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The Quantitative Evaluation Of Micro-Coating Composition Using Infrared Spectroscopy

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ABSTRACT

A technique has been developed through which micro-compositional and quantitative analysis of paper coatings are possible. The uniqueness of this method lies in its ability to isolate and measure paper-coating component distribution for a smaller sample than has been possible in the past. Paper coating characteristics are identifiable by combining common microscopy techniques with infrared spectroscopy. The internal structure of the sheet is preserved during analysis by allowing the paper sample to be embedded using traditional techniques and then sectioned using an ultra-microtome. This analysis procedure is unlike most methods for paper coating analysis and does provide accurate representation of paper coatings in isolated areas of cross-sectional samples.

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INTRODUCTION

Coatings are used in the paper industry to enhance the physical properties of the paper surface such as smoothness, ink holdout, etc. There is no such thing as a typical coating formulation. A coating is a complex mixture of ingredients similar in composition to indoor house paints. These ingredients and the method of application can be varied to produce specific coated-paper characteristics. Coating components are selected on the basis of several variables including the characteristics of the base stock, the capabilities of the equipment, the printing method chosen as well as the overall profitability obtainable. Therefore, the formulations are developed based on what you have to work with, what you intend to accomplish, and on how much you can afford. Although the combinations of coating ingredients vary greatly among paper grades, they all contain a combination of pigments, binders, and additives.

Coating Components

Pigments are used in paper coatings to build a fine porous structure that provides essentially two important properties. First, the pigment particles scatter light and secondly the particles help to level the paper surface. Common pigments include kaolin clay, calcium carbonate, titanium dioxide and plastic pigment as well as many others that are less commonly used.

Binders are used to hold individual pigment particles together and tend to fill in the fine porous pigment structure. The binder is responsible for adhering the coating to the base-paper and may also reinforce the surface of the basesheet. One common naturally extracted binder, starch, is produced from corn. Other binders however may be produced synthetically and comprise a complex polymer mixture.

Additives are the most diverse group in the coating formulation and are comprised of miscellaneous ingredients including dispersants, optical brighteners, defoamers, preservatives, dyes, rheology modifiers, etc. Additives are used to enhance the properties of the coated sheet, optimize the pigment dispersion, and control the viscosity of the slurry.

BACKGROUND AND THEORETICAL

Product and process advancements in the paper industry have dramatically changed coating raw materials and the ways in which coating components are used and applied to a fiber substrate. It is often necessary to analyze component interactions with one another as well as the overall effect on the paper sheet. Qualitative and quantitative analytical techniques have evolved over the decades for the analysis of both the physical and chemical coating properties in support of product and process developments.

Analytical Methods

Most analytical methods rely on a qualitative approach in identifying and comparing components within the coating structure. Quantitative techniques are less commonly utilized but are valuable for the evaluation of relatively large areas of interest. An example of a semi-quantitative method to determine the elemental composition of the pigments is a technique which uses a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). This method will determine the relative amount of different elemental pigments used in a coating formulation. Such a technique is used to show apparent filler or pigment concentrations. It does not take into account the actual concentration or amount per unit volume present on the sheet due to the fact that the volume is an unknown variable. The EDS analysis of coatings has the ability to measure only the inorganic components while the organic components such as binders and additives remain undetected.

In contrast to elemental quantitative methods, infrared (IR) analysis can evaluate the organic as well as many of the inorganic components found within a paper coating. IR analysis can be used as a qualitative as well as a quantitative technique through which generalizations can be proposed with regard to component concentration. IR techniques are commonly used within the industry to quantitatively evaluate the coating composition.

