Fourier Transform Raman Spectroscopy for the Analysis of Pigmented Acrylic Latex Films

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INTRODUCTION

Analysis of paints can be a complicated and time consuming procedure. To analyze the pigment content of a dried film would normally require the separation of the pigment from the polymer either through ashing or solvent washing and filtering.[1] This is a destructive and labor intensive method. Nondestructive methods usually involve spectroscopic techniques of which infrared (IR) is the most common. IR and other instrumental methods for the analysis of coatings have been described by Schernau et al.[2] Instrumental methods for the analysis of coatings is also the subject of a recent review.[3]

IR techniques can be conveniently divided into transmission and reflective techniques. Transmission infrared is not suitable for intact opaque films. Reflective techniques include attenuated total reflectance (ATR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and photoacoustic spectroscopy (PAS). ATR techniques are mainly suitable for qualitative analysis because of their low signal to noise ratio. DRIFTS is normally performed on powdered samples dispersed in a nonabsorbing matrix. However PAS has shown some promise in the study of coatings[4,5] and has been used to identify pigments in coatings.[5] These methods have been reviewed recently.[6] Raman spectroscopy is akin to IR in providing similar information although different selection rules apply making the two techniques complimentary. However, it enjoys three significant advantages over IR for the analysis of paints and paint films. Firstly, the Raman effect is due to the inelastic scattering of light by molecules and hence allows paints and paint films to be investigated directly without any sample preparation. Secondly, the requirement of a polarizability change for the Raman effect rather than a dipole moment change, as in the IR, means that symmetric stretches of inorganic pigments as well as the symmetric skeletal vibrations of the paint polymers are more prominent in the Raman spectrum than in the infrared. Thirdly, water-based paints can be studied directly as the H_2O vibrational bands have virtually no effect on Raman spectra. More importantly, the advent of commercial Fourier transform Raman (FTR) instrumentation using a near infrared laser of wavelength 1.064 micrometers (μm) has largely eliminated laser induced fluorescence, which was a problem in earlier Raman instrumentation. Thus, it is expected that FTR spectroscopy

Fourier transform Raman (FTR) spectra of some acrylic latices, rutile titanium dioxide, some common extender pigments, and some acrylic latex paint films were obtained. As expected, all FTR spectra obtained showed considerable differences to their published infrared spectra. It is shown that FTR spectroscopy is excellent for the qualitative analysis of dried acrylic latex paint films and has the added advantages that it is nondestructive and requires no prior sample preparation. Quantitative analysis of extender pigments in dried acrylic latex paint films has also been successful but good quantitative results for titanium dioxide were not obtained. The reason for this is not known.

will find many applications in the study of paints and paint films.

A schematic diagram of an FTR spectrometer is shown in *Figure* 1. A laser beam is directed onto the sample which can be a dry film or a liquid. The scattered light is collected and passed into an interferometer which consists of a beam splitter, a fixed mirror, and a continuously moving mirror. Half the beam travels a fixed pathlength. The other half of the beam travels a pathlength dependent on the position of the movable mirror. When the two are combined, constructive and destructive interference occurs. This is detected and amplified to give the interferogram, a plot of intensity of light versus distance moved by the movable mirror. The interferogram is Fourier transformed by the computer to give a Raman spectrum, a plot of intensity versus wavelength.

There are some previous reports on the use of FTR spectroscopy in the study of paints and coatings. Ley et al.[7] have shown that it is possible to distinguish between the anatase and rutile forms of titanium dioxide in paint films. However, other workers[8-13] have concentrated mainly on the polymeric components of paints. A recent publication describing the

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Table 1—Composition of Paints Used to Test the Analysis Method

