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Infrared Spectra of U.S. Automobile Original Finishes. VII. Extended Range FT-IR and XRF Analyses of Inorganic Pigments *In Situ*—Nickel Titanate and Chrome Titanate

ABSTRACT: The identification, analysis, and occurrence in U.S. automobile original finishes (1974–1989) of Nickel Titanate (yellow) and Chrome Titanate (yellow–orange) are described in this report. The titanate pigments are based on the rutile (titanium dioxide) structure and there are only minor differences between the infrared absorptions of rutile and the titanates. Titanate pigment absorptions in paint spectra can thus be easily mistaken for those of rutile. Each of the titanates, however, contains two elements in addition to titanium that can serve to distinguish them using elemental analyses. Fourier transform infrared (4000–220 cm^{-1}) and X-ray fluorescence instruments were used in combination for the *in situ* analysis of the titanates. In addition to titanium, nickel, and antimony, the three main detectable elements comprising Nickel Titanate, all of the commercial products of this pigment that were examined also contained impurities of zirconium, niobium, and usually lead. These elements were also detected in most of the monocoats in which Nickel Titanate was identified, as well as in the Chrome Titanate pigments, and the zirconium to niobium ratio was found to exhibit a wide variation. Nickel Titanate is a relatively common pigment that was identified in nearly three dozen U.S. automobile yellow nonmetallic monocoats (1974–1989), while Chrome Titanate appears to have been used in only a few yellow and orange nonmetallic monocoats. The use of the titanate pigments likely increased after this time period as they were replacements for lead chromate pigments (last used in a U.S. automobile original finish in the early 1990s), and are more amenable for use in basecoat/clearcoat finishes than in monocoats. Minor distortions of the infrared absorptions of rutile, anatase, and the titanates obtained using accessories with diamond windows were noted, and their origins are discussed.

KEYWORDS: forensic science, criminalistics, paint analysis, automotive paint, pigment identification, infrared spectroscopy, X-ray fluorescence spectrometry, Nickel Titanate, Chrome Titanate

In Parts I and II of this series, the identification, analysis, and occurrence in U.S. automobile original (OEM) finishes (1974–1989) of several inorganic pigments were described (1,2). The pigments were identified *in situ* using an extended range (4000–220 cm^{-1}) Fourier transform infrared (FT-IR) spectrometer, and the finishes consisted of monocoats from the Reference Collection of Automotive Paints. The color-imparting pigments that were identified included iron ferrocyanide (Prussian Blue, which has a dark blue hue), ferric oxide (rust-colored), hydrous ferric oxide (yellow), Chrome Yellow (bright orange–yellow), Molybdate Orange (red–orange), and silica-encapsulated Chrome Yellow and Molybdate Orange.

Ferric oxide and hydrous ferric oxide continue to be used in American automotive finishes, but formulations involving the lead chromate pigments (Chrome Yellow, Molybdate Orange, and the silica-encapsulated versions of these) were discontinued due to safety concerns about lead salts. Lead-containing pigments were last used in U.S. automobile OEM finishes in the early 1990s (2). For vehicles produced in Europe, however, lead pigments continued to be used after this period (3). Iron ferrocyanide also is no longer used much in U.S. automobile OEM finishes, although it continues to be used in refinishes (4).

The identification, analysis, and occurrence of two other inorganic pigments that were used in U.S. automobile OEM monocoats (1974–1989), Nickel Titanate (lemon yellow) and Chrome

Titanate (golden yellow–orange), are described in this paper. Both pigments may be used to help formulate hues formerly produced by Chrome Yellow, and they became more common after lead chromate pigments were phased-out (DuPont Automotive Products, Troy, MI, personal communication, December 1998). The use of titanate pigments likely also increased after the Reference Collection era because of the increasing prevalence of basecoat/clearcoat finishes (DuPont Automotive Products, personal communication, February 2005). As is the case for most inorganic pigments (5), the titanates have low tinctorial strengths (6–9) and heavy pigment loads are required to achieve the vivid colors characteristic of many automotive finishes. In monocoats, such heavy pigment loads make it difficult to achieve a high gloss finish, but this is not a problem when using basecoat/clearcoat systems (7).

The titanate pigments are based on the rutile (titanium dioxide) structure, and only minor differences are observed between the infrared absorptions of rutile and the titanates. Titanate pigment absorptions in paint spectra can thus be easily mistaken for those of rutile. Each of the titanates, however, contains three elements that can be detected using X-ray methods of elemental analysis (including X-ray fluorescence (XRF) spectrometry and scanning electron microscope/energy dispersive X-ray (SEM/EDX) analyses). The use of both infrared and elemental analysis methods thus provides an effective combination for the characterization, differentiation, and identification of these pigments *in situ*, and data obtained using FT-IR (4000–220 cm^{-1}) and XRF instruments are presented and discussed.

During the course of this study, minor distortions in the infrared spectra of rutile, anatase, and the titanates using the diamond anvil cell (DAC) accessory were noted. The distortions can contribute

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Received 23 July 2005; and in revised form 3 Dec. 2005; accepted 10 Dec. 2005; published 21 April 2006.

to the already difficult task of differentiating between the absorptions of these related pigments, and this effect was therefore investigated. The cause of the distortions has been identified and is discussed.

Titanate Pigments

Several different mixed phase pigments based on titanium dioxide are used in the paint, coatings, plastics, ceramics, and other industries. These pigments are formed by partial substitution of titanium by various metals in the titanium dioxide rutile lattice, which results in compounds having various shades of yellow, orange, or brown. Some of the metals that have been used (6–10) include nickel/antimony (Nickel Titanate, lemon yellow), chromium/antimony (Chrome Titanate, golden yellow–orange), manganese/antimony (Manganese Antimony Titanate, dark brown); nickel/niobium (Nickel Niobium Titanate, lemon yellow), and chromium/niobium (Chromium Niobium Titanate, golden orange). The “second” element of these formulations (antimony or niobium) serves to enhance the color development of the pigment (8).

Because they are formed at very high temperatures, the titanates are quite heat-resistant and they are used in plastics, ceramics and other materials that may be subjected to high temperatures. Nickel Titanate, Chrome Titanate, and Manganese Antimony Titanate are commonly used in poly (vinyl chloride) (PVC) siding products (8,9), and Nickel Titanate may also be common in artists' paints. The niobium-containing titanates are not widely used because of their relatively high costs (Cerdec Corp., Washington, PA, personal communication, July 1999; The Shepherd Color Company, Cincinnati, OH, and Ishihara Corp., San Francisco, CA, personal communications, January 2005). At least two of the titanates, Nickel Titanate and Chrome Titanate, are used in automotive finishes. Typical empirical formulas for the two are $20 \text{ TiO}_2 \text{ Sb}_2\text{O}_5 \text{ NiO}$ and $31 \text{ TiO}_2 \text{ Sb}_2\text{O}_5 \text{ Cr}_2\text{O}_3$, respectively (8,9), although it should be emphasized that the titanates are comprised of solid solutions rather than stoichiometrically constrained mixed salts, and they can exhibit essentially continuously variable compositions. (Another important group of mixed phase pigments results from partial substitution of various metals for magnesium or aluminum in the spinel (MgAl_2O_4) lattice, and spectra of four such pigments were presented in Fig. 14 of paper II in this series (2) to illustrate the variety of far-infrared absorptions of inorganic, pigments.)

Experimental

Extended Range FT-IR Analyses

Infrared spectra were acquired at a resolution of 4 cm^{-1} using a Digilab FTS-7 FT-IR spectrometer. This extended range ($4000\text{--}220 \text{ cm}^{-1}$) instrument has cesium iodide (CsI) optics and uses a deuterated triglycine sulfate (DTGS) detector. More information about this spectrometer and the acquisition parameters that were used for data collection are presented elsewhere (2).

All of the paint samples were analyzed as thin slices placed over a 1 mm diameter circular aperture in a metal disk, which was mounted in a Digilab 5X beam condenser (Bio-Rod Digilab Division, Cambridge, MA). Most of the slices, except for those having quite brittle textures, were pressed with a roller device to produce a more uniform thickness, and 1000 scans were averaged.

Spectra of all of the pigments were acquired using a single anvil (11,12) of a DAC mounted in the 5X beam condenser. The DAC is a specially-designed version of the miniature diamond cell (High Pressure Diamond Optics, Tucson, AZ) constructed so that the

beveled diamond edges are not included in the area encompassed by the apertures of the cell. Pigment powders were ground thoroughly with excess CsI and pressed onto a single anvil to form a semitransparent film. Reference spectra were obtained of CsI pressed onto this same anvil, and 2000 scans were averaged for both reference and sample spectra.

Some pigment powders were additionally analyzed either neat or diluted with excess CsI and pressed between both anvils of the DAC; diluted with CsI and analyzed with a Digilab diffuse reflectance (DRIFTS) accessory (13); or diluted with excess CsI and pressed into a pellet. Unless otherwise indicated, the pigment spectra that are depicted were obtained using the single anvil method.

Spectral data were processed using Spectra CalcTM software. Although spectra are presented in transmittance, all of the calculations were performed with data in the absorbance format. In most cases, paint and pigment spectral absorption intensities were adjusted so that the most intense peak had a transmittance value between 3% and 10%, with the highest points of the baselines set near 99%. Spectral baselines were not flattened, however. Reflectance spectra of pigments obtained using the DRIFTS accessory were converted to a transmittance format (13).

XRF Analyses

XRF analyses were performed using a Jordan Valley EX-6600 XRF spectrometer (Jordan Valley AR, Inc., Austin, TX) equipped with a rhodium primary target and various secondary targets. To secure samples, a $\frac{3}{4}$ "-wide strip of adhesive tape with the adhesive side down was pulled taut and attached to the top of a sample cup holder. Numerous slices of each monocoat were mounted onto the adhesive side of the tape covering a total surface area of approximately 2 cm^2 ; this configuration avoided having a substrate between the sample and the detector, which is located below the sample. Pigment powders were also spread onto tape strips covering similar surface areas. Data collected for a blank strip of tape were subtracted from each spectrum. X-rays from a tin secondary target were used for excitation, produced with an X-ray tube voltage of 50 kV and a current of 4.9 mA. The samples were run in air and data were collected for 30,000 s (total live time). Escape peaks were removed from all spectra using the instrument software.

Since each of the paint samples consisted of numerous individual slices having mostly flat orientations, differences arising from sample morphology and penetration effects were averaged, and very reproducible results were obtained. This was confirmed by running two separate samples of one particular paint, LC78G0513. This paint was chosen because it produces peaks of at least six elements over a wide energy range (and is discussed in detail later). Spectra of the two analyses were overlaid (after normalization) and the results were virtually identical. In addition, separate samples of most of the paints and pigments were analyzed using a tin secondary target on a Kevex 0700 XRF spectrometer, which has been described previously (2). Very similar peak intensity ratios were observed for data collected on the two systems as well.

U.S. Automobile OEM Finishes

All of the automotive finishes discussed in this work are monocoats from the Reference Collection of Automotive Paints (Collaborative Testing Services Inc., Herndon, VA). They will be referred to by their seven or nine character identification codes, which have been described previously (1). Before vehicle model

TABLE 1—Pigments used in this study.