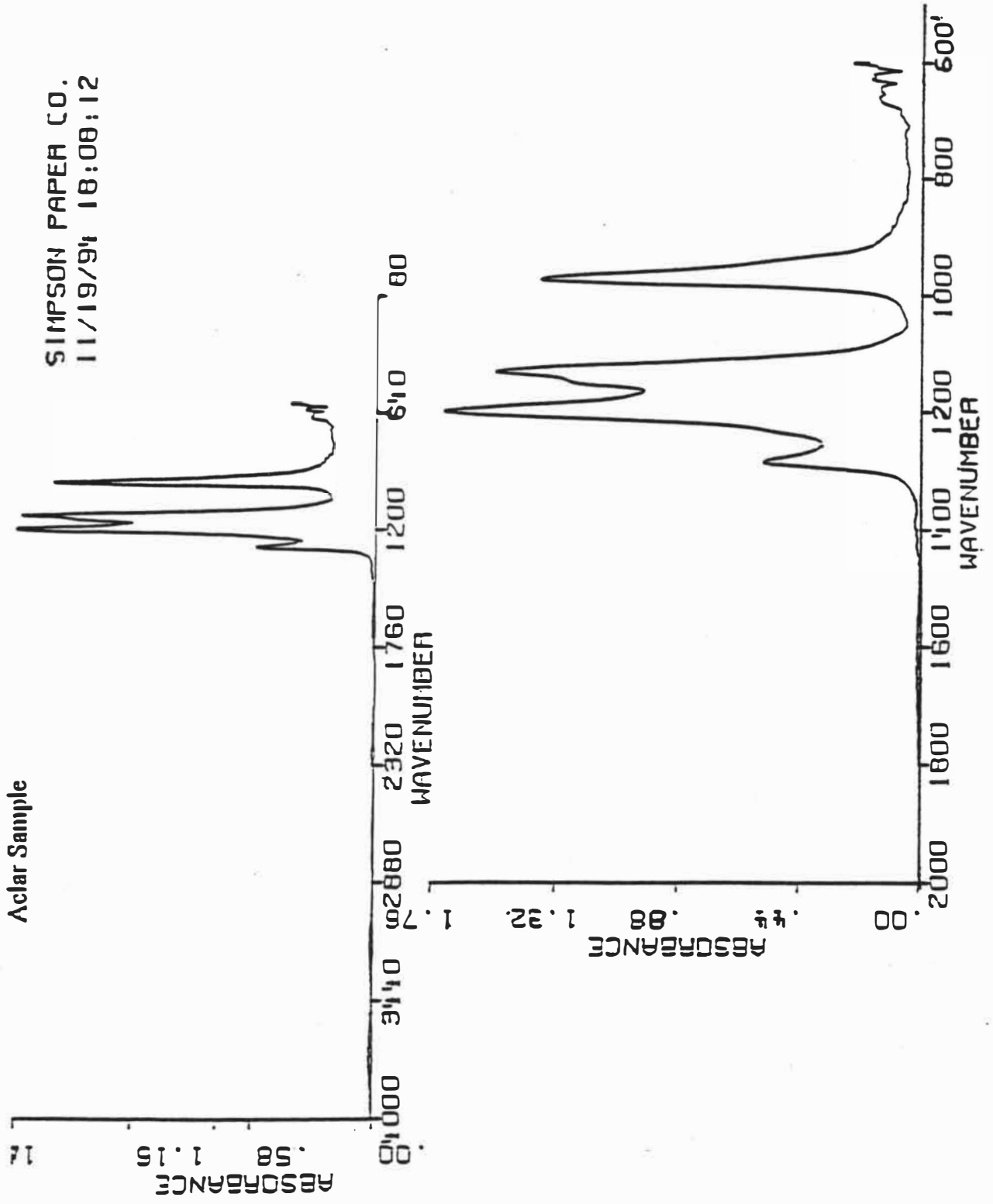
Statement Of Problem

There is a need for new methods which utilize the added capabilities of newer technology available today. The ability to quantify smaller areas of interest may provide valuable information in regard to the chemical composition of samples currently too small for conventional analysis methods. Rick Peterson of Simpson Paper Company proposed that with the combination of IR spectroscopy and conventional microscopy methods, micro-quantitative analysis of coating structures should be possible. The IR micro-spectroscopy project proposed relies on a microtome to cut cross-sectional samples and IR transmittance as the analysis method. The spectrophotometer to be used incorporates a Fourier transform infrared (FT-IR) spectrometer with a microscope attachment. The FT-IR microscope is used to analyze small samples, focusing the IR energy from the spectrophotometer.⁽¹⁾

Fourier Transform Infrared (FT-IR)

The FT-IR is used to generate a characteristic spectrum of absorbance bands over a range of wavelengths expressed as inverse wavelength. A typical spectrum illustrates the absorption of energy with respect to its wave number, generated from a unique molecular property of the sample. An IR spectrum of a commercially manufactured poly-fluoro film is illustrated in **Figure 1 - Aclar™ Sample** (see following page). The spectrum is shown with a wave number range from 4000 to 640, with units of inverse centimeters. The lower plot is an expansion of the spectrum to further show the 2000 to 600 wave number range. An absorption spectrum has two primary characteristics, the wave number at which the maximum absorption occurred and the intensity of absorption at this wave number as compared with the baseline absorption. This absorption spectrum serves to fingerprint as well as quantify components within the sample volume analyzed.

Figure 1 - Aclar Sample



A spectrum provides quantitative and qualitative information as related to the Beer-Lambert laws of Physical Science. Unique to this proposed method is the quantification of coating components which are evaluated on a volume basis and analyzed as the coating exists on the paper surface. Assuming that common volumes are analyzed within a particular sample, the changes in the absorbance can be directly attributed to the quantity or concentration of the individual coating components present within the sample volume. Multiple measurements of the coatings are necessary and variations in the absorbance levels of a known component is of particular interest among spectra for the context of this report. Clay is easily isolated from the other components and will be the focus of this project.

EXPERIMENTAL PROCEDURE

Instrumentation

All infrared spectra were recorded on a Nicolet® Model 740 Fourier transform infrared spectrometer equipped with a Spectra-Tech IR-PLAN® microscope. All IR spectra reported were collected by co-adding 128 scans at a resolution of 8 cm⁻¹.

Experimental Basis

The experimental basis of this project is the analytical comparison of a laboratory-prepared-control or standard-coated sample with that of commercially-produced coated paper samples. The standard-coating sample will be further described later. The ability to correlate results among these samples should show the practicality of the proposed method. Planned work included the analysis of various coated samples and the effect of component density due to calendering.

The initially porous coating is often pressed using machine finishing rolls or supercalendering rolls which ultimately reduces the void volume of the coating structure. Pressing theoretically makes the coating more dense. It is believed that this proposed method has the ability to indicate the relative void volume within coating structures. The void volume of the coating is believed to affect print quality, ink drying rate, print mottle, etc. This method attempts to quantify and correlate these properties with actual coating density.

Experimental Approach

In general, coating thickness varies from sample to sample but are typically between the range of five and fifteen microns thick on the paper surface. Considerable variation in thickness occurs from one area to another as a function of the basesheet structure. An example of how the basesheet may influence the coating structure is illustrated in **Figure 2**, which shows an SEM photomicrograph of the cross-sectional structure of four coated-one-side samples. Traditional microscopy methods have been used for decades to evaluate the internal structural characteristics of paper.^(2,3,4,5) The coated paper sample is preserved in its original state by using typical embedding methods and procedures.⁽⁶⁾ Once the sample is preserved in the fixing media, sections can then be cut from the sample to expose the cross-sectional area of the base paper and coating structure for evaluation. This technique is commonly referred to as paper cross-sectioning and has been practiced for decades. The sections are a few microns in thickness and are cut with an Ultra-microtome® using either glass or diamond knives. This sectioning technique exposes the coating structure thereby allowing traditional transmitted infrared analysis through the Z-direction of the coating. This is more easily understood by examining **Figure - 3**, which shows a two-dimensional photomicrograph (illustrating two surface planes) of a coated paper sample.⁽⁴⁾

The sample volume is calculated from the projected sample area and the section thickness. The sample area is easily measured by restricting the IR energy to a specific area of interest. This is accomplished by what can be referred to as masking the field of view. The IR-PLAN® microscope apparatus uses dual apertures to allow for constant-area sampling. An aperture, with a characteristic circular area of approximately five hundred micrometers², first projects energy through the sample. After the energy is passed through the sample the other aperture is used to eliminate the diffracted or scattered energy resulting from the transmitted IR beam. Since the sections are cut using a microtome and are typically uniform but not of predictable thickness, a method was developed to accurately determine the sample thickness.