	Gloss	Sheen
	kg	kg
Material		
Water	30.0	50.0
Propylene glycol	37.0	50.0
Aqueous ammonia (14M)	1.0	—
Orotan 731 (25%)	—	16.0
Orotan 1124 (50%)	6.0	—
Triton CF10	—	2.0
Triton X45	3.0	—
Foamaster VL	3.0	2.0
Proxel GLX20	1.0	1.5
Primal RM1020	10.0	—
Omyacarb 2	—	50.0
Omyacarb 5	—	50.0
Tioxide RHD2	300.0	300.0
Water	10.0	—
Water	165.3	206.8
Primal AC6501M	659.9	540.0
Texanol	33.0	27.0
Foamaster VL	—	2.0
Aqueous ammonia (14M)	—	2.0
Primal RM1020	—	20.0
Total	1259.2	1318.2
PVC	20.3	31.8
Volume (1)	1000.0	1000.0

principles and the analytical applications of FTR spectroscopy in general has been edited by Grasselli and Bulkin.[14] A more recent review of the use of FTR spectroscopy in the study of synthetic polymers and rubbers has been published by Smith et al.[15]

As the average diameter of paint pigments may range in size from about 0.03 μm to about 100 μm,[16] it is of interest to know the effect of particle size on FTR spectra. Martin and Genzel[17] have shown that, for modes which are both IR and Raman active, and for which the particle size is small compared with the wavelength of the incident radiation, the absorption frequency can change with size. Also, a new band can appear due to surface effects. The intensity of this new band increases with decrease in particle size. Hayashi and Kanamori[18] have confirmed the existence of this new band due to surface effects in gallium phosphide crystals. The particle size of rutile titanium dioxide has been optimized for its hiding power at about 0.25 μm and significant variation from this value is unlikely to be found in paint compositions. Extender pigments, such as calcium carbonate, are likely to be found over a much wider particle size range and are more likely to be larger than 1 μm which is close to the wavelength used for Raman excitation. There are no known reports of the effect of particle size in these size ranges on Raman peak intensities, although it is well known from Mie theory[19] that scattering depends on particle size. Hence, the relative Raman peak intensity of a component in a paint film might also be expected to vary with particle size. In addition, the possibility of latex particles remaining discrete above the critical pigment volume concentration (PVC) may contribute to scattering variations depending on latex particle size. Even below the critical PVC, coalescence may be incomplete and,

therefore, lead to scattering variations also depending on latex particle size.

The aim of this paper is to show that FTR spectroscopy can be used to qualitatively identify pigments used in paints and to semiquantitatively analyze for rutile titanium dioxide and extender pigments in acrylic latex paint films. The method is semiquantitative because it does not allow for the unknown effects of latex composition, extender particle size, or latex particle size.

EXPERIMENTAL

FTR spectra of extender pigments and paint films were recorded using a Bruker IFS 88 interferometer system with an FRA 106 Raman attachment equipped with a near infrared Adlas Nd:YAG laser operating at 1.064 μm. Data acquisition was performed and stored using Bruker OPUS software (version 1.4). All samples were run over a wavenumber range 4,000-50 cm^{-1} using a scanner velocity of 0.17 cm s^{-1} at 4 cm^{-1} resolution with 300 mW laser power at the sample and 180° scattering geometry. Noise reduction for each spectrum was achieved by averaging 250-1,000 scans. A Blackman-Harris three term apodization was used and all spectra were corrected for instrumental effects using the appropriate Bruker software.