Name	Alternative Names	Colour Index Code	Source	Product Name	Infrared Spectrum	XRF Spectrum
Nickel Titanate	Nickel Antimony Titanium Yellow Rutile, Nickel Titanate Yellow, Nickel Antimony Titanate, Nickel Antimony Titanate Yellow, Titanium Yellow, Titanium Nickel Yellow, Titan Yellow, Sun [®] Yellow	Pigment Yellow 53 and Pigment Yellow 118	Bayer Corp.	Light Yellow 7G	Fig. 1c	Fig. 8c
			Cerdec Corp.	Yellow 10401	Fig. 1e	Fig. 8e
			Engelhard Corp. (Cleveland, OH)	Meteor Plus [®] Bright Golden 9350	Fig. 1d	Fig. 8d
			Ferro Corp.	V-9415 Yellow	Fig. 1b	Fig. 8b
			Ishihara Corp.	Tipaque [®] TY-50	Fig. 1a	Fig. 8a
Chrome Titanate	Chromium Antimony Titanium Buff Rutile, Chrome Antimony Titanium Buff Rutile, Chrome Titanate Yellow, Chrome Antimony Titanate Buff	Pigment Brown 24	Bayer Corp.	Light Yellow 3R		Fig. 9c
			Bayer Corp.	Light Yellow 5R		Fig. 9h
			Cerdec Corp.	Yellow 10406		Fig. 9e
			Engelhard Corp.	Meteor Plus [®] Yellow Buff 9371	Fig. 2a	Fig. 9d
			Ferro Corp.	V-9118 Bright Golden Yellow	Fig. 2b	Fig. 9b
Nickel Niobium Titanate	Nickel Niobium Titanium Yellow Rutile, Nickel Niobium Titanate Yellow	Pigment Yellow 161	The Shepherd Color Company	Tipaque [®] TY-100 Yellow 341		Fig. 9a
					Fig. 3c	Fig. 9i
Chromium Niobium Titanate	Chrome Niobium Titanate, Chrome Niobium Titanate Buff, Chrome Niobium Titanium Yellow Rutile	Pigment Yellow 162	Cerdec Corp.	RD-1019 Yellow	Fig. 3d	
Manganese Antimony Titanate Rutile, Silica-Encapsulated Rutile, Zirconia-Encapsulated Anatase	Manganese Antimony Titanium Buff Rutile	Pigment Yellow 164	The Shepherd Color Company	Indian Brown 221	Fig. 3e	
	Titanium Dioxide		DuPont	Ti-Pure [®] R902	Fig. 3b	
	Titanium Dioxide		Ishihara Corp.	Tipaque [®] CR-97		Fig. 9j
	Titanium Dioxide		Aldrich Chemical Co. (Milwaukee, WI)		Fig. 3a	

year 1983, finishes in this collection (14) were divided into general color categories according to the Inter-Society Color Council—National Bureau of Standards method of designating colors (15). The description of topcoat color used in the present work is based on this classification system.

Pigments

Table 1 provides a summary of information about the pigments that were analyzed in this study. In addition to the various common names that have been used for the titanates, *Colour Index* (16) generic codes are also listed.

Nickel Titanate

Extended Range FT-IR Analyses

Infrared spectra of Nickel Titanate from Ishihara, Ferro, Bayer, Engelhard, and Cerdec are depicted in Figs. 1a, b, c, d, and e, respectively. As a comparison, infrared spectra of Chrome Titanate from two manufacturers, Nickel Niobium Titanate, Chromium Niobium Titanate, and Manganese Antimony Titanate are depicted in Figs. 2a–b, 3c, 3d, and 3e, respectively. Like rutile (Fig. 3b), all of the titanates have a pair of low-frequency peaks below 430 cm^{-1} in their spectra. Anatase, a polymorph of rutile, has a single peak in this region (Fig. 3a).

Minor differences in the absorptions of the five Nickel Titanate products are observed, mainly in the shapes, relative intensities, and frequencies of the two low-frequency peaks, and these appear to be real since replicate analyses indicate that they are reproducible. The differences may reflect the variable nature of the com-

position of Nickel Titanate, but they could also reflect particle size/particle size distribution differences.

Although the Nickel Titanate absorptions are qualitatively similar to those of rutile, the frequencies of the low frequency pair can serve to distinguish them. The rutile pair occurs at $424\text{--}422$ and 357 cm^{-1} and these values do not vary much. The frequencies of the Nickel Titanate pair occur at somewhat lower values, which are much more variable; they occur between 403 and 386 cm^{-1} and between 345 and 338 cm^{-1} in spectra of the five products tested.

With the possible exception of the Ishihara product, spectra of the other Nickel Titanate pigments have another conspicuous feature that may also serve to distinguish them from that of rutile. The four spectra all have pronounced slopes in their baselines (see Fig. 1; note that the apparent discontinuities in the slopes of the baselines at 2000 cm^{-1} result from a change in the abscissa scale by a factor of two). It is evident that an optical or physical property of the pigment formulation is responsible for this effect since (1) a baseline slope of similar extent is observed in all of the replicate transmittance spectra of the four Nickel Titanate products; (2) pronounced baseline slopes also occur in spectra of Nickel Titanate depicted in the First Edition (17) of *An Infrared Spectroscopy Atlas for the Coatings Industry* (but not in the Fourth Edition (10), as the baselines of spectra in this newer compilation were flattened); (3) comparable baseline slopes occur in spectra of all of the paints in which large amounts of this pigment were identified; (4) the extent to which a slope occurs increases as the thickness of the pigment or paint sample increases; for paint samples in particular, poor sample preparation usually results in scattering losses from the irregular surfaces of the sample, and a simple correlation with thickness does not necessarily occur; and

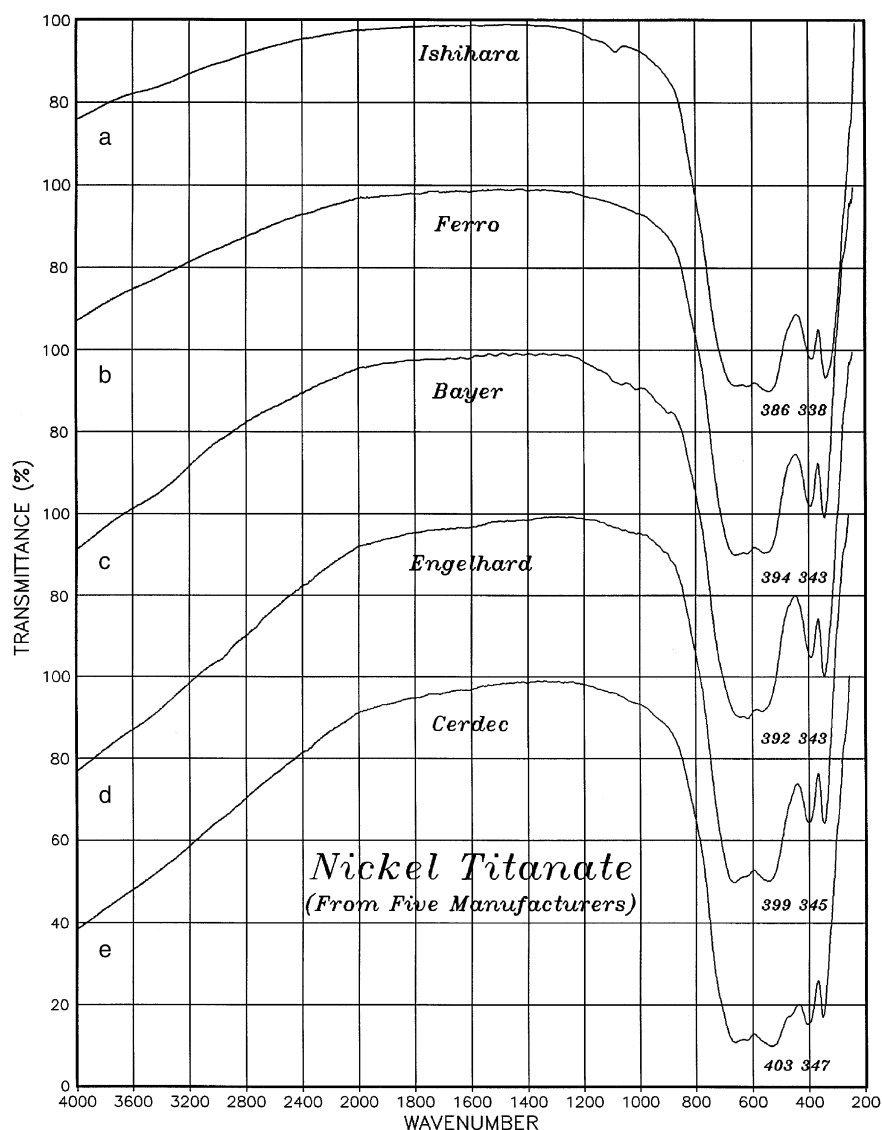


FIG. 1—Infrared spectra of Nickel Titanate from five manufacturers: (a) Ishihara; (b) Ferro; (c) Bayer; (d) Engelhard; and (e) Cerdec. The frequencies of the two titanate peaks are listed for each spectrum.

(5) the spectra of some other titanates, including Nickel Niobium Titanate (Fig. 3c) and Chromium Niobium Titanate (Fig. 3d), also exhibit this effect.

The pronounced baseline slope is thus a characteristic—and conspicuous—feature of transmittance spectra of the four Nickel Titanate products and of paints that contain large amounts of such high scattering formulations. Observation of this feature in the spectrum of a *yellow nonmetallic finish* can thus serve as a prompt to examine in more detail the low frequency region of the spectrum. Although a prominent baseline slope occurs in spectra of all of the Reference Collection monocoats in which this pigment was identified in large quantities, this may not necessarily be true in every case, as a composition of the type produced by Ishihara (or others) could be encountered. Also, it should be noted that a pronounced baseline slope can result from a poorly prepared paint sample.

Pigment Absorptions in Spectra of Acrylic Melamine Enamels—The spectrum of a yellow nonmetallic acrylic melamine enamel, PN76H0037, which contains a heavy pigment load of Nickel Titanate, is depicted in Fig. 4d, together with the spectrum of Nickel Titanate from Engelhard (Fig. 4c). As a comparison, the

spectrum of a similar white nonmetallic enamel, PN82A0123, which contains rutile, is shown in Fig. 4b, together with data for rutile (Fig. 4a). The slope of the baseline of Fig. 4b is typical of that of a paint that contains a large amount of rutile, and can be contrasted with that of Fig. 4d.

Spectra of three other yellow nonmetallic enamels that contain heavy pigment loads of Nickel Titanate are depicted in Figs. 5b (NC83 0506), 5c (CC78H0506), and 6c (NW80H0697). Spectra of NC83 0506 (Fig. 5b) and CC78H0506 (Fig. 5c) should be compared with that of KC83 0506 (Fig. 5a), another enamel of this same color that does not contain Nickel Titanate. KC83 0506 contains rutile and a small amount of Isoindolinone Yellow 3R, which produces (18) the two very weak sharp peaks at 1657 and 855 cm^{-1} . All three enamels of color 0506 contain hydrous ferric oxide (Fig. 5d), as evidenced by the weak peaks or shoulders near 276 cm^{-1} . NW80H0697 (Fig. 6c) also contains a small amount of Isoindolinone Yellow 3R, with peaks at 1674, 1657, 1308, and 853 cm^{-1} .