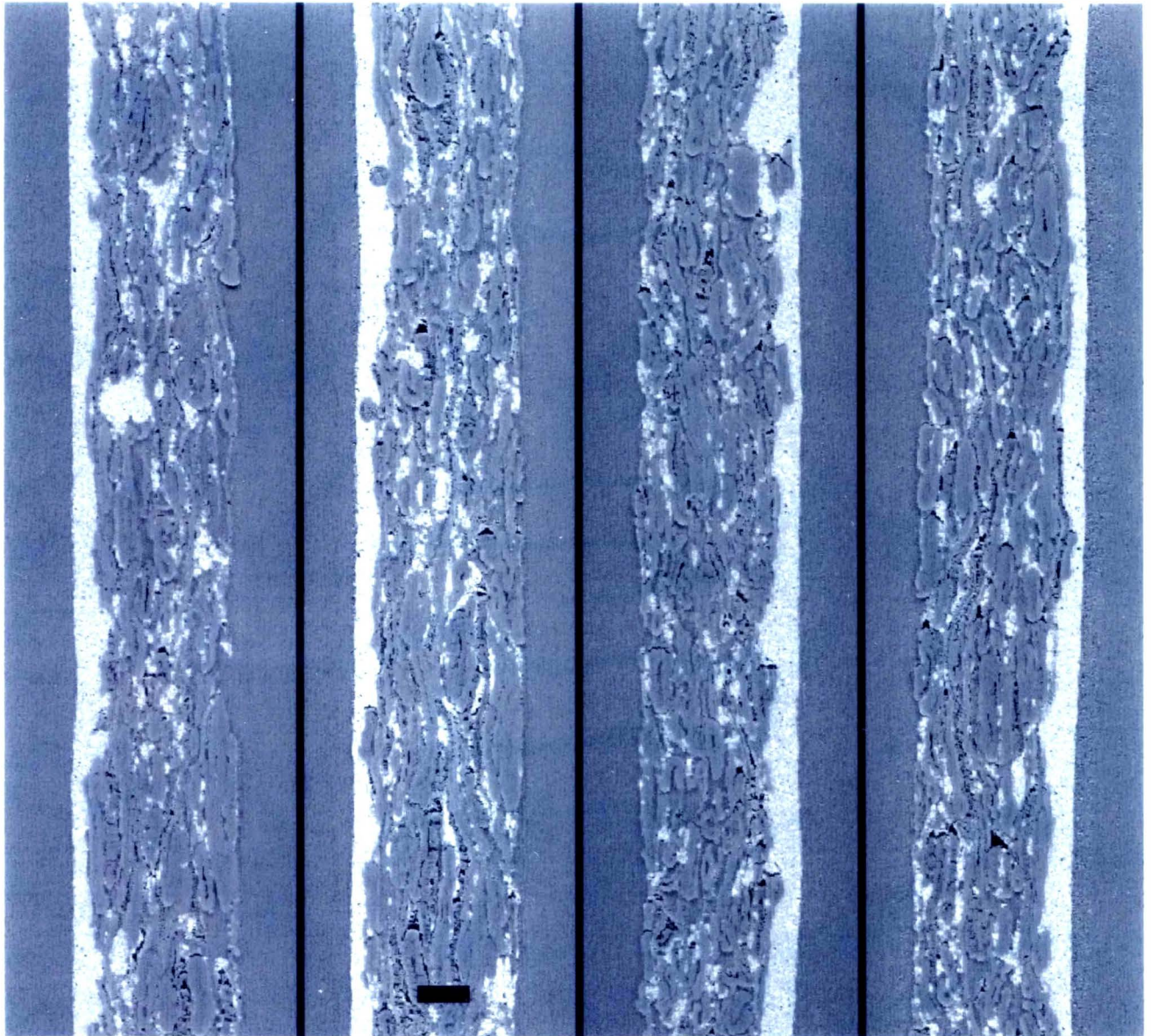


Figure 2 - Typical Coating Structure

Coated One Side Samples

Bright Areas Represent Elemental Filler And Coating Pigments

Scale Bar = 25 Micrometers

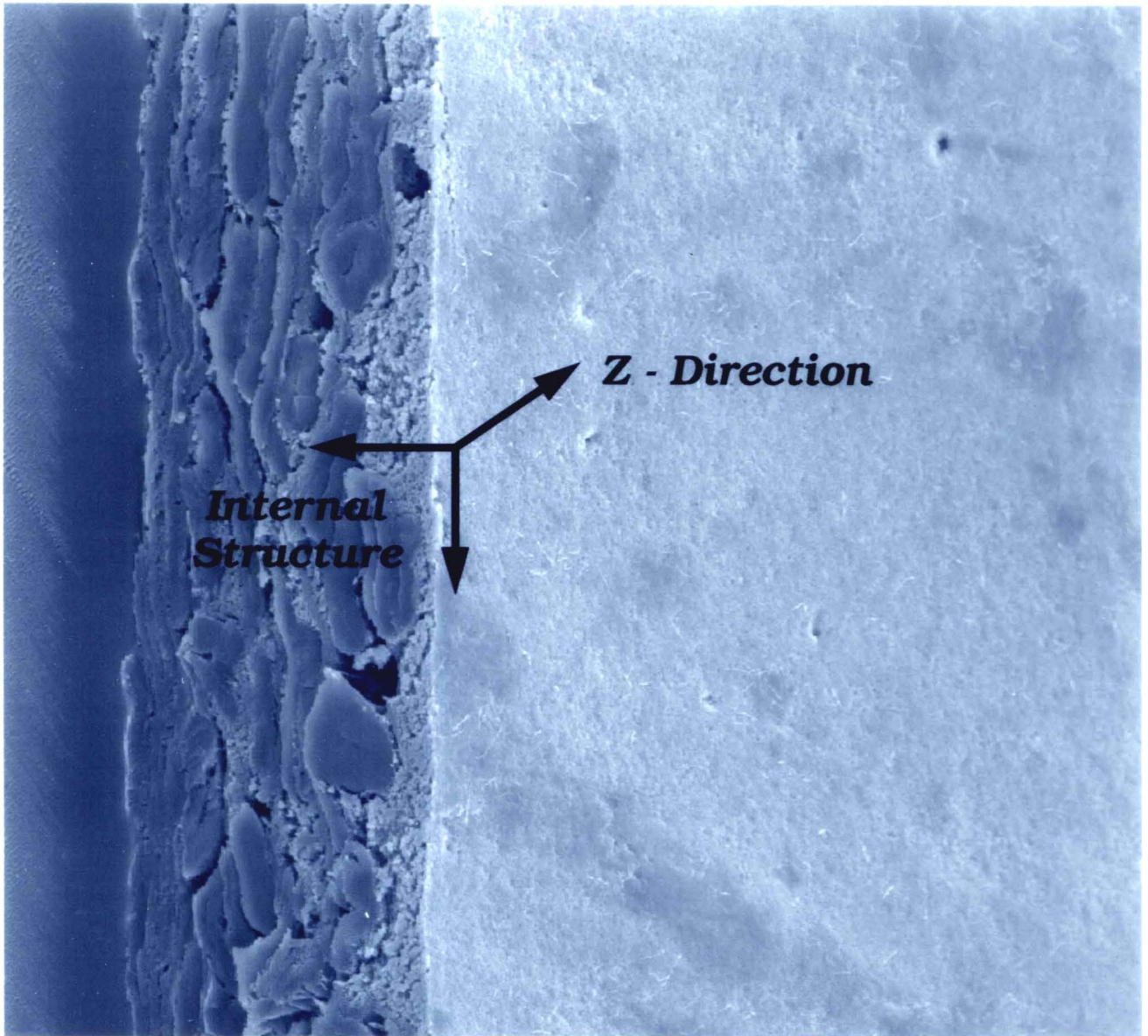


Figure 3 - Two Dimensional Representation

Coated One Side Sample

Quantitative Basis

The determination of thin-film thickness using FT-IR micro-spectroscopy is a well established method.⁽⁷⁾ Application of the Beer-Lambert Law for spectral absorbance provides an easy and more efficient method for determining the thickness of the section using an IR spectrophotometer. In brief, the law states that the absorbance of the spectrum at characteristic wavelengths will be directly related to the mass of the exposed sample. Since the paper and the embedding media cannot be considered homogeneous, to apply this law for section thickness determination, a homogeneous polymer film Aclar is embedded within the section for similar analysis. The sole purpose of this film is to provide an area in which Beer's Law can be applied within the section to determine the sample thickness. The film is placed on top of the coated paper sample and embedded as usual. If the sample area through which the IR energy is transmitted remains constant, according to Beer's Law, the spectral absorbance at characteristic wavelengths would be directly linear to the section thicknesses.