The extender pigments studied were calcium carbonate (Omyacarb 10, Omya Southern Pty. Ltd., Melbourne, Victoria, Australia), barytes (Lakabar Micro Barytes), silica (Silica 400WQ), mica (Mica DF), and kaolin (Kaolin K37G). The last four extenders were all from Commercial Minerals Pty. Ltd., Melbourne, Victoria, Australia. Concentrations of pigments in paint are commonly indicated by the PVC defined as the percentage volume of the dry film occupied by the pigment. Paints for quantitative investigations were prepared by making high PVC paints with rutile titanium dioxide and calcium carbonate pigments and diluting these with latex to produce PVC ladders. The rutile titanium dioxide used was RHD2 (Tioxide Australia Pty. Ltd., Burnie, Tasmania, Australia). The acrylic latex used was Primal AC6501M, (Rohm and Haas Australia Pty. Ltd., Geelong, Victoria, Australia). This latex had a nonvolatile content of 50%. The monomer composition was not stated. These paints were used to construct calibration curves and contained no coalescents or other additives except 2% of surfactant (based on pigment) required for pigment dispersion, and ammonia to give pH 8.0-9.0. Two sets of calibration paints were made. The first set contained titanium dioxide and latex with PVC values ranging from 0 to 45%. The second set contained titanium dioxide, calcium carbonate, and latex. The titanium dioxide, in this set, was held constant at 15% PVC and the calcium carbonate varied from 0 to 45% PVC. These paints were drawn down at 47% volume solids and 0.38 mm wet film thickness. They were allowed to dry at

Table 2—Monomer Compositions

Latex Monomer	Methyl Methacrylate	Butyl Methacrylate	Butyl Acrylate	2 Ethyl Hexylacrylate	Acrylic Acid
AC6501M	N/A	—	—	—	—
A	45%	15%	39%	—	1%
B	54.5%	—	—	44.5%	1%
C	54.5%	—	44.5%	—	1%
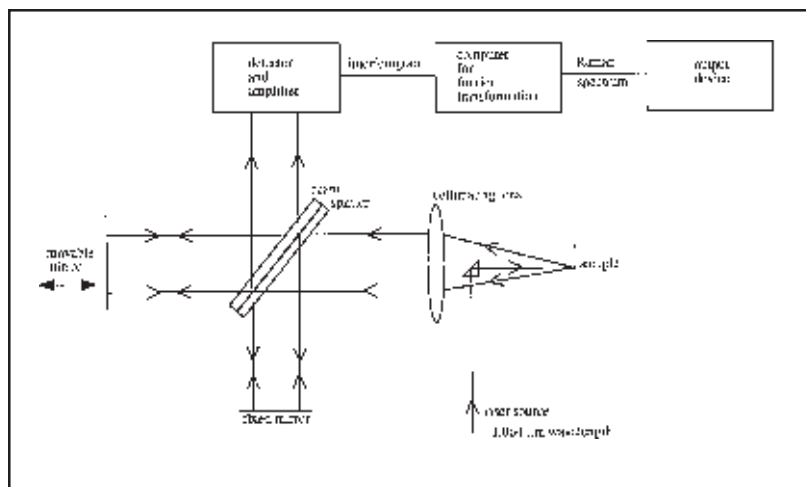
be excessive because of the constraints of coalescence and tackiness required of a latex film suitable for paint formulations. These three latices were designated latex A, latex B, and latex C. The compositions of these latices are shown in *Table* 2.

RESULTS AND DISCUSSION

Individual FTR spectra of a dry acrylic latex film (AC6501M), titanium dioxide, and calcium carbonate are shown in *Figure* 2. FTR spectra of barytes and kaolin are shown in *Figure* 3. Spectra of silica and mica are shown in *Figure* 4. All spectra show features significantly different from their corresponding IR spectra.[20] In the acrylic spectrum, the FTR C=O stretch shows considerably less intensity than in the IR. Also in the region between 1,400 and 900 cm^{-1} lower FTR band intensities are observed. The Raman bands of the polymer, centered at 1,470, 1,750, and 2,900 cm^{-1}, are assigned respectively to the C–C bending, C=O stretching, and C–H stretching modes, and these are used to measure relative concentrations of the latex in the paint films. The titanium dioxide FTR spectra shows much sharper bands than the IR spectrum and is consistent with that reported by Ocana et al.[21] This spectrum shows two weak bands at 144 and 233 cm^{-1} and two intense peaks at 446 and 610 cm^{-1} whose assignments have been previously reported.[22] The latter two intense bands were employed to quantitate titanium dioxide in the latex paints studied.