The absorptions of rutile and Nickel Titanate in spectra of several other finishes are depicted in Fig. 7. These figures depict the region from 850 to 250 cm^{-1} with the rutile or titanate absorption

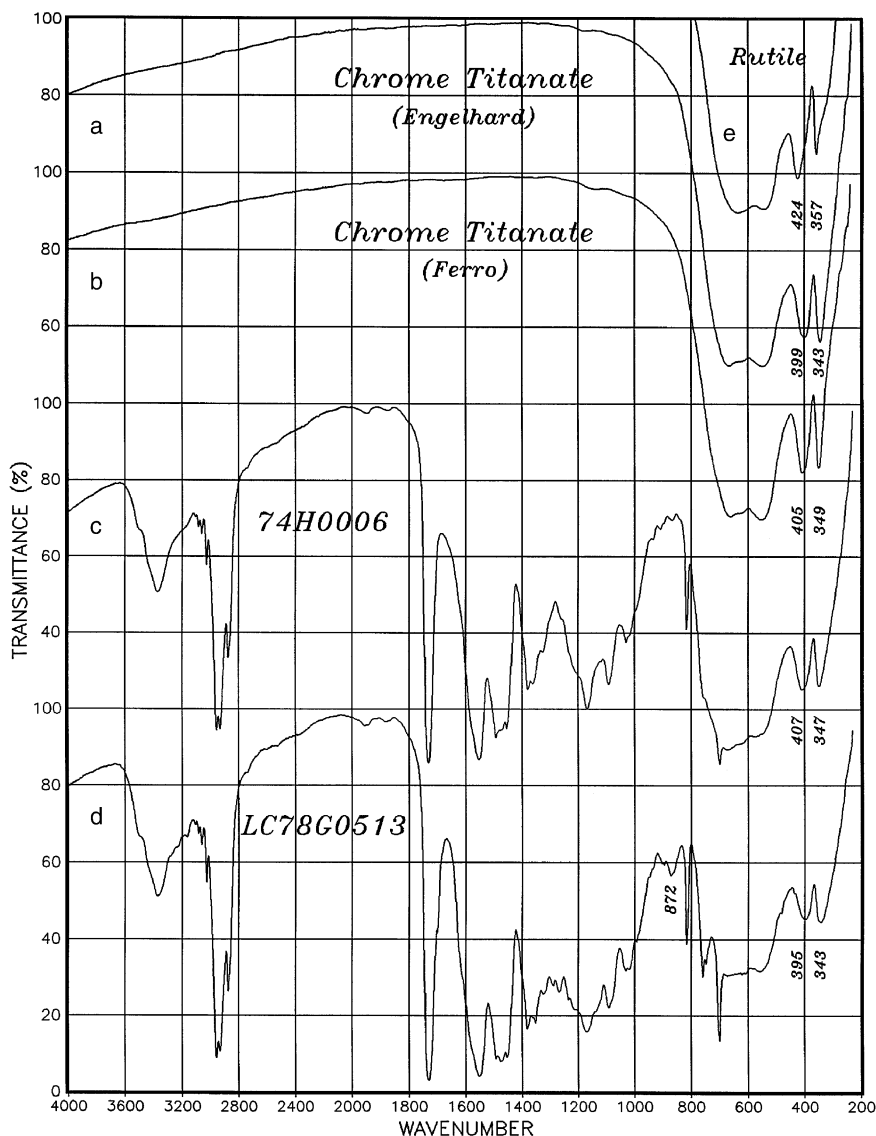


FIG. 2—Infrared spectra of (a) Chrome Titanate from Engelhard; (b) Chrome Titanate from Ferro; (c) a yellow nonmetallic acrylic melamine enamel monocoat, 74H0006, which contains Chrome Titanate; (d) an orange nonmetallic acrylic melamine enamel monocoat, LC78G0513, which contains Chrome Titanate and a small amount of Molybdate Orange; and (e) a portion of the spectrum of rutile. The frequencies of the two rutile or titanate peaks are listed for each spectrum.

having a maximum intensity of 10% transmittance. The frequencies of the rutile or titanate low frequency pair are indicated for each figure. Spectra of three white and three yellow nonmetallic enamels that contain rutile are shown in Figs. 7a–c and 7e–g, respectively, while data for five yellow nonmetallic enamels that contain Nickel Titanate are shown in Figs. 7j, k, m, n, and o.

As observed for the pigments themselves, the frequencies of the rutile pair ($424\text{--}422$ and 357 cm^{-1}) show little variation in paint spectra. Those of Nickel Titanate occur between 417 and 394 cm^{-1} and between 353 and 336 cm^{-1} (note that the 419 cm^{-1} frequency for the rutile peak of Fig. 7g results from the presence of hydrous ferric oxide—see Fig. 5d). Although they are not pronounced features, the lower frequency rutile peak has a more sharply pointed tip than the rounded ones of Nickel Titanate, and its relative intensity is always weaker compared with the higher frequency rutile peak (this is based on the %T value of the peak tip and not on the intensity of this absorption as measured from its base). The relative intensities of the two peaks of Nickel Titanate exhibit more variability, but the lower frequency member

often has a comparable or greater intensity (see also Fig. 1) unlike that of rutile.

Pigment Absorptions in Spectra of Acrylic Lacquers—The spectrum of a yellow nonmetallic acrylic lacquer (NB80H0697) that contains Nickel Titanate and a small amount of Isoindolinone Yellow 3R is shown in Fig. 6b; the absorptions of the latter pigment occur as very weak sharp peaks at 1657 , 1308 , and 1084 cm^{-1} (18). This spectrum should be compared with that of PA81H0697 (Fig. 6a), another lacquer of this same color that contains rutile and Benzimidazolone Yellow 3G (the absorptions (5) of which occur at 3407 , 3187 , 3133 , 1701 , 1669 , 1640 , 1622 , 1582 , 1539 , 1111 , 1036 , 951 , 934 , 882 , 858 , 816 , 733 , 702 , 648 , 625 , 611 , 583 , 571 , 395 , and 305 cm^{-1}).

Acrylic lacquer binders have a weak peak at 365 cm^{-1} as illustrated by the spectrum of PA81L0780 (Fig. 6d), a blue metallic finish that lacks pigment absorptions. This 365 cm^{-1} binder feature occurs at a somewhat higher frequency than the low-frequency member of the rutile (357 cm^{-1}) or Nickel Titanate ($353\text{--}336\text{ cm}^{-1}$) pair. Consequently, spectra of acrylic lacquers that

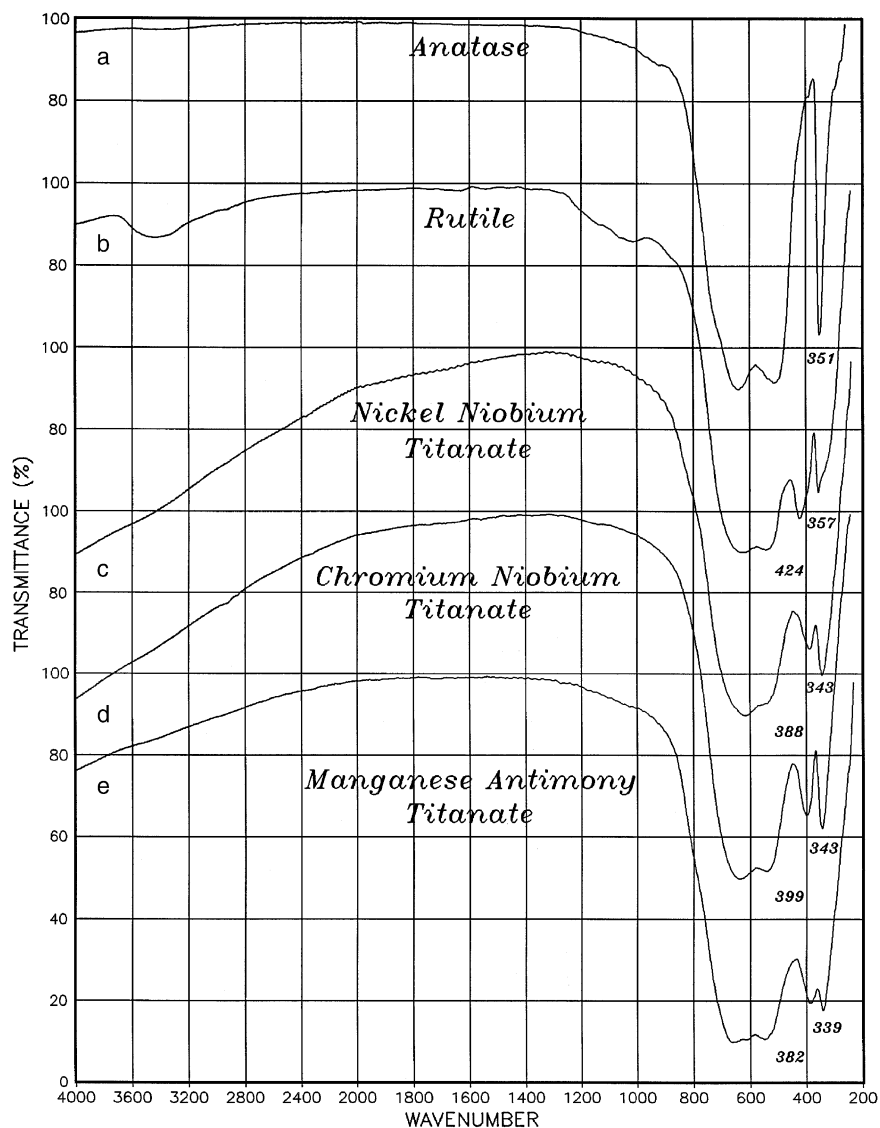


FIG. 3—Infrared spectra of (a) anatase; (b) rutile (from DuPont); (c) Nickel Niobium Titanate; (d) Chromium Niobium Titanate; and (e) Manganese Antimony Titanate. The frequencies of the titanium dioxide or titanate peaks are listed for each spectrum.

contain rutile or Nickel Titanate may appear to have an enhanced intensity, and possibly a slightly higher frequency, than expected for the lower frequency member of the pair. With rutile, the frequency shift is usually small but an intensity enhancement is usually observed; compare, for example, the low-frequency rutile pair of Figs. 4b and 6a (for the latter, the rutile 422 cm^{-1} peak is also shifted to 428 cm^{-1} due to the presence of an overlapping Benzimidazolone Yellow 3G absorption at 430 cm^{-1} (5)).

The minor differences between the absorptions of rutile and Nickel Titanate may thus be partially obscured in spectra of acrylic lacquers, but the higher frequency member of the pair is unaffected, and a strongly sloping baseline may occur if Nickel Titanate is present.

Pigment Combinations—In addition to binder absorptions, peaks of both organic and inorganic pigments that are used together with Nickel Titanate might also occur in the same region as the titanate low-frequency pair. For organic pigments, these are likely to be sharp features and they may appear as fine structures superimposed on the somewhat broader pair. The sharp tip of the high-frequency member of the Nickel Titanate pair of

NW78H0461 (Fig. 7o), for example, is due to Isoindolinone Yellow 3R (18). The possibility that the frequencies of the Nickel Titanate pair may be affected by these peaks should be considered, but the presence of an organic pigment (or pigments) is usually not difficult to discern since sharp absorptions will be observed in other spectral regions as well. The rutile low-frequency pair may also be affected by organic pigment absorptions, as noted for PA81H0697 (Fig. 6a).