In order to develop an accurate correlation between sample volume and absorbance, a series of Aclar sections of varying thickness was cut and analyzed using a constant circular sample area of twenty-five micrometers in diameter. The absorbance at a characteristic wave number was then compared to the corresponding film thickness to obtain a prediction model for sample thickness determination and associated excitation volume calculations. The side-to-side thickness of individual sections was also determined by taking two spectra from opposite ends and comparing the absorbance at a characteristic wave number. The average absorbance resulting from the two areas of the section was used for determining an absorbance-to-thickness relationship. If the difference between the two similar absorbance peaks for the section was significant (defined as anything greater than 10% error), the data were voided. Thickness values between three and seven micrometers were generally found to be acceptable.

RESULTS AND DISCUSSION

Sample Thickness Verification And Analysis

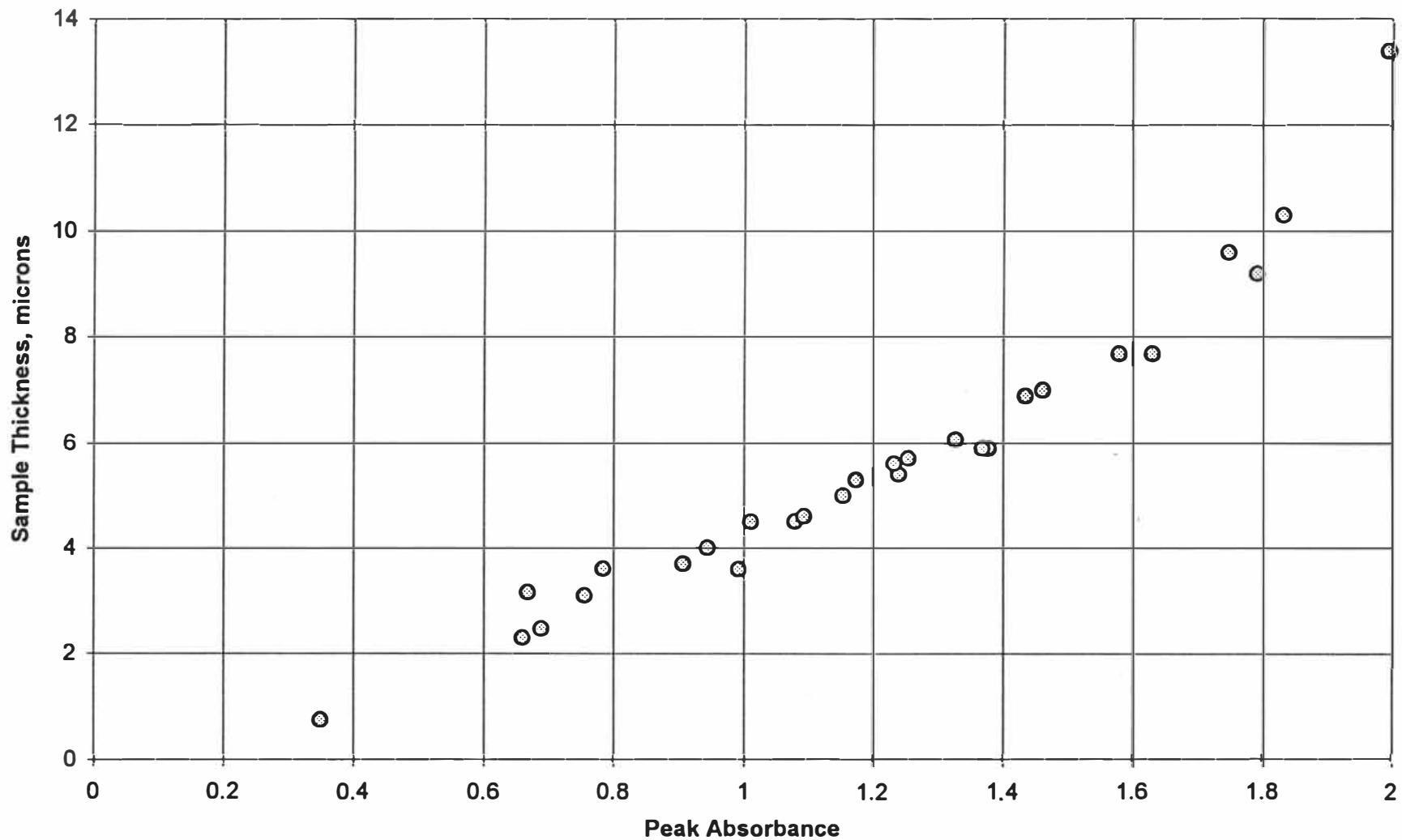
The actual thickness of each Aclar section was measured with an SEM and an image analysis system. The individual sections were embedded between two paper samples acting as supports, sealed, and preserved in a similar fashion as the coating samples were. The sample blocks were then cut to expose the cross-sectional structure of the individual sections. Twenty eight sample sections were evaluated this way to provide an accurate thickness representation for future samples.

The correlation of Aclar section thickness to the absorbance at a characteristic wave number yielded a range from 0.8 to 13.4 microns. The data are listed in **Table I** - Thickness Determination Raw Data. To illustrate the relationship between the sample thickness and the absorbance at a characteristic wave number, the data were plotted (see **Figure 4** - CS Thickness Vs. Absorbance). The plot is fairly linear with a correlation coefficient of 0.97 within the 3 to 7 micron range. The data behaved as expected and should provide accurate section thickness determinations using standard or constant area apertures.

Sample Pre-analysis

To establish a standard basis for the coating evaluation, a laboratory-prepared coated sample was obtained from DuPont® consisting of a 100% clay coating applied to a Mylar™ film substrate of uniform caliper which provided an ultra-uniform coated sample. The binder used for this particular formulation was not reported. The density of this coating was reported as 1.56 gram per cubic centimeter ⁽⁸⁾, with a coating thickness of approximately 6.5 microns on the surface of concern. A structural comparison of this laboratory prepared coated structure to the commercially-produced coated paper sample is illustrated in **Figure 5** - Structural Comparison. Note the obvious natural structural variations within the commercially-produced coated paper structure.