The calcium carbonate pigment also shows significant differences between the FTR and IR spectra. Without invoking crystal effects, the vibrational spectrum of the carbonate ion would be expected to show four bands v1, v3, v4 (Raman), and v2, v3, v4 (infrared). In the infrared spectrum,[20] the broad peak observed at 1,445 cm^{-1} and the band at 875 cm^{-1} are respectively due to v3 and v2. The 1,087 cm^{-1} (v1) dominates the FTR spectrum and is used here for quantitation of

30°C for 24 hr. FTR spectrometry was carried out on these films.

Two separate acrylic latex paints of known composition were supplied by Rohm and Haas Australia Pty. Ltd. and were used to test the method of analysis. The first was an acrylic gloss paint containing titanium dioxide as the only pigment at 20% PVC and Primal AC6501M latex. The second was an acrylic sheen paint containing titanium dioxide and calcium carbonate pigments. The titanium dioxide was at 21% PVC and latex was also Primal AC6501M. The calcium carbonate was a mixture of 2 μm and 5 μm average particle size at 10.5% PVC. These formulations are shown in *Table* 1. These formulations contained high boiling coalescing agent and so, the films cast from these materials were aged at 110°C for 24 hr before analysis.

Three latices of known, but varying composition, were provided by Taubmans Pty. Ltd. (Villawood, New South Wales, Australia), and were used to investigate the sensitivity of the method towards variation of monomer content of the acrylic latex. This was done because acrylic latices vary in monomer type and content depending on source and application. The variation in monomers will cause a variation in the intensities of the C=O and C–C bands which were used to quantitate the latex in the film. This variation, however, is not expected to
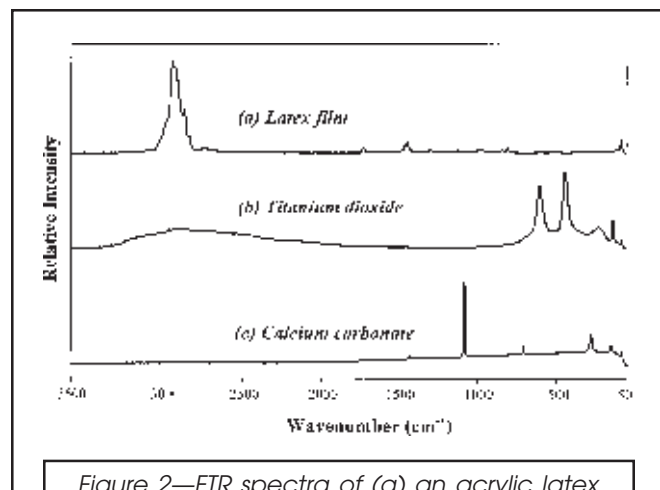

Figure 2—FTR spectra of (a) an acrylic latex film (AC6501M), (b) rutile titanium dioxide, and (c) calcium carbonate.
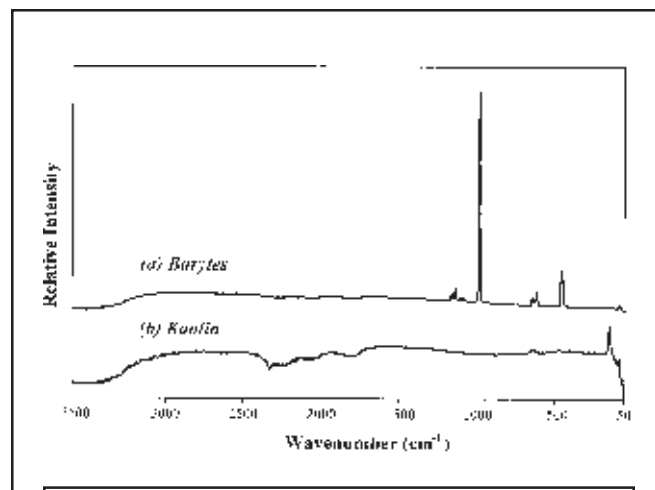