The pigment that appears to have been most commonly used with Nickel Titanate is hydrous ferric oxide. For this combination, the hydrous ferric oxide serves to adjust the tint of the finish, as well as to provide additional hiding power and opacity (DuPont Automotive Products, personal communication, December 1998). The two strongest absorptions of hydrous ferric oxide occur at 405 and 278 cm^{-1} (Fig. 5d), and spectra of many yellow nonmetallic monocoats that contain strong rutile or Nickel Titanate absorptions also have shoulder peaks of hydrous ferric oxide ($2,5,18$) near 276 cm^{-1} ; see, for example, Figs. 5a–c, and 7g. The presence of the hydrous ferric oxide 405 cm^{-1} absorption may distort the higher frequency member of the rutile or titanate pair; the

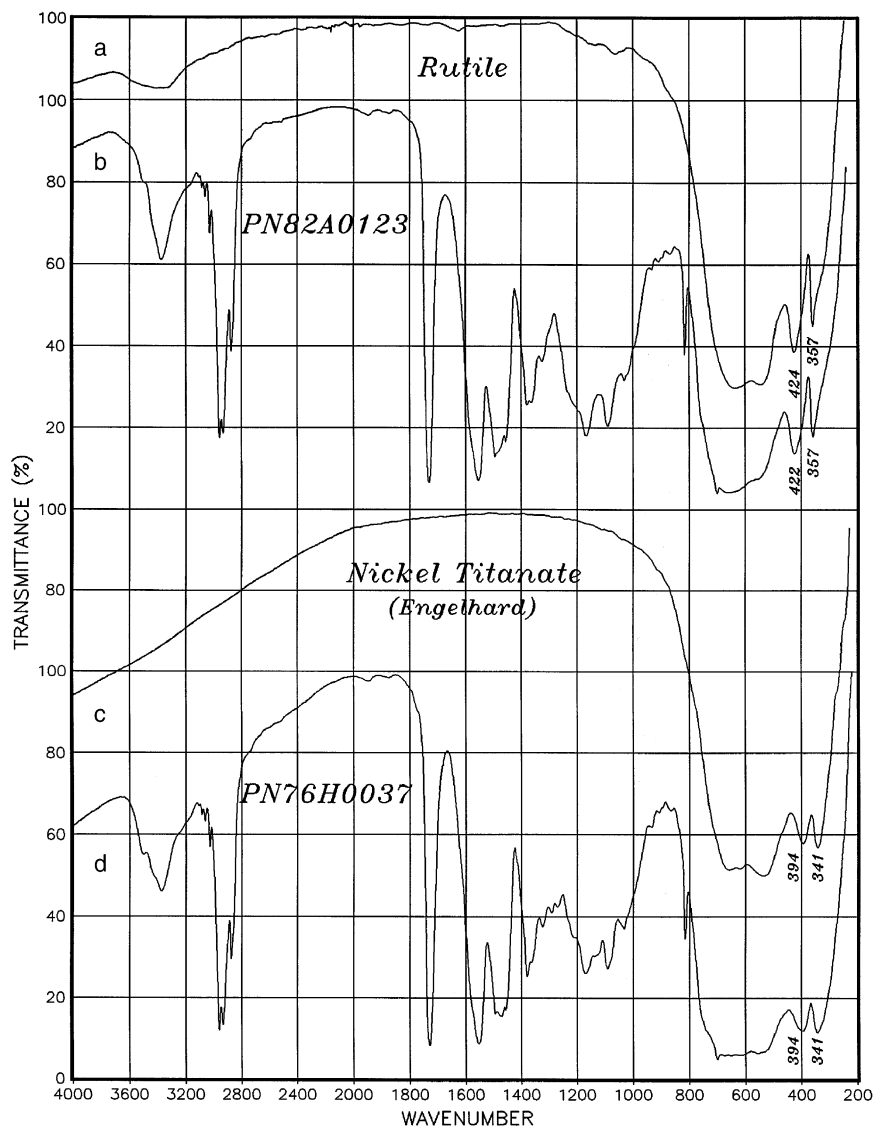


FIG. 4—Infrared spectra of (a) rutile; (b) a white nonmetallic acrylic melamine enamel monocoat, PN82A0123, which contains rutile; (c) Nickel Titanate from Engelhard; and (d) a yellow nonmetallic acrylic melamine enamel monocoat, PN76H0037, which contains Nickel Titanate. The frequencies of the two rutile or titanate peaks are listed for each spectrum.

rutile 422 cm^{-1} absorption of Fig. 5a, for example, has a low-frequency shoulder compared with the rutile peak of Fig. 4a. This should be expected, however, if the 278 cm^{-1} hydrous ferric oxide peak is present.

XRF Analyses

Even when all of the cited features of Nickel Titanate are observed clearly in paint infrared spectra, elemental analysis is still a critical aspect of pigment identification since the differences between the absorptions of rutile and Nickel Titanate—and especially between the titanates themselves—are minor at best. As noted, these minor differences are often obscured by the presence of other components in infrared spectra of paints.

XRF spectra (shown between 1 and 20 keV) of Nickel Titanate from Ishihara, Ferro, Bayer, Engelhard, and Cerdec are depicted in Figs. 8a, b, c, d, and e, respectively. As expected from the approximate empirical formula for this pigment ($20\text{ TiO}_2\text{ Sb}_2\text{O}_5\text{ NiO}$), the K lines of titanium are more intense than the K lines of nickel and

the L lines of antimony, but the ratios of the titanium and nickel K lines and the antimony L lines are similar for the five products. Very small amounts of zirconium and niobium were identified in the pigments, with the ratio of the zirconium to niobium varying over a relatively wide range. Small amounts of lead were observed for four of the products, and the fifth (Fig. 8a) also appears to contain this element, but with peaks at the detection limits.

XRF spectra of five monocoats that contain Nickel Titanate are depicted in Figs. 8f–j (the figure number of the infrared spectrum of each paint is indicated in parentheses): 8f-PN76H0037(4d), 8g-NC83 0506(5b), 8h-CC78H0506(5c), 8i-NB80H0697(6b), and 8j-NW80H0697(6c). Very small amounts of zirconium, niobium, and lead were identified in all five monocoats and as observed for the pigments, the ratio of the zirconium to niobium varies over a fairly wide range.

PN76H0037 (Fig. 8f) also contains small amounts of chromium, iron, and probably arsenic. The chromium may reflect the presence of Chrome Titanate. A common source of chromium in yellow, orange, red, and brown nonmetallic Reference Collection

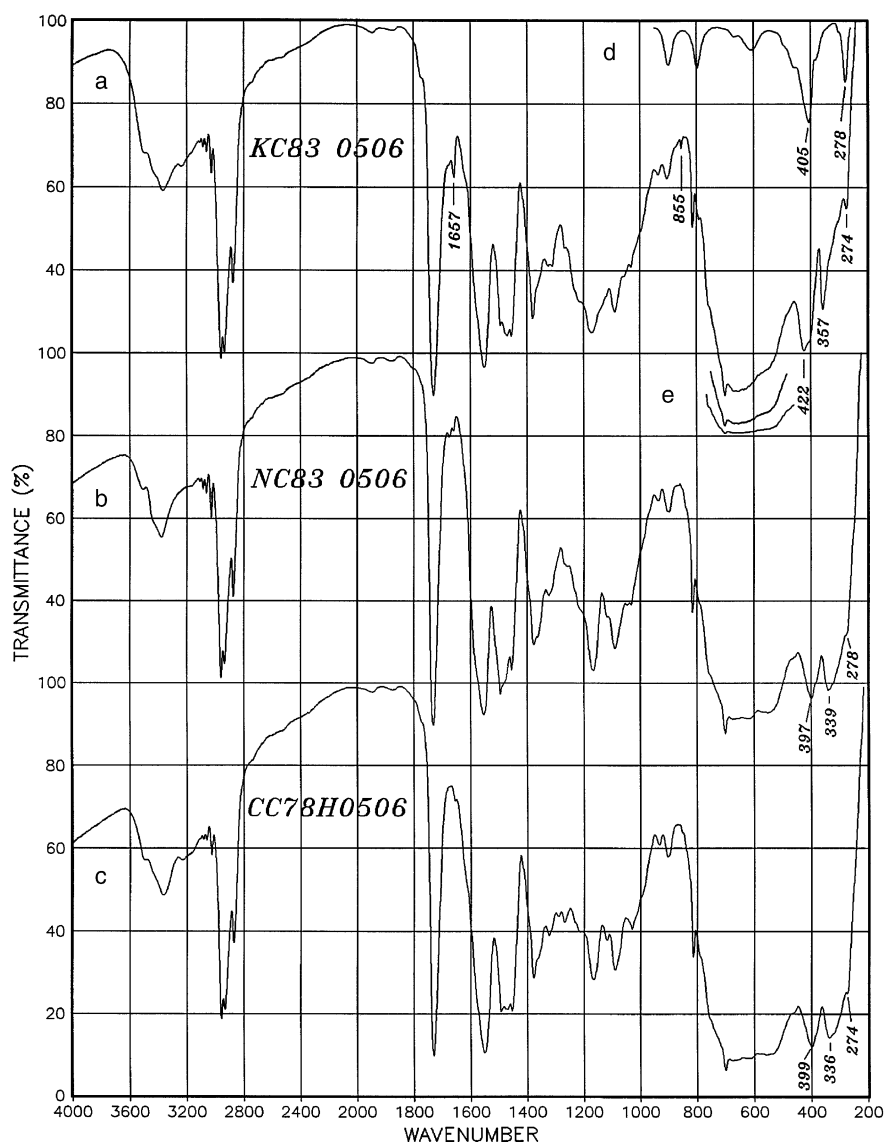


FIG. 5—Infrared spectra of three yellow nonmetallic acrylic melamine enamel monocoats of color 0506: (a) KC83 0506, which contains rutile, hydrous ferric oxide and Isoindolinone Yellow 3R; (b) NC83 0506, which contains Nickel Titanate and hydrous ferric oxide; (c) CC78H0506, which contains Nickel Titanate and hydrous ferric oxide; and (e) portions of the spectra of KC83 0506 scaled by factors of 1.5 (top) and 2.3 (bottom) to illustrate the shapes of the rutile absorptions for thicker samples. (d) A portion of the spectrum of hydrous ferric oxide. The frequencies of the two rutile or titanate peaks are listed together with those of some other pigments.

monocoats is lead chromate pigments. If such a pigment were present, however, much stronger peaks of lead, or lead and molybdenum, would also occur, based on the ratio of the lead to chromium lines (or the ratios of the lead, molybdenum, and chromium lines) observed for such pigments (2,19,20).

NC83 0506 (Fig. 8g) and CC78H0506 (Fig. 8h) both contain iron from hydrous ferric oxide. Note that infrared spectra of the two paints (Figs. 5b and c) might suggest that only small amounts of hydrous ferric oxide are present, but the observed intensities of the hydrous ferric oxide peaks near 276 cm^{-1} may be misleading since the absorptions occur as shoulders on the sides of the strong titanate absorptions and a logarithmic scale is involved. NC83 0506 also contains a small amount of strontium, and CC78H0506 contains a small amount of zinc. Small amounts of zinc are likewise present in NB80H0697 (Fig. 8i) and NW80H0697 (Fig. 8j), along with very small amounts of iron; both also contain chlorine from Isoindolinone Yellow 3R (18). As discussed below, the zinc and strontium may be from Nickel Titanate.

Compared with the pigments (Figs. 8a to e), the ratios of the nickel to titanium peaks are lower for PN76H0037 (Fig. 8f), NB80H0697 (Fig. 8i), and NW80H0697 (Fig. 8j). For PN76H0037, this may reflect the presence of Chrome Titanate, as discussed. For NB80H0697 and NW80H0697, this is probably due to the presence of some rutile.

In Paper VI in this series (18), infrared and XRF data for NW78H0461, a yellow nonmetallic enamel, were presented to illustrate the identification of Isoindolinone Yellow 3R. At that time, it was noted that this monocoat also contains Nickel Titanate, and a very small amount of niobium was detected. Closer examination of the XRF data, as well as further analyses, indicate that very small amounts of zirconium and lead are also present.