Figure 4 - CS Thickness Vs. Absorbance (All Data)



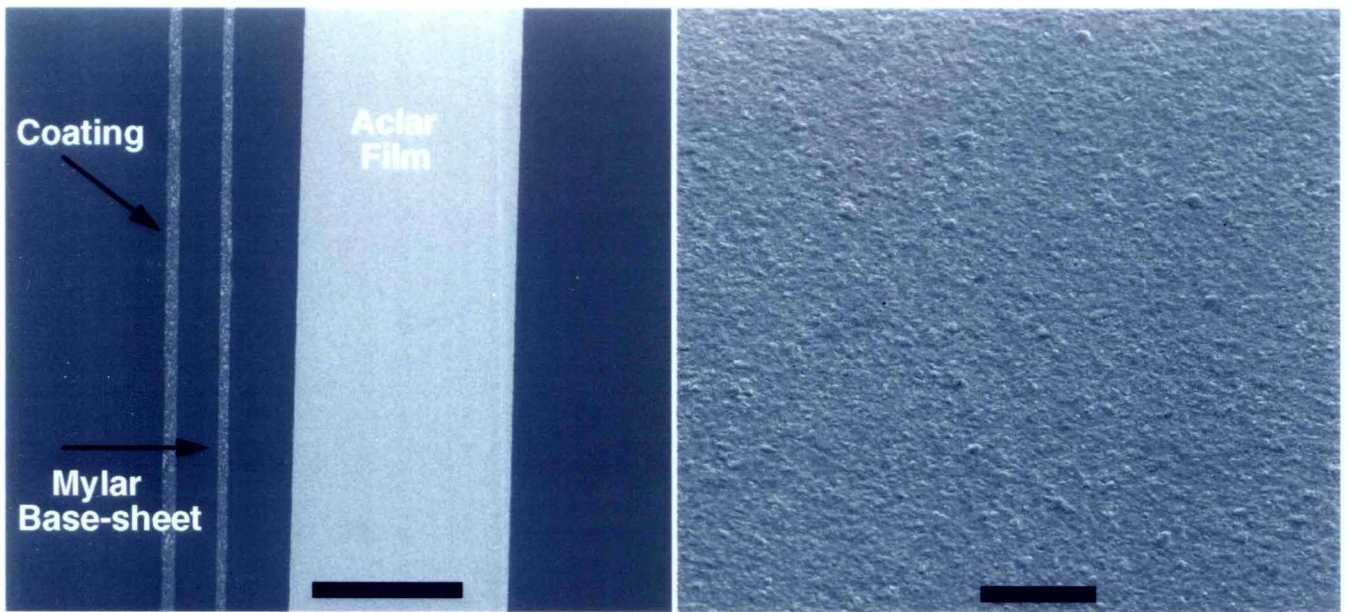
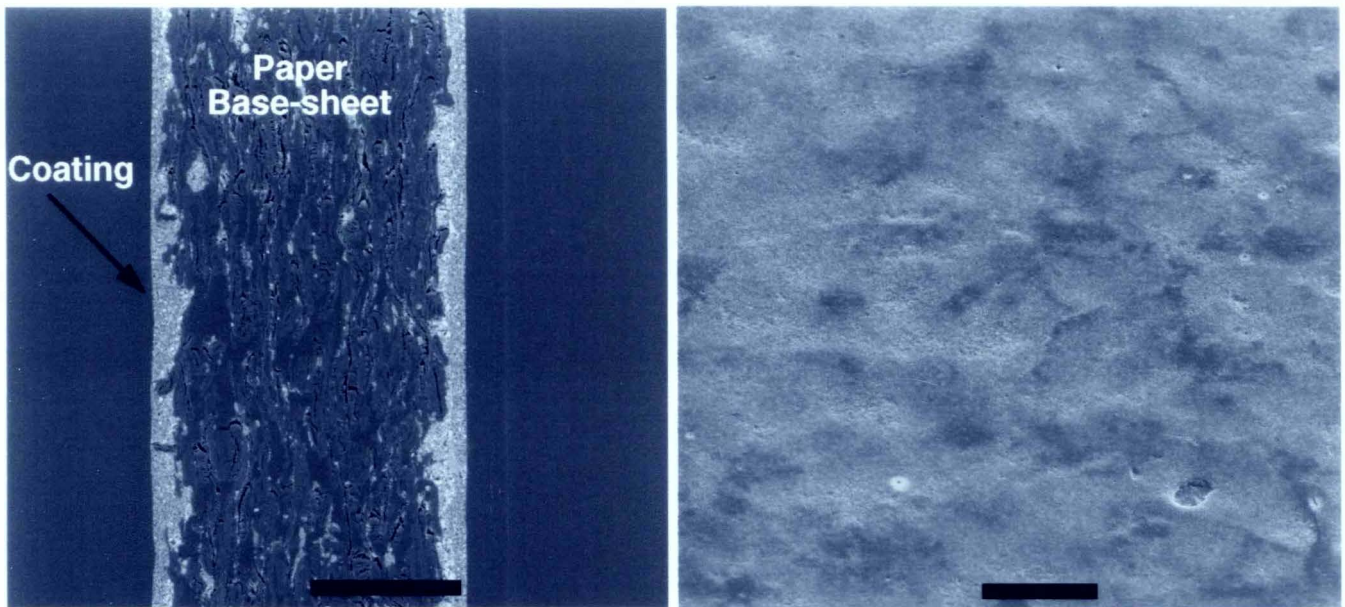


Figure 5 - Structural Comparison
Laboratory Prepared Sample



Commercially Produced Sample

Internal Structure And Surface Topography

Scale Bar = 100 Micrometers

Aperture Configuration

In the development of a constant aperture size to be used for coating analysis, the theoretical limits of the instrumentation were taken into consideration. The IR uses a sinusoidal energy wave and is known to have a wavelength of approximately five to six microns. The Heisenberg Uncertainty Principle would state that the minimum threshold for accurate data is that of the incident IR wavelength. Additionally, this minimum threshold must not be larger than the actual thickness of the coating layer itself for quantitative purposes. The aperture for coating analysis was therefore designed to provide a projected rectangular sample area with a width of 6 microns and a length of 30 microns. The width is at the minimum threshold while the length may be shortened if desired. To put this in perspective, this sample area, (excluding the sample thickness) is approximately 75 times smaller than the smallest dirt speck on the TAPPI dirt chart. At this size, small areas such as mottle and other areas of interest may be easily evaluated without any fiber or other basesheet interference.