*Figure 3—FTR spectra of (a) barytes, and (b) kaolin.*

Table 3—Comparison of Formulated and Analyzed Pigment Percentages

	Formulated			Analyzed				
	$CaCO_3/TiO_2$	$CaCO_3$/Latex	TiO_2/Latex	$CaCO_3/TiO_2$	$CaCO_3$/Latex		TiO_2/Latex	
					C=O	C–C	C=O	C–C
Sheen Paint	25%	27%	52.6%	26.5%	26%	24%	46.5%	44%
Gloss Paint	—	—	47.5%	—	—	—	36%	39.5%

the carbonate. The weaker Raman bands at 712, 1,445, and 1,740 cm^{-1} are due respectively to the v4, v3, 2v2 of the carbonate,[23] while the low energy intense bands at 281 and 155 cm^{-1} are due to the cooperative latice modes.[24] The v3 and 2v2 bands of the carbonate pigment are close to the C=O and C–C bands of the latex but are fortuitously extremely weak compared to these polymer bands. This makes the FTR a more suitable method of analysis than IR for calcium carbonate.

The FTR spectrum of barytes (*Figure* 3a) shows intense sharp peaks at 1,000 and 460 cm^{-1}. The main peaks in the IR occur between 1,050 and 1,200 cm^{-1} which overlap with IR absorption by the acrylic polymer in this region. Kaolin shows only one small sharp peak at 100 cm^{-1}. The silica (*Figure* 4a) shows only one intense peak at 470 cm^{-1}. The mica (*Figure* 4b) shows two weak bands at 600 and 470 cm^{-1}. Barytes, silica, and mica all show a peak close to 470 cm^{-1} near the titanium dioxide peak. Although the FTR band chosen to characterize each pigment is sufficiently separated in frequency for use in pigment identification, there could be some band overlap which would affect pigment quantitation work. Our results indicate that, although it may be difficult to detect small amounts of mica and kaolin in a paint film, the FTR technique is clearly excellent for rapid qualitative analysis of titanium dioxide, calcium carbonate, barytes, and silica pigments in latex paints.

The capability of FTR, using near infrared excitation, to quantitate paint film constituents was investigated with titanium dioxide and calcium carbonate pigmented films. Unlike most methods of spectroscopic analysis, the paint film need not be destroyed when using the FTR analytical method. The normal practice of adding an internal standard for quantitative analysis cannot be used without destroying the paint film.

Figure 4—FTR spectra of (a) silica, and (b) mica.
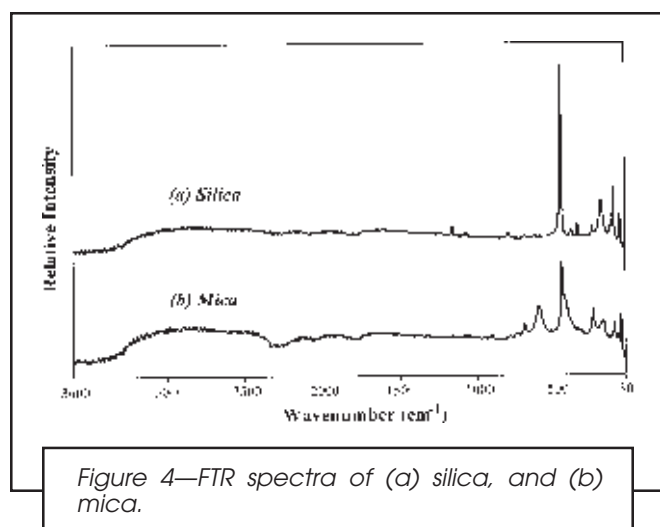
However, if two different substances are present in the film, their relative concentrations can be estimated by comparison of the relative intensities of the respective peaks. *Figure* 5 shows a plot of the ratio of area intensities of calcium carbonate to titanium dioxide against the percentage by mass of calcium carbonate in the pigment for the set of calibration paints using these pigments. The calibration graph has a slight curvature. To test the method of analysis, a sheen paint (*Table* 1) provided by Rohm and Haas Australia Pty. Ltd. was analyzed. The percentage of calcium carbonate to titanium dioxide was found to be 26.5% by mass, compared with the formulated value of 25%. This agreement between the analyzed and