Infrared and XRF data for DB82H0870, a yellow nonmetallic acrylic lacquer, were also discussed in paper VI and the presence of Nickel Titanate was indicated from the XRF data. The ratios of the nickel and antimony peaks to the titanium peaks are much lower than observed for the pigment spectra of Fig. 8, and only a

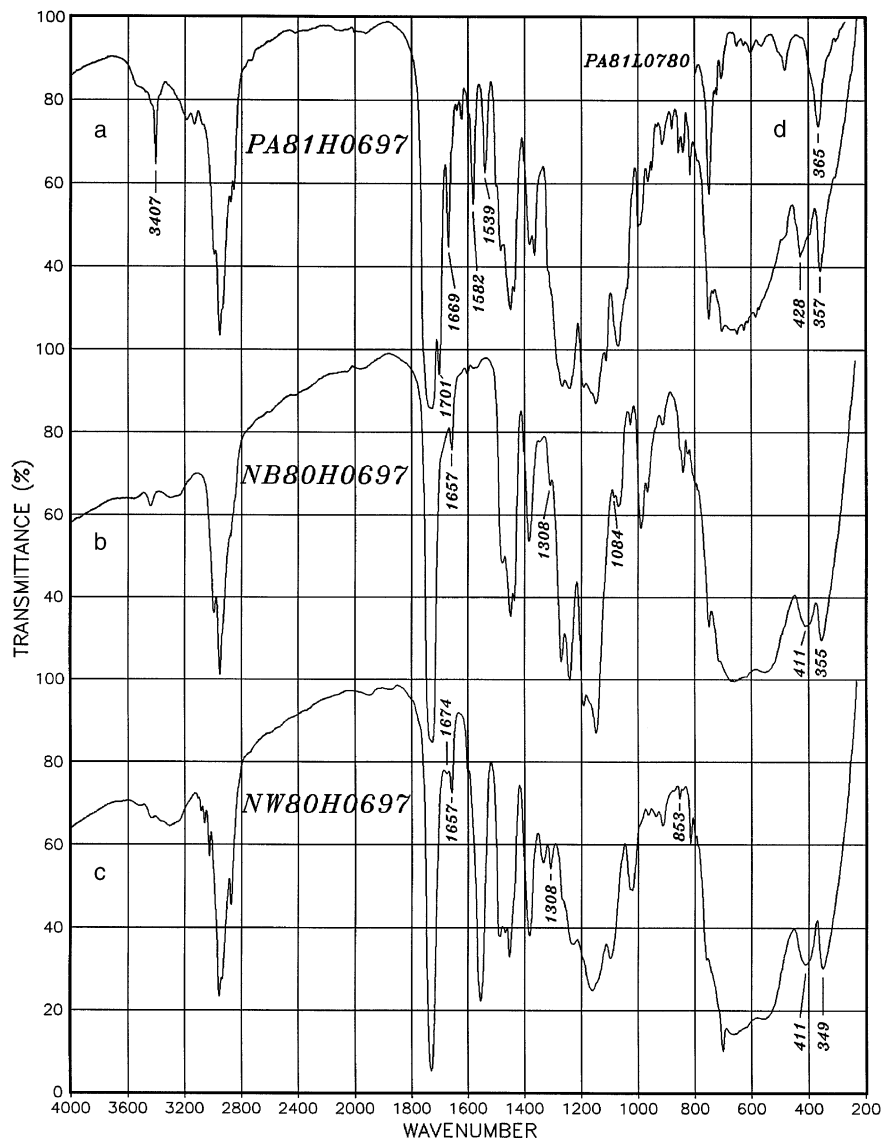


FIG. 6—Infrared spectra of three yellow nonmetallic monocoats of color 0697: (a) PA81H0697, an acrylic lacquer that contains rutile and Benzimidazolone Yellow 3G; (b) NB80H0697, an acrylic lacquer that contains Nickel Titanate and a small amount of Isoindolinone Yellow 3R; and (c) NW80H0697, an acrylic melamine enamel that contains Nickel Titanate and a small amount of Isoindolinone Yellow 3R. (d) A portion of the spectrum of a blue metallic acrylic lacquer monocoat, PA81L0780, which does not contain pigment absorptions. The frequencies of the two rutile or titanate peaks are listed together with those of some other pigments.

barely discernable niobium peak was observed (this paint was re-analyzed in the present study and a very small amount of zirconium was also detected). The infrared spectrum of DB82H0870 appears to be typical of that of an acrylic lacquer containing a large amount of rutile, and this spectrum has an inconspicuous baseline slope that is only slightly more pronounced than might be expected for a paint containing rutile. DB82H0870 is thus consistent with a finish that contains mainly rutile with a lesser amount of Nickel Titanate.

The infrared spectrum of another finish of this same color, NW82H0870, an acrylic melamine enamel, has a pronounced baseline slope with absorptions typical of that of a titanate (Fig. 7m). The ratio of the nickel to titanium peaks in the XRF spectrum of NW82H0870 is similar to those observed for Figs. 8i and j. The pigment loads of Nickel Titanate used in DB82H0870 and NW82H0870 thus appear to be quite different, although the two paints have the same color.

The levels of zirconium, niobium, and lead found in the titanate pigments are quite low, and some of the observed peaks of these elements are at the detection limits for the particular conditions used to obtain data. These conditions favor the higher energy peaks, particularly the K lines of niobium and zirconium, since excitation efficiencies are highest for elements having ionization energies close to the K_{α} line of tin. Detection efficiencies also favor these elements since higher energy X-rays penetrate deeper, and the effective sampling depths are greater. Consequently, the peak intensities observed in Fig. 8 are highly skewed relative to the actual concentrations of the elements. This can be seen clearly from Fig. 9i, which depicts the XRF spectrum of Nickel Niobium Titanate. Although the molar ratio of niobium to titanium in this pigment is quite low, the niobium K lines are stronger than those of titanium; for the same reason, the nickel lines are stronger compared with those of titanium than would be the case if their intensities were proportional to molar concentrations. Figure 9i

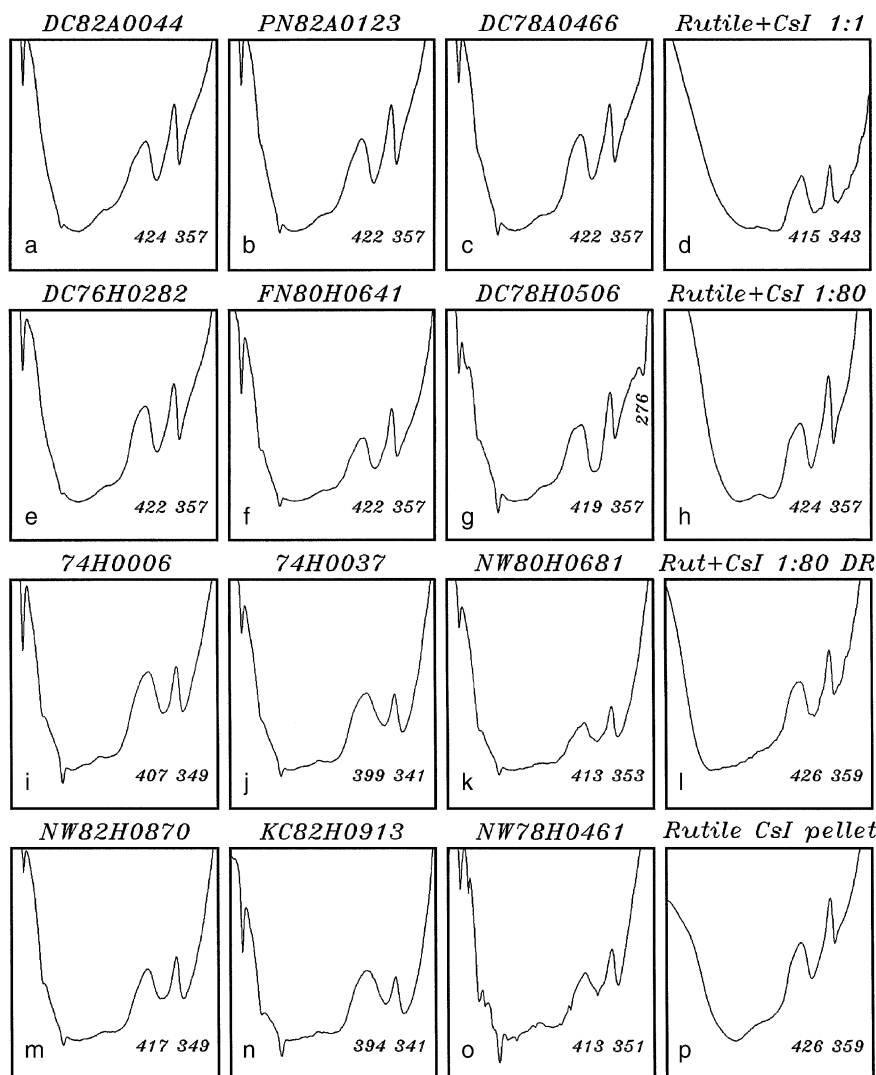


FIG. 7—Infrared absorptions in the $850\text{--}250\text{ cm}^{-1}$ spectral region, depicted between 0% and 60%T. Spectra of three white and three yellow nonmetallic acrylic melamine enamel monocoats that contain rutile: (a) DC82A0044; (b) PN82A0123; (c) DC78A0466; (e) DC76H0282; (f) FN80H0641; and (g) DC78H0506, which also contains hydrous ferric oxide. (i) The spectrum of 74H0006, which contains Chrome Titanate. Spectra of five yellow nonmetallic acrylic melamine enamel monocoats that contain Nickel Titanate: (j) 74H0037; (k) NW80H0681; (m) NW82H0870; (n) KC82H0913; and (o) NW78H0461, which also contains Isoindolinone Yellow 3R. Spectra of rutile diluted with CsI: (d) 1:1 mixture analyzed with a single anvil of the DAC; (h) 1:80 mixture analyzed with a single anvil of the DAC; (l) This same 1:80 mixture analyzed using DRIFTS; and (p) 1:100 mixture pressed into a pellet. The frequencies of the two rutile or titanate peaks are listed for each spectrum.

may also provide the analyst with some idea of the relative peak intensity ratios to expect (using a tin secondary target) if a paint containing this particular titanate pigment is encountered.

Because zirconium and niobium are adjacent elements in the periodic table, their excitation and detection efficiencies are quite similar, although niobium is slightly favored since its ionization energy is closer to that of the tin K_{α} line. As such, the observed intensity ratios of the K lines of zirconium and niobium provide a fairly good estimate of the relative molar concentrations of the two elements in paint and pigment samples.

Sources of Zirconium, Niobium, and Lead in Titanate Pigments—Niobium and zirconium minerals, especially zircon, are often associated with the ilmenite and rutile ores used to produce titanium dioxide, although the amounts of these minerals are very dependent on specific locations and deposit histories (21). One of the main sources of niobium and zirconium in Nickel Titanate (and other titanates) is thus titanium ore (Ferro Corp., Independence, OH, Ishihara Corp., and The Shepherd Color Company,

personal communications, January 2005). Rutile (at least for the grades used in automotive finishes) is produced from the ore by the chloride process (7), which involves the formation of titanium tetrachloride; the tetrachloride is distilled, which removes most of the niobium, zirconium, and other impurities. The titanates, in contrast, are produced from anatase manufactured by the sulfate process (7), which does not involve a distillation step, so more of the niobium, zirconium, and other impurities is retained (anatase is converted to rutile during the titanate manufacturing process). According to one in-house study of the impurities in commercial anatase used to manufacture titanates, the levels of niobium (calculated as Nb_2O_5) varied between 0.01% and 0.33% (by weight), while those of zirconium (calculated as ZrO_2) varied between 0.00% and 0.03% (Ferro Corp., personal communication, January 2005). A very small amount of zirconium was detected in the sample of Nickel Niobium Titanate, although the K_{α} line of this element is not easily observed for the ordinate scale used for Fig. 9i.