Since this standardized area is so small, the apertures require precise alignment in addition to maintaining near constant spectrophotometer operating conditions. To provide a check of the apparatus conditions and aperture alignment, a reference measurement was taken of the Aclar sample after every coating measurement. If a large deviation was observed between the reference areas of concern, the data were voided.

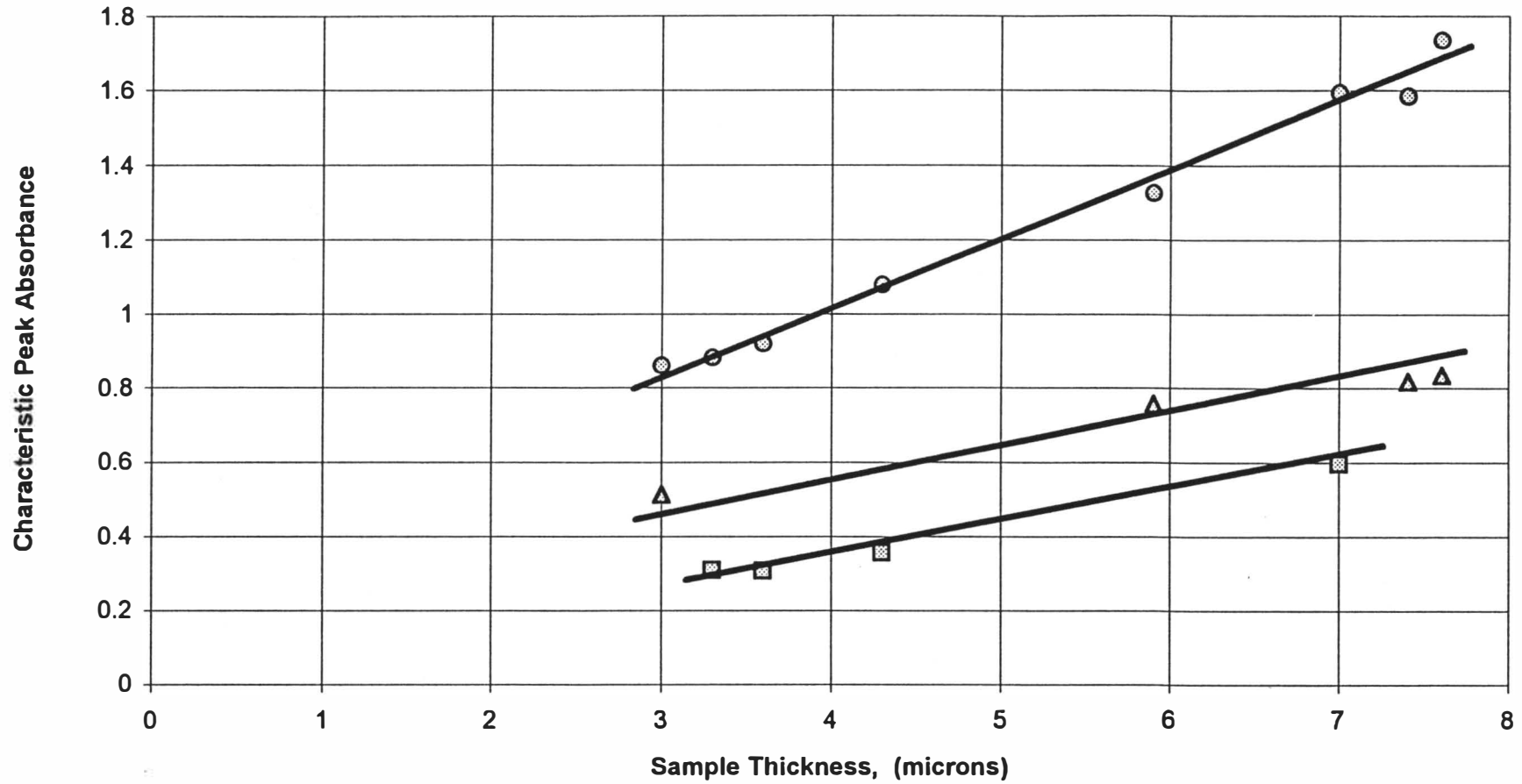
Sample Analysis

The coating component concentration in the standard-coating sample is considered to be uniform and of known density. To check the analysis method for apparent component variances, four areas were analyzed from four separate sections of varied thickness. The variance was determined by calculating the standard deviation from a specific clay absorbance peak and calculating the percent change from this average for each section. The reference Aclar data were also evaluated in a similar fashion for comparison purposes. An example of raw data is illustrated in **Table II** - Absorbance Data For Real And Standard Coated Samples.

The coating component variance for a commercially-produced paper coating sample was evaluated in a similar fashion as the standard sample. The coated paper sample is not as uniform and showed areas of coating which were less than 6 microns thick. Only sample areas with more than 6 microns of coating were experimentally evaluated for variance comparison with the standard-coating sample. Four different sections from the commercially produced coating sample were evaluated for the characteristic clay concentration per unit volume. EDS spectra were obtained for both the standard and commercially-produced paper samples which verified that the laboratory standard sample was comprised of 100% clay while the commercially-produced coated sample showed a relative 50:50 ratio of calcium carbonate and clay. Assuming nearly constant densities between the two coated samples, the standard sample should show approximately twice the clay concentration per unit volume.

Each sample section was analyzed using IR-transmittance at four different locations. The representative clay absorption peak was averaged for each section and plotted against its' associated coating thickness (see **Figure 6**). The absorbance from clay with respect to sample volume was consistently greater for the standard sample as compared with the commercially-produced paper sample which contained a lower amount of clay (see **Table III - Characteristic Absorbance Vs. Sample Thickness**). The importance of this analysis lies in its ability to quantitatively verify an individual component on a volume basis. Analysis of known peaks of other substances may also be evaluated in a similar fashion, but only the clay component was quantified for this project.

Figure 6 - Characteristic Absorbances Vs. Sample Thickness



■ Clay Component of Paper Sample ● Aclar Reference ▲ Clay Component of Standard Sample

Clay Component Evaluation And Comparison

The clay-absorbance average was used for the graphical analysis of the data and the standard deviation from the four sample areas for each section was also evaluated. The standard deviation as calculated from the commercially-produced paper sample data was consistently greater than the standard deviation as calculated from the standard-coated sample. This can mean several things, but may indicate component distribution variance from one area to another on a micro level. This is believed to be reasonable since the control sample displayed greater structural uniformity than the commercially-produced coated paper sample. This particular aspect may be explored in more detail at a later date.