Table 4—Variation in Intensity Ratios and Analyzed Mass Percent for Paints with 47% by Mass of Titanium Dioxide and Latices of Different Composition

Latex	TiO_2/C=O Area Ratio	TiO_2/C–C Area Ratio	Mass Percent Analyzed From	
			TiO_2/C=O	TiO_2/C–C
AC6501M 47.9		15.45	51.5	51.5
A 37.8		12.42	41.2	43.8
B 39.8		12.08	43.8	43.2
C 39.4		13.02	43.5	45.6

the formulation value is good, especially as the calcium carbonate was a mixture of 2 μm and 5 μm particle sizes, both of which were smaller than the 10 μm calcium carbonate used in the calibration curve paints.

Relative quantities of pigment to polymer can be estimated by comparing areas of pigment peaks with the C–H stretch at 2,900 cm^{-1}, the C=O stretch at 1,750 cm^{-1}, and/or the C–C bend at 1,470 cm^{-1}. *Figure* 6 shows a plot where the x-axis gives the percentage of calcium carbonate to latex solids and the y-axis denotes area ratios of the calcium carbonate peak (1,086 cm^{-1}) to the C–H stretch, C=O stretch, and the C–C bend, respectively. The area ratio of calcium carbonate to C–H does not show a monotonic increase with the percentage of calcium carbonate to latex solids. The reason for this unexpected result is not known, and it does not allow the C–H peak to be used for quantitative analysis. The C=O and C–C peak ratios give slightly curved calibration plots. To test the method, the same sheen paint was used and found to have a percentage of calcium carbonate to latex solids of 25% compared to the formulated value of 27%. The found percentage is the average of using both the C=O and C–C bands.

The titanium dioxide to latex solids percentage can also be estimated from calibration curves shown in *Figure* 7. The percentage titanium dioxide to latex solids is given on the x-axis while the y-axis represents area ratios of the combined titanium dioxide peaks (610 and 446 cm^{-1}) to the C–H, C=O,

and C–C peaks. Again the titanium dioxide/C–H peak ratio does not show a monotonic increase with percentage of titanium dioxide to latex solids. The reason for this is unknown and does not allow the C–H band to be used for analysis. To test the method of analysis, a formulated gloss paint (*Table* 1), as well as the sheen paint, was used. These results are shown in *Table* 3 along with the previous quantitative results. The measured titanium dioxide content was found to be lower by as much as 20% compared to that of formulated values. The gloss paint shows a greater discrepancy than the sheen paint. These results are certainly not as good as those obtained for the calcium carbonate to titanium dioxide percentage or the calcium carbonate to latex solids percentage in spite of good calibration curves in all cases. The reasons for low values of percentage titanium dioxide to latex solids are uncertain. One possible explanation is the continued presence of 2,2,4, trimethyl pentanediol monobutyrate coalescing agent which also possesses both the C=O and C–C bonds. The persistence of this coalescing agent in the film was not tested but simply assumed to be absent after curing 24 hr at 110°C. However, if some coalescing agent were still present, the calcium carbonate to latex percentage in the sheen paint would be similarly affected and should show a low value as this coalescing agent was also employed in this formulation. The fact that this is not the case suggests that other factors, as yet unidentified, may be more important.