Other possible sources of zirconium and niobium in the titanates are: (1) Zirconium from zircon grinding beads, which are used by at least one of the titanate manufacturers for pigment particle sizing; some other manufacturers have indicated, however, that they do not use this grinding medium; (2) Zirconium from the kiln or furnace used to produce the titanates; and (3) Niobium from a prior production of Nickel Niobium Titanate, although not all of the manufacturers of Nickel and Chrome Titanate produce Nickel Niobium Titanate.

The lead impurity likely originates primarily from antimony ore. Small amounts of magnesium, calcium, zinc, strontium, and other elements might also be found in some titanates, as salts of these elements can be used by certain manufacturers when producing the titanates.

Other Sources of Zirconium in Automotive Paints—To date, niobium has not been identified by XRF in any of the other automotive pigments or paints discussed in this series (2,5,18–20), except for paints containing Nickel Titanate (18). Widely varying levels of zirconium, however, have previously been identified in both acrylic lacquers and acrylic melamine enamels (19,20) that

do not contain Nickel Titanate. As discussed, the likely source of zirconium for these paints is from wear of the zirconium oxide dispersion beads used during the paint manufacturing process, as these beads must be periodically replaced (22) because of degradation (wear of the dispersion medium may also contribute to the silicon and iron levels in a paint, depending on the composition of the beads). Zirconium introduced from the paint manufacturing process can thus add to that already present in paints containing titanates, and this might be the case for PN76H0037 (Fig. 8f), which has a relatively high level of zirconium compared with that observed for the pigments (Figs. 8a–e).

Zirconium has been used as a drier for alkyds (7), although alkyd binders have not been used in a U.S. OEM finish for several decades. No alkyd-based paints were identified in panels from the Reference Collection of Automotive Paints, which began in 1974. It is also possible that zirconium might be found in a few two-component urethane finishes, since transition metals are common catalysts for the isocyanate-alcohol reaction, although tin compounds are more likely to be used for this (Bayer Material Science LLC, Pittsburgh, PA, personal communication, February 2005).

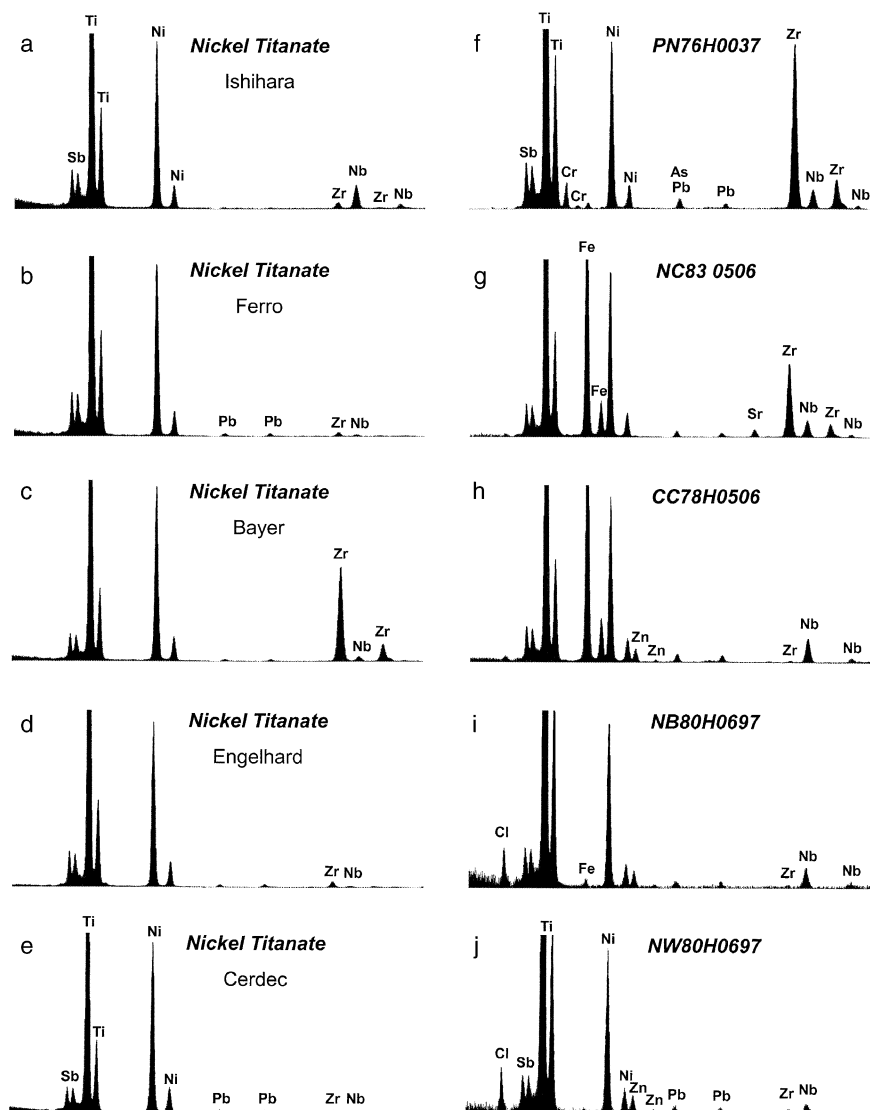


FIG. 8—X-ray fluorescence spectra (1–20 keV) of Nickel Titanate and some monocoats that contain Nickel Titanate obtained using a tin secondary target: (a) Nickel Titanate from Ishihara; (b) Nickel Titanate from Ferro; (c) Nickel Titanate from Bayer; (d) Nickel Titanate from Engelhard; (e) Nickel Titanate from Cerdec; (f) PN76H0037; (g) NC83 0506; (h) CC78H0506; (i) NB80H0697; and (j) NW80H0697.

Certain paints containing rutile might also contain zirconium. The surface of titanium dioxide consists of hydroxyl groups, and these can catalyze the production of free radicals from water and oxygen when exposed to ultraviolet light (23). This, in turn, may initiate the degradation of the paint binder. The most durable grades of rutile are therefore comprised of encapsulated TiO_2 particles to prevent this reaction, and common surface treatment compounds used for this include (23) silica, alumina, zirconia, and hydrous titania (the weak broad absorption near 1100 cm^{-1} in Fig. 3b is from the silica used to encapsulate rutile). Rutile pigments used in OEM automotive finishes always consist of such surface-treated particles because of the demanding durability requirements of such paints (DuPont White Pigment and Mineral Products, Wilmington, DC, Ishihara Corp., and Ciba Specialty Chemicals Corp., Newport, DE, personal communications, May 1999).

Figure 9j depicts the XRF spectrum of an Ishihara zirconia-encapsulated rutile pigment used in automotive finishes. Tin oxide may be used with zirconia in rutile grades used for automobile finishes (24), and tin was also identified in this Ishihara pigment; the K lines of this element occur above 20 KeV so they are not

observed in Fig. 9j. The presence of tin and zirconium in an automotive paint containing rutile would thus be consistent with the use of this type of titanium dioxide. Although the titanate pigments are based on the rutile structure, they are not encapsulated (Bayer Corp., Pittsburgh, PA, Ferro Corp., and The Shepherd Color Company, personal communications, January 2005; and BASF Corp., Southfield, MI, personal communication, March 2005).

Trace Elemental Analyses—The elemental analysis data collected in this study suggest that paints containing titanate pigments can be usefully characterized to a degree beyond that of specifying which particular titanate pigment is present. Not only do the low levels of zirconium, niobium, and lead vary between different pigment products—especially the zirconium to niobium ratio—but additional zirconium may be introduced during the paint manufacturing process. The latter contribution can also reflect some degree of individuality since the extent of wear of the dispersion beads may vary between different paint batches, and dispersion media other than zirconium oxide may be used.

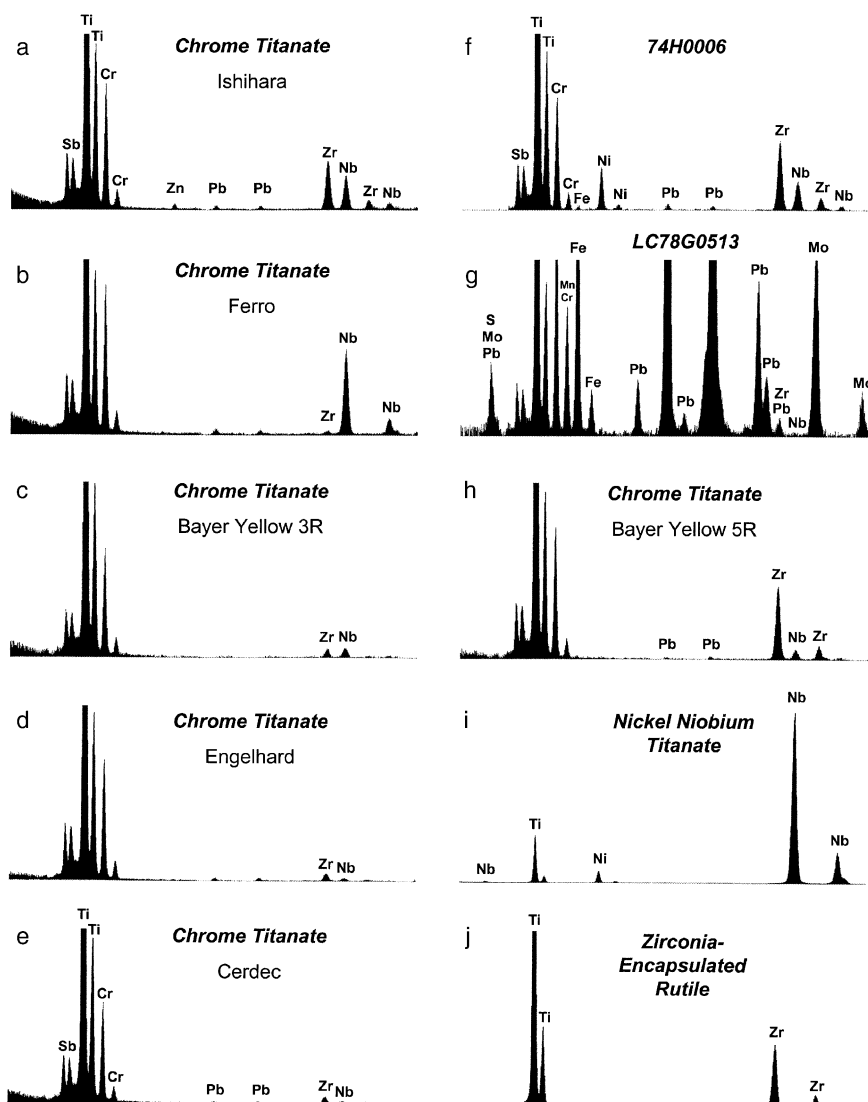


FIG. 9—X-ray fluorescence (XRF) spectra (1–20 keV) of Chrome Titanate and two monocoats that contain Chrome Titanate obtained using a tin secondary target: (a) Chrome Titanate from Ishihara; (b) Chrome Titanate from Ferro; (c) Chrome Titanate from Bayer, Light Yellow 3R; (d) Chrome Titanate from Engelhard; (e) Chrome Titanate from Cerdec; (f) 76H0006; (g) LC78G0513; and (h) Chrome Titanate from Bayer, Light Yellow 5R. XRF spectra of (i) Nickel Niobium Titanate; and (j) Zirconia-encapsulated rutile from Ishihara.

