	14.25
13		8.16	0.25	0.37
14	AM3	8.96	15.04	15.72
15	(VM)	9.13	0.00	0.13
16	AM4	9.42	6.40	5.70
17	PI2	9.91	5.96	5.60
18	(AM2)	10.85	0.70	0.69
19		11.59	0.15	0.32
20	(AM3)	11.70	0.16	0.17
21	(AM3)	11.80	0.67	0.56
22	(AM3)	11.85	0.29	0.25
23		12.11	1.32	0.97
24	(AM4)	12.19	0.77	0.43
25	(AO)	12.53	5.68	4.69
26		12.76	0.25	0.00
27	(AM2)	14.61	1.59	1.31
28	(AM3)	16.00	1.19	1.01
29	(AM4)	16.57	1.21	1.12
30	(AO)	16.77	0.61	1.21
31		19.74	0.00	0.00
Totals:			100.00	100.00

Entries in boldface type indicate the major peak associated with each component in the coating formulation. Entries in parentheses indicate minor peaks that represent minor additives or impurities in that component.

The concentrations of each GC peak, calculated as a percentage of the total area of all peaks detected in the GC chromatogram, are compared in Table 2 for the A1 and B1 coating formulations. In general, each peak in the GC chromatogram represents a unique chemical compound. Sometimes two or more compounds will have the same or very similar retention times, so a GC peak can represent more than one compound. Thus, the 31 peaks listed in Table 2 represent at least 31 different volatile chemical compounds present in the coating samples. Of these 31 peaks, 6 represent major components in the coating formulation. These are listed in boldface type in Table 2.

The remaining peaks, listed in parentheses, represent impurities and minor additives in the major components of the coating formulations.

The high level of similarity in area percent values between the A and B coating formulations are remarkable, even for the minor peaks in the chromatograms. This information indicates that the chemical compositions of the volatile fractions of the A1 and B1 coatings are almost identical.

Comparisons of the area percents of the major peaks in the GC chromatograms are shown in Table 4. The differences in area percents ranged between 0.1% and 1.5% for the A1 and B1 samples, again showing a very high degree of similarity between the A and B coating formulations. It should be noted that the GC analysis does not measure the concentration of non-volatile components in the coating samples.

Table 4. Comparison of the major GC peaks of the A1 and B1 Coating Samples

Peak ID or Origin	Retention Time (minutes)	Area Percent		Area Percent Difference
		A1	B1	
(AO)	5.70	6.0	5.6	0.4
AM1	5.91	7.0	7.2	-0.1
AM2	7.63	29.0	30.5	-1.5
PI1	8.05	13.2	14.2	-1.1
AM3	8.96	15.0	15.7	-0.7
AM4	9.42	6.4	5.7	0.7
PI2	9.91	6.0	5.6	0.4
(AO)	12.53	5.7	4.7	1.0

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