There are many possible combinations of monomers that can be used in the manufacture of acrylic latices. Most latices will show a C–H, C=O, and a C–C absorption and the ratios of the C–H, C=O, and C–C absorbances will vary depending on the composition. When attempting to determine the pigment content of an acrylic latex of unknown composition using FTR, the results can only be approximate unless the calibration curves used are constructed from a latex with the same composition as the unknown. However, the uncertainty introduced by not knowing the composition is not expected to be excessively large as monomers must be chosen to give a narrow range of physical properties. Other monomers with different chemical groupings, such as acrylonitrile or styrene, which could be used in latices, would be easily detected by FTR. To estimate the range of results which could be expected due to variation in composition of the latex, three titanium dioxide paints were made with acrylic latices of three different monomer compositions. These compositions are listed in *Table* 2. The paints all have a titanium dioxide to latex solids percentage of 47%. The area intensity ratios of titanium dioxide to latex and the determined compositions are shown in *Table* 4. It can be seen that all the latices of known composition give measured titanium dioxide values which are up to 15% lower than the actual value of 47%. However, these results are not as low as those obtained for the formulated paints. In *Table* 5, the estimated mol per gram of latex solids, of C=O and C–C bonds is shown for the three latices of known composition. The determined percentages of titanium dioxide to latex should inversely correlate with these concentrations. They do not and this indicates that experimental error is likely to be larger than the effects of latex composition. There is a 7% variation for C=O and a 5% variation for C–C for the three latices A, B, and C. Both variations are considerably lower than the variation in the analyzed results and, therefore, it appears that variation in monomer composition cannot be considered as the major source of inaccuracy.
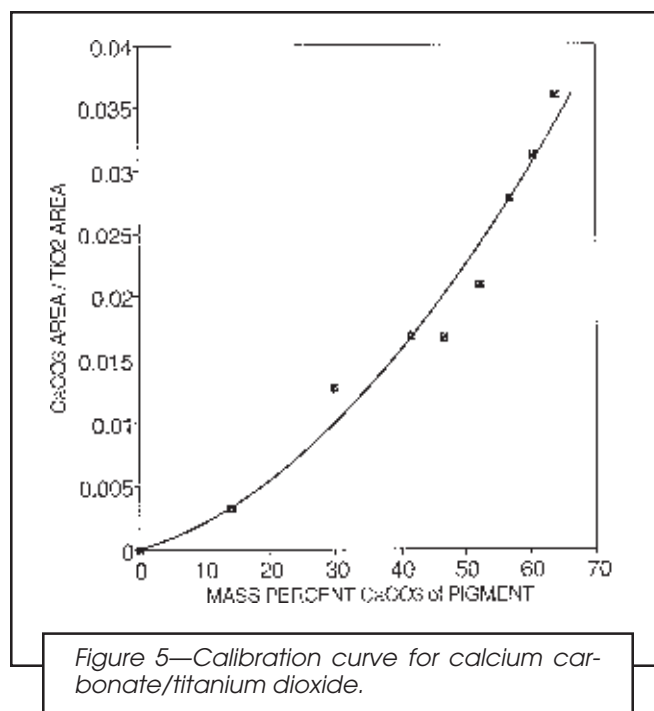

Figure 5—Calibration curve for calcium carbonate/titanium dioxide.