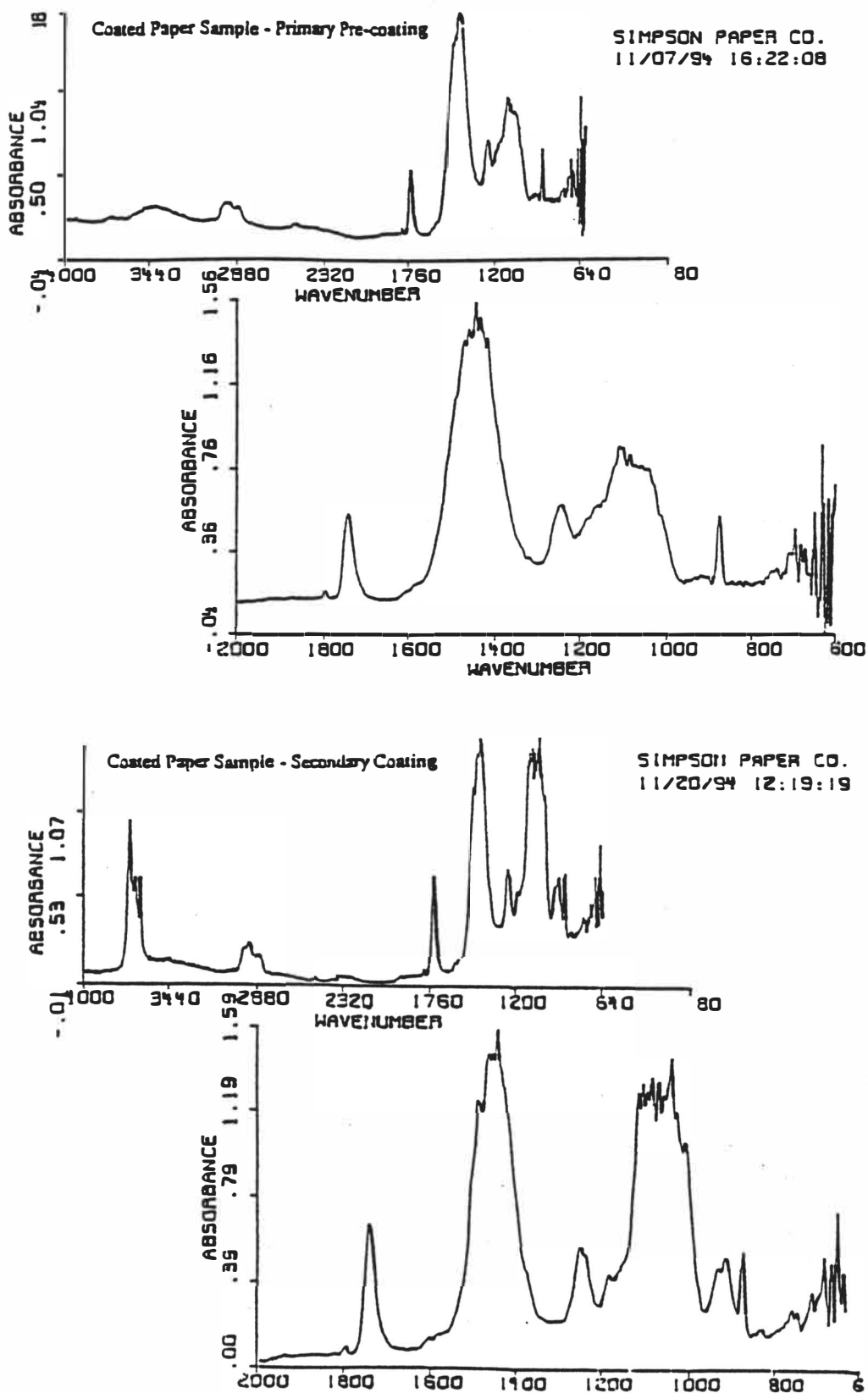
Multiple Coating Layer Identification

Qualitative analysis of separate coating layers on the same surface was also evaluated for a sample having two coating layers on a similar surface. A spectrum was obtained from an area within the thick primary coat layer (applied first), revealing no clay. Another spectrum was obtained from the outer coating layer showing significant clay content. **Figure 7** illustrates this spectral difference observed between the two different coating layers. The wave number absorbance range of 3600 to 3700 is used for the determination of the clay content, particularly at the characteristic 3640 wave number.

Micro-Density Pre-analysis

Preliminary analysis of individual density measurements from one area to another on a single coated sample was not pursued vigorously. The limitations due to the minimum width of the aperture was found to severely limit the usefulness of the technique for this purpose. The surface characteristics resulting from basesheet interference is typically the result of a lack of coating. Most, if not all, areas from the particular sample analyzed where higher density areas were suspected typically had an associated coating thicknesses less than seven microns. The preliminary density analysis work stressed the limitations of the technique but should prove successful if applied to coating areas with thicknesses in excess of six microns.

Figure 7 - Multi-Coating Layer Differentiation



CONCLUSIONS

A technique has been developed through which micro-compositional and quantitative analysis of paper coatings are possible. What makes this method unique is its ability to isolate and measure paper-coating-component distribution and density for a smaller sample than has been possible in the past. Coating-component characteristics were identifiable by combining common microscopy techniques with infrared spectroscopy. The internal structure of the sheet is preserved during analysis using traditional embedding techniques and then sectioned using an ultra-microtome. This is unlike most methods for paper coating analysis and should provide accurate representation of paper coatings in isolated areas of a cross-sectional sample in the future.

The application of this technique was successfully used to determine and verify the clay concentration in coated samples. Differences in the component concentration of clay between a commercially-produced coated paper sample and a laboratory prepared standard-coated sample was consistent with comparable EDS data. This method provided a means to quantitatively evaluate component densities within very small volumes. The application of this method differs from other conventional methods in that it can measure and calculate the actual sample volume. Although the application of this method was successful for clay concentration analysis, it could be applied to other coating components such as binder content if there exists a unique IR wavelength for the component in question.

RECOMMENDATIONS

Plans for future work include the analysis of samples with thicker coat thicknesses and an analysis of the effect which calendering has on component density since void volume of the coating is believed to strongly effect print quality, ink drying, mottle, etc. The ability to quantify and correlate these properties with coating density data using this technique should prove valuable in future applications.