At present, this potential is not likely to be utilized much since SEM/EDX, a common method used in forensic science laboratories for the elemental analysis of paint evidence, does not permit the detection of such low levels of niobium, zirconium, lead, and other heavy elements. The sample sizes required to detect these elements using an XRF instrument are much larger than normally encountered in casework, and secondary targets are not used with micro-XRF systems. Low levels of these and other elements are readily detected using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). This was demonstrated in a recent paper (25) on the analysis of automotive paints using this technique; although lead was one of the elements examined in this work, zirconium and niobium were not. Such levels can also be detected using total reflection X-ray fluorescence (TXRF) spectrometry, which has been used for the analysis of pigments in works of art and in manuscript inks (26–32).

Trace elemental analyses for niobium, zirconium, and some other elements might also prove useful for distinguishing materials that contain significant amounts of anatase, such as certain types of paper or paper-based products, some architectural coatings, and other evidence.

Use in U.S. Automobile OEM Nonmetallic Monocoats (1974–1989)

A survey of the infrared spectra of all of the available yellow and orange nonmetallic monocoats in the Reference Collection of Automotive Paints was conducted to determine the frequency of occurrence of Nickel Titanate in U.S. Automobile OEM nonmetallic monocoats (1974–1989). Each spectrum was examined for both strongly sloping baselines and for the far-infrared absorption characteristics that have been described. In most cases, those spectra having pronounced baseline slopes were also found to have the absorptions that were sought, and XRF analyses were performed directly on each such panel. For every panel where the infrared data indicated the presence of Nickel Titanate, the characteristic elements of this pigment were also found.

Nickel Titanate was identified in nearly three dozen yellow nonmetallic monocoats by this means, but not in any orange nonmetallic monocoats. The majority of paints in which this pigment was identified have various shades of lemon yellow. As discussed earlier, similar colors can be produced using other pigments or pigment combinations not involving Nickel Titanate, or with varying levels of Nickel Titanate. Nickel Titanate is used primarily in nonmetallic finishes, although it may also be used in certain metallic finishes (Cerdec Corp., personal communication, January 1998, and DuPont Automotive Products, personal communication, April 1998).

Most of the monocoats in which Nickel Titanate was identified contain heavy pigment loads. The method that was used to screen Reference Collection samples in this survey, however, would tend to favor paints containing such heavy loads. The actual use of this pigment in finishes of the Reference Collection period is thus likely to be higher than cited. As noted for DB82H0870, lighter pigment loads of Nickel Titanate are possible, and rutile is often used with Nickel Titanate in such cases to help produce opacity (Cerdec Corp., personal communication, January 1998, and DuPont Automotive Products, personal communication, April 1998). For these paints, the primary indication that Nickel Titanate is present is provided by elemental analyses.

Nickel Titanate is still used in automotive paints, primarily to formulate nonmetallic lemon yellow hues in the more pastel shades (DuPont Automotive Products, personal communication,

February 2005). It may be more common for some specialty finishes, such as paints for fleet or commercial vehicles, taxicabs, and buses (BASF, personal communication, March 2005).

Chrome Titanate

Extended Range FT-IR Analyses

Infrared spectra of Chrome Titanate from Engelhard and Ferro are shown in Figs. 2a and b, respectively, and a portion of the spectrum of rutile is shown in Fig. 2e for comparison. Only very minor differences are observed between the spectra of the Engelhard and Ferro products and they are similar to spectra of Chrome Titanate from Ishihara, Bayer, and Cerdec (which are not depicted). Spectra of the different products of this pigment thus exhibit considerably less variability than observed for Nickel Titanate (Fig. 1).

The Chrome Titanate absorptions are quite similar to absorptions of some of the Nickel Titanate pigments (Fig. 1). As observed for Nickel Titanate, the wavenumber values of the Chrome Titanate low frequency pair vary, and they occur between 411 and 395 cm^{-1} , and between 349 and 340 cm^{-1} in spectra of the five products. These values are lower than those of rutile, but fall within the range of frequencies observed for Nickel Titanate. The absorptions of Nickel Titanate and Chrome Titanate are thus essentially indistinguishable, and the main difference that is usually observed is a strongly sloping baseline in spectra of Nickel Titanate and paints containing Nickel Titanate.

The spectrum of a yellow nonmetallic acrylic melamine enamel, 74H0006, which contains Chrome Titanate is depicted in Fig. 2c. The titanate absorptions of 74H0006 are also depicted in Fig. 7i, and they can be compared with absorptions of Nickel Titanate (Figs. 7j, k, m, n, and o) and rutile (Figs. 7a, b, c, e, f, and g) as they occur in spectra of various paints. As discussed below, 74H0006 may also contain a lesser quantity of Nickel Titanate.

The spectrum of an orange nonmetallic enamel, LC78G0513, which contains Chrome Titanate is shown in Fig. 2d. This enamel also contains a small amount of Molybdate Orange, as indicated by the weak absorption at 872 cm^{-1} (2) and elemental analysis data (discussed below). In Part VI of this series (18), infrared and XRF data for several monocoats of Reference Collection color G0513 were presented to illustrate the diversity of pigment compositions that are possible. A number of organic and inorganic pigments in various combinations were identified in the paints of this bright red–orange nonmetallic color, including Quinacridone Red Y (19), Benzimidazolone Orange (5), Isoindolinone Yellow 3R (18), Perinone Orange (18), Molybdate Orange (2), ferric oxide (2), and hydrous ferric oxide (2). Curiously, spectra of all of these finishes were observed to have prominent absorptions of color-imparting pigments except for that of LC78G0513, which appeared to have only the one weak lead chromate peak. The identification of a strong titanate absorption in this spectrum—which was previously assumed to be due to rutile—explains this apparent anomaly.

XRF Analyses

XRF spectra of Chrome Titanate from Ishihara, Ferro, Engelhard, and Cerdec are depicted in Figs. 9a, b, d, and e, respectively. Bayer manufactures two grades of Chrome Titanate that may be used in automotive paints, Light Yellow 3R and Light Yellow 5R, and spectra of the two are depicted in Figs. 9c and h, respectively. As observed for Nickel Titanate, very small amounts of zirconium and niobium were identified in all six products in varying levels,

including a difference between the two Bayer products. Very small amounts of lead were also found in most, and a very small amount of zinc was detected in the Ishihara product (Fig. 9a).

The XRF spectrum of 74H0006 is shown in Fig. 9f. The relative ratios of the antimony, titanium, and chromium peaks of Fig. 9f are similar to those observed for Chrome Titanate, and peaks of zirconium and niobium are readily observed. Nickel is also present along with very small amounts of iron and lead.

In paper VI in this series (18), data for all of the available yellow organic pigments that might be used in an automotive paint were compiled. Only one such pigment, Pyrimidine Yellow, contained nickel, and it was not identified in any Reference Collection monocoats (it is used mostly for industrial paints). Although the nickel of 74H0006 might be from an orange or red pigment, it may also be from Nickel Titanate.

The detection of chromium in paints that contain Nickel Titanate and nickel in paints that contain Chrome Titanate could thus reflect the presence of a second titanate, especially if indications of other pigments that might account for these elements are lacking (as discussed earlier for PN76H0037 regarding lead chromate pigments). Such cases illustrate the desirability of having a third method, which might possibly consist of polarized light microscopy or X-ray diffraction, to clarify the situation when two titanates, a titanate and rutile, or two titanates and rutile, are used in a paint.

During a recent study of automotive paint inorganic pigments using Raman spectroscopy, Raman spectra of Nickel Titanate and Chrome Titanate were obtained, although they were not included in the published paper (4). Both spectra, collected down to 160 cm^{-1} , were found to be nearly identical to that of rutile. The spectral bandwidth that was used in this study was relatively large ($c. 10\text{ cm}^{-1}$), however, and it is conceivable that minor differences might be observed using higher spectral resolutions.

The XRF spectrum of LC78G0513 is depicted in Fig. 9g. The strong L lines of lead and K lines of molybdenum dominate the spectrum, which also has peaks of antimony, titanium, chromium, and iron. Judging from the ratio of the K_{α} and K_{β} lines of chromium, manganese is also indicated, although the K_{β} line of manganese overlaps the K_{α} line of iron so this could not be readily confirmed. The highest energy L line of lead (at 15.8 keV) has a greater relative intensity than normally observed for lead, consistent with the presence of a weak K_{α} peak of zirconium, which occurs in this same region. A very weak peak of niobium, at essentially the detection limit, also appears to be present.

Since Molybdate Orange makes a significant contribution to the chromium peaks of Fig. 9g, the spectrum of this pigment (2) was subtracted from that of LC78G0513. A residual chromium K_{α} line resulted that had a relative intensity (compared with the K lines of titanium and the L lines of antimony) similar to those observed for Chrome Titanate; a very weak K_{α} line of zirconium also resulted from this.

Use in U.S. Automobile OEM Nonmetallic Monocoats (1974–1989)

Chrome Titanate was a less common pigment in automotive finishes than Nickel Titanate, as the green shade hues of yellow produced by Nickel Titanate were more prevalent in nonmetallic automotive finishes than the red shade hues produced by Chrome Titanate (Cerdec Corp., personal communication, January 1998). In addition, these red shades were more likely to have been formulated with Chrome Yellow, which was a very common pigment during that period (2). Consistent with this, Chrome Titanate (in

heavy pigment loads) was only identified in the two Reference Collection monocoats discussed earlier, 74H0006 (orange–yellow) and LC78G0513 (red–orange), although it more than likely was used in lesser quantities in other finishes (including its use with Nickel Titanate, as discussed).

When use of Chrome Yellow was discontinued just after the time period covered by the Reference Collection of Automotive Paints, Chrome Titanate became more common (Cerdec Corp. and DuPont Automotive Products, personal communications, January 1998). One formulation that is currently used to produce the orange–yellow “school bus yellow” hue that was formerly produced with Chrome Yellow consists of a mixture of Isoindoline Yellow (18) and Chrome Titanate (DuPont Automotive Products, personal communication, February 2005).

Rutile and Titanate Absorptions in DAC Spectra

An examination of the absorptions of rutile, Nickel Titanate, and Chrome Titanate in Figs. 1–7 shows clearly that there is a minor but noticeable difference between these features observed in spectra of pigments versus paints. The main rutile/titanate absorption has two lobes and the lower frequency lobe (centered near 530 cm^{-1}) is stronger in all of the pigment spectra compared to paint spectra. This is an artifact produced with the DAC, and is not observed in spectra of rutile obtained using DRIFTS (Fig. 7l), CsI pellets (Fig. 7p; references (17) and (33)), or KBr pellets (10). The same sample used to obtain the CsI pellet spectrum of Fig. 7p was pressed between both anvils of the DAC, and results similar to Fig. 7h were obtained. The DAC is thus clearly the source of this effect. Three different low-pressure diamond anvil cells and a high-pressure diamond anvil cell (13) were used on five different FT-IR instruments/beam condensers over the course of two decades. All of these configurations produced similar results, so specific analysis geometry is not a factor.

The effect is dependent on the concentration and particle sizes of rutile. It is more pronounced in DAC spectra of neat pigments, in spectra of pigments mixed with CsI where the dilution ratio is low (Fig. 7d), and in spectra produced when the rutile particles are not ground thoroughly. The enhancement effect is also stronger when both anvils of the DAC are used compared with when a single anvil is used. These observations are all consistent with the enhanced intensity of the lower frequency lobe resulting from differences in the amount of light reflected from the diamond/rutile interface across the absorption band.