Table 5—Variation in C=O and C–C Content for Latices of Different Compositions

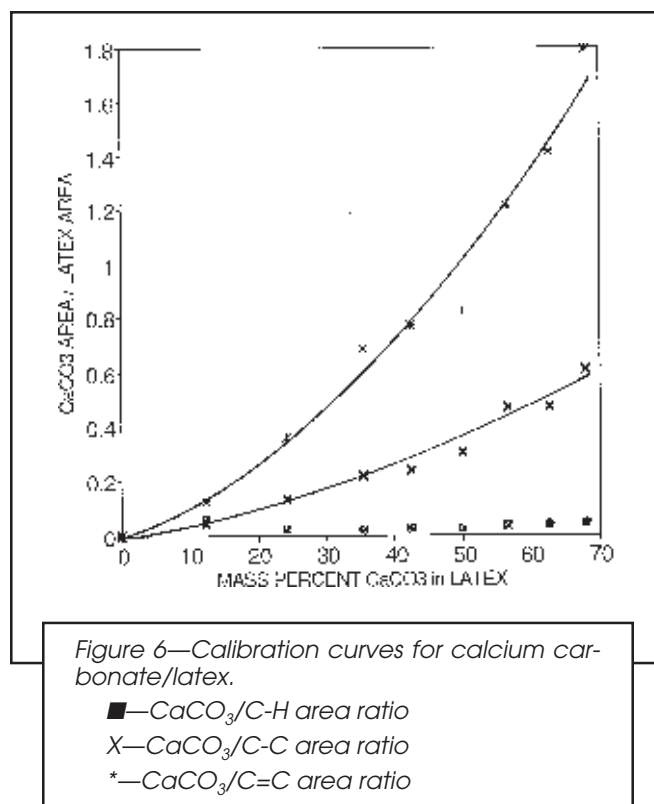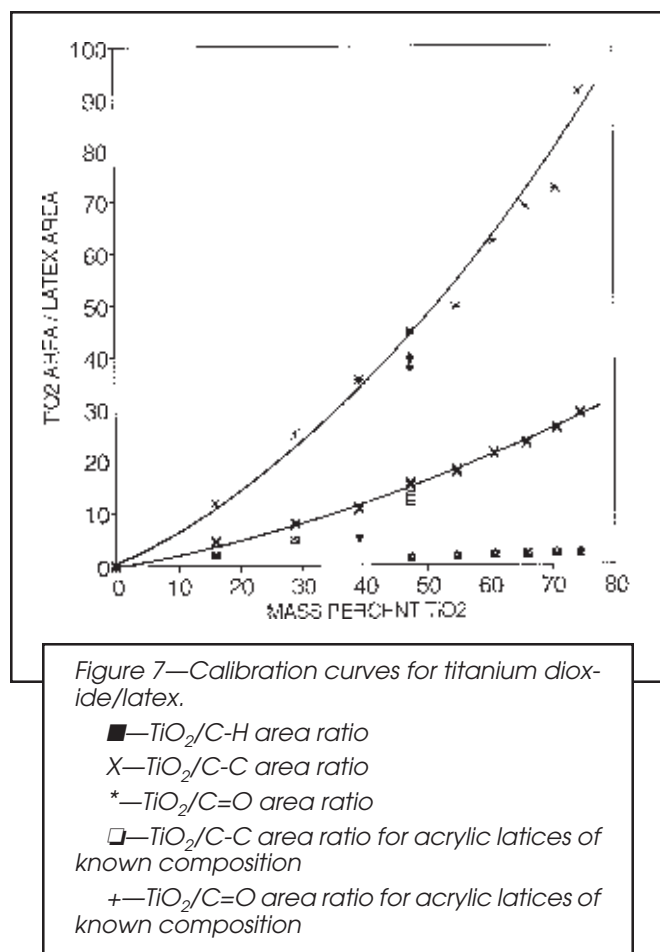| Latex	Mol C=O/g Latex	Mol C–C/g Latex
A	0.0085	0.044
B	0.0078	0.047
C	0.0090	0.043

Figure 6—Calibration curves for calcium carbonate/latex.

■—CaCO₃/C-H area ratio

X—CaCO₃/C-C area ratio

*—CaCO₃/C=C area ratio

Figure 7—Calibration curves for titanium dioxide/latex.

■—TiO$_2$/C-H area ratio

X—TiO$_2$/C-C area ratio

*—TiO$_2$/C=O area ratio

□—TiO$_2$/C-C area ratio for acrylic latices of known composition

+—TiO$_2$/C=O area ratio for acrylic latices of known composition

CONCLUSION

This study has shown that FTR spectroscopy can be used for qualitative and semi-quantitative analysis of pigment content of acrylic latex paint films. The technique used is nondestructive and requires no sample preparation. Quantitative results on real paint formulations produce pigment concentrations that are in excellent agreement for calcium carbonate and up to 20% lower than the formulated values for titanium dioxide. Variation in monomer content would be a contributing factor to poor quantitative results when calibration curves are made with latices of different composition to those analyzed. However, there are other contributory factors which need to be identified and investigated.

ACKNOWLEDGMENTS

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