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APPENDICES

TABLE I - Thickness Determination Raw Data

Section ID	Uncorrected Peak Absorbance	Baseline Absorbance	Corrected Peak Absorbance	Average Absorbance	Measured SEM Thickness, (Microns)	% Change
S	0.317	0.016	0.301	0.349	0.8	27.51 %
	0.385	-0.012	0.397			
T	0.630	0.014	0.616	0.659	2.3	13.05 %
	0.694	-0.008	0.702			
U	0.621	0.005	0.616	0.688	2.5	20.80 %
	0.764	0.005	0.759			
KK	0.738	-0.019	0.757	0.755	3.1	0.66 %
	0.768	0.016	0.752			
V	0.635	0.001	0.634	0.667	3.2	9.90 %
	0.690	-0.010	0.700			
JJ	0.844	0.051	0.793	0.779	3.6	3.59 %
	0.786	0.021	0.765			
Z	1.067	0.053	1.014	0.993	3.6	4.33 %
	0.997	0.026	0.971			
R	0.931	0.034	0.897	0.906	3.7	1.99 %
	0.955	0.040	0.915			
PP	0.946	0.017	0.929	0.944	4.0	3.07 %
	0.919	-0.039	0.958			
BB	1.068	0.005	1.063	1.079	4.5	2.97 %
	1.100	0.005	1.095			
FF	1.108	0.066	1.042	1.011	4.5	6.13 %
	1.047	0.067	0.980			
GG	1.182	0.027	1.155	1.174	5.3	3.15 %
	1.213	0.021	1.192			
HH	1.295	0.038	1.257	1.240	5.4	2.74 %
	1.214	-0.009	1.223			
EE	1.312	0.058	1.254	1.233	5.6	3.41 %
	1.212	0.000	1.212			
II	1.298	0.000	1.298	1.254	5.7	7.02 %
	1.214	0.004	1.210			
OO	1.372	-0.002	1.374	1.377	5.9	0.36 %
	1.350	-0.029	1.379			
LL	1.387	-0.018	1.405	1.368	5.9	5.48 %
	1.317	-0.013	1.330			
Y	1.351	0.000	1.351	1.327	6.1	3.69 %
	1.313	0.011	1.302			
NN	1.517	0.052	1.465	1.434	6.9	4.32 %
	1.347	-0.056	1.403			
DD	1.493	-0.008	1.501	1.461	7.0	5.55 %
	1.399	-0.021	1.420			
X	1.647	0.041	1.606	1.630	7.7	2.94 %
	1.687	0.033	1.654			
Q	1.547	0.100	1.447	1.579	7.7	16.72 %
	1.744	0.033	1.711			
P ₁	1.756	-0.002	1.758	1.790	9.2	3.58 %
	1.797	-0.025	1.822			
P ₁	1.708	0.050	1.658	1.747	9.6	10.13 %
	1.822	-0.013	1.835			
W	1.828	-0.011	1.839	1.831	10.3	0.93 %
	1.834	0.012	1.822			
MM	2.012	-0.044	2.056	1.994	13.4	6.27 %
	1.895	-0.036	1.931			

Table II - Data For The Laboratory And Commercially Produced Coated Samples

(I) - Data Representing The Standard Laboratory Prepared Coating Clay Absorbance Characteristics

H1B-E		H1B-E		Calculated Thickness 5.9	
BASLINE	0.020	CORRECTED	0.030		
971	1.215	1.195	1.161		1.131
1128	1.318	1.298	1.313		1.283
1187	1.496	1.476	1.517		1.487
1284	0.568	0.548	0.460	0.430	

H1B-E		H1B-E		Standard Coating Results	
BASLINE	-0.033	CORRECTED	0.004		
3621	0.744	0.777	0.789		0.785
3653	0.737	0.770	0.760		0.756
3883	1.073	1.106	1.048		1.044

H1B-E		H1B-E		WAVENUMBER	Total AVG.	STD. DEV.	Total Change	
BASLINE	0.035	CORRECTED	0.024					
3620	0.776	0.741	0.825					0.801
3653	0.804	0.769	0.759					0.735
3883	1.184	1.149	1.107					1.083
3883				1.096	0.044	4.01%		

H1B-E		H1B-E		Reference Aclar Results	
BASLINE	0.000	CORRECTED	-0.010		
971	1.200	1.200	1.154		1.164
1128	1.324	1.324	1.304		1.314
1187	1.642	1.642	1.496		1.506
1284	0.462	0.462	0.469	0.479	

H1B-E		H1B-E		WAVENUMBER	Total AVG.	STD. DEV.	Total Change	
BASLINE	0.001	CORRECTED	0.002					
971	1.255	1.254	1.269					1.267
1128	1.386	1.385	1.285					1.283
1187	1.783	1.782	1.522					1.520
1284	0.469	0.468	0.460	0.458				
971				1.221	0.048	3.93%		
1128				1.327	0.043	3.24%		
1187				1.613	0.128	7.94%		
1284				0.467	0.009	1.93%		

(II) - Data Representing The Commercially Manufactured Paper Coating Clay Absorbance Characteristics

Y1B-C		Y1B-C		Calculated Thickness 3.6	
BASLINE	-0.040	CORRECTED	-0.024		
971	0.785	0.825	0.785		0.809
1128	0.864	0.904	0.875		0.899
1187	0.961	1.001	0.975		0.999
1284	0.260	0.300	0.268	0.292	

Y1B-C1		Y1B-C2		Real Paper Coating Results	
BASLINE	0.043	CORRECTED	0.016		
3621	0.359	0.316	0.319		0.303
3653	0.378	0.335	0.317		0.301
3883	0.775	0.732	0.662		0.646

Y1B-C3		Y1B-C4		WAVENUMBER	Total AVG.	STD DEV	Total Change	
BASLINE	0.024	CORRECTED	0.055					
3621	0.312	0.288	0.397					0.342
3653	0.318	0.292	0.363					0.308
3883	0.682	0.658	0.713					0.658
3883				0.674	0.039	5.79%		

Y1B-C		Y1B-C		Reference Aclar Results	
BASLINE	-0.021	CORRECTED	-0.017		
971	0.841	0.862	0.891		0.908
1128	0.907	0.928	0.933		0.950
1187	1.006	1.027	0.963		0.980
1284	0.294	0.315	0.302	0.319	

Y1B-C		Y1B-C		WAVENUMBER	Total AVG.	STD DEV	Total Change	
BASLINE	-0.009	CORRECTED	-0.025					
971	0.832	0.841	0.852					0.877
1128	0.865	0.874	0.908					0.933
1187	0.974	0.983	1.015					1.040
1284	0.303	0.312	0.297	0.322				
971				0.872	0.028	3.21%		
1128				0.921	0.033	3.58%		
1187				1.008	0.031	3.08%		
1284				0.317	0.004	1.26%		

Table III - Characteristic Absorbance Vs. Sample Thickness

Sample ID	Measured Thickness, (microns)	Clay Component Absorbance Of Paper Sample	Clay Component Absorbance Of Standard Sample	Reference Aclar Absorbance
STD C	3		0.513	0.861
Real A	3.3	0.31		0.883
Real C	3.6	0.309		0.921
Real B	4.3	0.357		1.078
STD E	5.9		0.758	1.327
Real D	7	0.597		1.594
STD D	7.4		0.818	1.584
STD F	7.6		0.835	1.735