Because of anomalous dispersion, the index of refraction of rutile is not constant throughout this absorption, but changes rapidly and reaches a maximum on the low-frequency side of the band. Differences between the indices of refraction of rutile and diamond for various wavelengths of this band result in differences in the amount of reflection that occurs at the interface (the amount of reflection is also determined by the absorption coefficient of rutile, but this is not changing rapidly in the vicinity of the broad absorption band maximum where this effect occurs). The apparent absorption intensity increase for the lower frequency rutile lobe in DAC spectra indicates that more light is being reflected (and hence lost) for these wavelengths. The difference in index of refraction between diamond and rutile is thus greater here than for the higher frequency lobe. This is consistent with the index of refraction of rutile reaching a maximum value in the vicinity of the low-frequency lobe, and becoming greater than that of diamond.

It is important to note that this effect actually occurs for *all* samples regardless of whether a diamond window is used, and

there is always some distortion of an absorption band because of it. The effect is usually more pronounced for inorganic compounds, however, since they tend to have higher indices of refraction and absorption coefficients than organic compounds, and reflection from the sample particle surface is consequently greater. The effect is also more evident with diamond windows since the high index of refraction of diamond results in a substrate having an index of refraction closer to those of inorganic compounds (for certain wavelengths), accentuating reflection differences. DAC spectra of all of the inorganic pigments discussed in this study (1,2) were therefore taken of pigment powders diluted with CsI and thoroughly ground.

None of these other inorganic pigments produced an effect as pronounced as that of rutile and the titanates, but there appear to be at least two reasons for this: (1) there is a wavelength term in the Fresnel equation (13) for specular reflection that indicates that reflection increases somewhat with wavelength; this effect is thus likely to be more evident for a far-infrared band than one that occurs at higher frequencies; and (2) the very wide breadth of the rutile/titanate absorption permits this effect to be more noticeable (the index of refraction is normally changing most rapidly near the peak of an absorption band, but for most compounds, a relatively sharp peak is involved).

A comparison of the DAC spectrum of anatase (Fig. 3a) and that of a CsI pellet of this pigment (17,33) indicates that the lower frequency absorption lobe is also enhanced, so this effect is observed for this second polymorph of titanium dioxide as well.

This effect is not evident in DAC spectra of paints that contain rutile or titanates, since for paints (1) the formation of pigment agglomerates has been minimized, reducing the average particle size (larger particles increase specular reflection); and (2) the individual pigment particles are well dispersed in a binder medium, so little or no pigment/diamond contact occurs. Consequently, rutile/titanate absorptions in DAC spectra of paints containing these pigments are similar to those obtained by other means.

Owing to the logarithmic nature of the transmittance scale, the relative intensities of the two absorption lobes of rutile/titanate may appear to vary depending on the absorption intensity. For most of the data presented, the intensities of the rutile/titanate absorptions were adjusted to 10% transmittance to facilitate comparisons, but Fig. 5e shows how the two rutile absorption lobes appear to have more similar intensities as their transmittance values approach 0%.

Concluding Comments

This study has served to clarify four minor mysteries that arose during the course of examining infrared spectra of finishes from the Reference Collection of Automotive Paints: (1) spectra of certain yellow nonmetallic monocoats had very pronounced baseline slopes that were reproducible and did not appear to be due to poor sampling techniques; the pronounced slopes did not occur in spectra of some other monocoats of this same color, and absorptions of a pigment that might be responsible for this effect were not apparent; (2) these particular monocoats all had what appeared to be strong rutile absorptions in their spectra, but these absorptions differed slightly from those of rutile observed in most other spectra; (3) the spectrum of one particular bright red–orange monocoat (LC78G0513) seemed to suggest that only a small amount of pigment was used, whereas spectra of all of the other paints of this same color had very prominent pigment absorptions (and due to optical considerations (5,18), prominent pigment absorptions are the norm for most red nonmetallic automotive fin-

ishes); and (4) DAC spectra of rutile, anatase, and the titanates consistently resulted in absorptions that exhibited minor differences compared to CsI pellet spectra of these same materials, and to absorptions of these same pigments observed in paint spectra.

Acknowledgments

The authors would like to thank Bayer Corp., Cerdec Corp., DuPont White Pigment and Mineral Products, Engelhard Corp., Ferro Corp., Ishihara Corp., and The Shepherd Color Company for providing samples and information; BASF Corp., Bayer Material Science LLC, Ciba Specialty Chemicals Corp., Clariant Corp., Consolidated Research Inc., Cookson Pigments Inc., DuPont Automotive Products, Edward E. Jaffe Associates Inc., Ford Motor Co., Pigments Consultants Inc., PPG Industries Inc., Sun Chemical Corp., and Wayne Pigment Corp. for providing information; Ms. Drexie Malone and Ms. Kitty Jacob (both of the WSP Forensic Laboratory Services Bureau) for their assistance with graphics; and Dr. JoAnn Buscaglia (FBI Counterterrorism and Forensic Science Research Unit), Ms. Helen Griffin (Ventura County Sheriff's Department Forensic Sciences Laboratory), Ms. Andria Hobbs (FBI Laboratory Chemistry Unit), Dr. Kim Mooney (FBI Counterterrorism and Forensic Science Research Unit), Dr. David Northrop (WSP Crime Laboratory, Marysville), Ms. Marianne Stam (California Department of Justice Forensic Science Laboratory, Riverside), and Dr. Diane Williams (FBI Counterterrorism and Forensic Science Research Unit) for taking the time to review this manuscript.

References

1. Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): I. Differentiation and identification based on acrylonitrile and ferrocyanide C \equiv N stretching absorptions. *J Forensic Sci* 1996;41:376–92.
2. Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): II. Identification of some topcoat inorganic pigments using an extended range (4000–220 cm^{-1}) Fourier transform spectrometer. *J Forensic Sci* 1996;41:393–406.
3. Massonnet G, Stoecklein W. Identification of organic pigments in coatings: applications to red automotive topcoats. Part III: Raman spectroscopy (NIR FT-Raman). *Sci Justice* 1999;39:181–7.
4. Suzuki EM, Carrabba M. In situ identification and analysis of automotive paint pigments using line segment excitation Raman spectroscopy: I. Inorganic topcoat pigments. *J Forensic Sci* 2001;46:1053–69.
5. Suzuki EM, Marshall WP. Infrared spectra of U.S. automobile original topcoats (1974–1989): III. In situ identification of some organic pigments used in yellow, orange, red, and brown nonmetallic and brown metallic finishes—benzimidazolones. *J Forensic Sci* 1997;42:619–48.
6. Lambourne R. Paint and surface coatings: theory and practice. New York: Halsted Press; 1987.
7. The Oil and Colour Chemists' Association Australia, Surface coatings, Vol. 1—raw materials and their usage. 2nd ed. Randwick, Australia: Tafe Educational Books; 1983.
8. Hackman JR. Nickel antimony titanate yellow. In: Lewis P, editor. Pigment handbook, Vol. 1. New York: John Wiley & Sons; 1988:375–81.
9. Hackman JR. Chrome antimony titanate buff. In: Lewis P, editor. Pigment handbook, Vol. 1. New York: John Wiley & Sons; 1988:383–88.
10. Infrared Spectroscopy Atlas Working Committee. An infrared spectroscopy atlas for the coatings industry. 4th ed, Vols. I and II. Blue Bell, PA: Federation of Societies for Coatings Technology; 1991.
11. Lin-Vien D, Bland BJ, Spence VJ. An improved method of using the diamond anvil cell for infrared microprobe analysis. *Appl Spectr* 1990; 44:1227–8.
12. Suzuki EM. Fourier transform infrared analyses of some particulate drug mixtures using a diamond anvil cell with a beam condenser and an infrared microscope. *J Forensic Sci* 1992;37:467–87.
13. Suzuki EM, Gresham WR. Forensic science applications of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS): I. Principles, sampling methods, and advantages. *J Forensic Sci* 1986; 31:931–52.

14. Collaborative Testing Services Inc. Reference collection of automotive paints technical data. Herndon, VA: Collaborative Testing Services; 1989.
15. Judd DB, Wyszecki G. Color in business, science, and industry. 3rd ed. New York: John Wiley & Sons; 1975.
16. The Society of Dyers and Colourists. Colour index. 3rd ed, Vols. 1–7. Bradford, Yorkshire: The American Association of Textile Chemists and Colourists; 1982.
17. Infrared Spectroscopy Committee of the Chicago Society for Coatings Technology. An infrared spectroscopy atlas for the coatings industry. Philadelphia: Federation of Societies for Coatings Technology; 1980.
18. Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): VI. Identification and analysis of yellow organic automotive paint pigments—Isoindolinone Yellow 3R, Isoindoline Yellow, Anthrapyrimidine Yellow, and miscellaneous yellows. *J Forensic Sci* 1999; 44:1151–75.
19. Suzuki EM, Marshall WP. Infrared spectra of U.S. automobile original topcoats (1974–1989): IV. Identification of some organic pigments used in red and brown nonmetallic and metallic monocoats—quinacridones. *J Forensic Sci* 1998;43:514–42.
20. Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): V. Identification of organic pigments used in red nonmetallic and brown nonmetallic and metallic monocoats—DPP Red BO and Thioindigo Bordeaux. *J Forensic Sci* 1999;44:297–313.
21. Force ER. Geology of titanium-mineral deposits. Special paper 259. The Geological Society of America, Inc. Boulder, CO. 1971.
22. Goldberg S. A study of bead mills and media, part 2: bead optimization. *Paint Coatings Industry* 1997;13:80–3.
23. Morgans WM. Outlines of paint technology. 3rd ed. New York: Halsted Press; 1990.
24. Tyler FK. Tailoring TiO₂ chemistry to achieve desired performance properties. *Paint Coatings Industry* 2000;16:32–8.
25. Hobbs AL, Almirall JR. Trace elemental analysis of automotive paints by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *Anal Bioanal Chem* 2003;376:1265–71.
26. Klockenkamper R, von Bohlen A, Moens L, Devos W. Analytical characterization of artists' pigments used in old and modern paintings by total-reflection X-ray fluorescence. *Spectrochim Acta* 1993;48B: 239–46.
27. Moens L, Devos W, Klockenkamper R, von Bohlen A. Total reflection X-ray fluorescence in the ultramicro analysis of artists' pigments. *Trends Anal Chem* 1994;13:198–203.
28. Devos W, Moens L, von Bohlen A, Klockenkamper R. Ultra-microanalysis of inorganic pigments on painted objects by total reflection X-ray fluorescence analysis. *Stud Conserv* 1995;40:153–62.
29. von Bohlen A, Meyer F. Microanalysis of old violin varnishes by total-reflection X-ray fluorescence. *Spectrochim Acta* 1997;52B:1053–6.
30. Vandenabeele P, Wehling B, Moens L, Dekeyser B, Cardon B, von Bohlen A, et al. Pigment investigation of a late-medieval manuscript with total reflection X-ray fluorescence and micro-Raman spectroscopy. *Analyst* 1999;124:169–72.
31. Van Hooydonk G, De Reu M, Moens L, Van Aelst J, Milis L. A TXRF and micro-Raman spectrometric reconstruction of palettes for distinguishing between scriptoria of related medieval manuscripts. *Eur J Inorg Chem* 1998;639–44.
32. Klockenkamper R, von Bohlen A, Moens L. Analysis of pigments and inks on oil paintings and historical manuscripts using total reflection X-ray fluorescence spectrometry. *X-ray Spectrom* 2000;29:119–29.
33. Afremow LC, Vandeberg JT. High resolution spectra of inorganic pigments and extenders in the mid-infrared region from 1500 cm⁻¹ to 200 cm⁻¹. *J Paint Technol* 1966;38:169–201.

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