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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

ABSTRACT: A number of strong unidentified absorptions were observed in infrared spectra of some U.S. automobile original topcoats (1974–1989) from the Reference Collection of Automotive Paints. Most of these absorptions appeared to arise from specific color-imparting pigments, but with the exception of ferric oxide (Fe$_2$O$_3$), talc, and diatomaceous silica, they could not be attributed to any pigments previously identified in automobile paint using infrared spectroscopy. All of those previously identified, however, were pigments used in undercoats. This paper describes the infrared identification of several inorganic pigments used in automobile topcoats. Lead chromate pigments, which were found in many Reference Collection yellow, orange, and red nonmetallic topcoats, are no longer used in U.S. original finishes. Their presence can thus serve as both a means to differentiate between topcoats and provide some indication of when certain topcoats may have been produced. The far-infrared region below 700 cm^{-1}, which cannot be observed when using a narrowband mercury cadmium telluride (MCT) detector, was found to be important for the analysis of topcoats containing certain pigments.

KEYWORDS: forensic science, criminalistics, paint analysis, infrared spectroscopy, pigment identification, ferric oxide, hydrous ferric oxide, Chrome Yellow, Molybdate Orange, silica-encapsulated chromate pigments, talc, diatomaceous silica, synthetic silica

In their pioneering work on the forensic analysis of automobile paint using infrared spectroscopy, Rodgers et al. identified and presented spectral data for a number of common binders and pigments that were used in these paints (1). Their spectra were collected on a dispersive instrument using a high pressure diamond anvil cell (DAC) accessory and data were presented from 2000 to 200 cm^{-1}. The identified pigments were limited to those used in undercoats and all were inorganic compounds. They included titanium dioxide (anatase), barium sulfate, kaolin, talc, crystalline silica, diatomaceous silica, calcium carbonate, and ferric oxide (Fe$_2$O$_3$). Except for the last compound, none of these pigments are used for imparting color.

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During the course of this paint study (2), a number of prominent unidentified absorptions were observed in infrared spectra of some U.S. automobile original topcoats (1974–1989) from the Reference Collection of Automotive Paints. These absorptions did not appear to arise from binders or binder-related components, and with the exception of ferric oxide, talc and diatomaceous silica, they could not be attributed to any of the pigments previously identified by Rodgers et al. in undercoats. Often, a particular group of unknown absorptions appeared only in the spectra of some topcoats having certain colors, which suggested that they arose from pigments responsible for, or contributing to, those colors. Less frequently, the same absorptions occurred in spectra of topcoats of widely different colors. These spectra sometimes had absorptions of what appeared to be a second pigment; a combination of two primary colors to produce a third color was one likely explanation for this. Pigments were therefore indicated as probable sources of these types of absorptions as well.

In some cases, the apparent pigment absorptions occurred in the spectra of topcoats of a particular Reference Collection color, but not in those of others having a similar color. In a few cases, they occurred for some topcoats of a given color, but not for others of this same color. These observations suggested that the unknown absorptions potentially could be useful for differentiation and identification, especially if they could serve to provide distinctions between some topcoats having both similar colors and similar binder compositions. To be able to utilize these absorptions for this purpose in a less empirical fashion and with less ambiguity, as well as to better classify topcoats of the Reference Collection, it was deemed desirable to identify the pigments (or other components) producing these absorptions. Also, some information about the type and range of topcoat colors that are associated with each of these pigments, as well as their frequencies of occurrence, could be useful in assessing how the spectral data may complement or augment the microscopic observations.

Because a number of pigments were identified in this study and they consist of two distinct types having very different spectral absorption characteristics, this work is presented in two parts. This paper deals exclusively with inorganic pigments, which as a group have relatively simple spectra, while the identification of organic pigments will be described in a subsequent paper.

Because of their inertness and low volatilities, inorganic pigments cannot normally be identified by pyrolysis methods. They are, however, usually strong infrared absorbers and their peaks are often quite apparent in topcoat spectra (as already noted). These

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pigments can thus be identified *in situ* for paint films without the need to isolate the pigment from the binder, and as was found to be the case for undercoats (1,3,4), simultaneous identification of both binders and pigments is possible for many topcoats.

As noted earlier (2), use of the infrared microscope has become a popular method for the forensic analysis of paint because this accessory permits considerably smaller specimens to be examined than is possible with alternative infrared methods. There is a trade-off involved with the increased sensitivity, however, since less spectral information is obtained. The sensitivity of this accessory results, in large part, from the use of mercury cadmium telluride (MCT) detectors, especially the narrowband MCT detector which is most often used with the microscope. The low frequency cut-off points for the narrowband and wideband MCT detectors occur near 700 cm^{-1} and 425 cm^{-1}, respectively. Like other inorganic compounds, some of the characteristic absorptions of inorganic pigments may occur in the low frequency region. This is particularly true for ionic type oxides used as pigments, which typically have all of their absorptions below 700 cm^{-1} (5). Another purpose of this study, therefore, was to evaluate the importance of the spectral region below 700 cm^{-1} for topcoat analysis, and all infrared data for this work were collected from 4000 to 220 cm^{-1}.

Experimental

Instrumentation

Infrared spectra were acquired on a Digilab FTS-7 Fourier transform infrared (FT-IR) spectrometer equipped with cesium iodide (CsI) optics and a deuterated triglycine sulfate (DTGS) detector. A resolution of 4 cm^{-1} was used and data were collected in the single-sided interferogram mode at a mirror velocity of 2.5 kilohertz (0.08 cm/s). The optical housing and sampling compartment were purged with dried and carbon dioxide-free air from a Balston air drying system. Between 500 and 1000 scans were averaged for all samples.

U.S. Automobile Topcoats

All of the topcoat samples used for this study were from the Reference Collection of Automotive Paints (Collaborative Testing Services, Inc., Herndon, Virginia). Topcoats will be referred to by their nine character identification codes, which have been described previously (2).

Pigments

The following pigments were used: ferric oxide (Fe$_2$O$_3$), talc, and lead oxide (Pb$_3$O$_4$), J.T. Baker Inc.; Yellow Iron Oxide, Chrome Yellow, titanium dioxide (rutile) and diatomaceous silica, Farwest Paint Mfg. Co.; lead chromate, lead molybdate, titanium dioxide (anatase), and chromium (III) oxide (Cr$_2$O$_3$), Aldrich Chemical Co.; Molybdate Orange, Cookson Pigments Inc. and Wayne Pigment Corp.; Krolor® Orange (silica-encapsulated lead chromate molybdate), Heubach Inc.; synthetic silica, J.M. Huber Corp.; zinc iron ferrite brown spinel ([Zn,Fe]Fe$_2$O$_4$:TiO$_2$), cobalt aluminate blue spinel (CoAl$_2$O$_4$), cobalt chromite blue-green spinel (Co[Al, Cr]$_2$O$_4$), and zinc iron chromite brown spinel ([Zn,Fe][Fe,Cr]$_2$O$_4$), Ferro Corp.; and Black Iron Oxide, Pfizer, Inc.

Sampling

Thin slices of Reference Collection topcoats were sampled with a low pressure diamond anvil cell (DAC) accessory (High Pressure Diamond Optics, Inc.), or they were placed over a 1 mm diameter circular aperture and sampled without a substrate. Both methods used a Digilab 5X beam condenser. With the DAC, some slices were pressed between both anvils, while others were analyzed using the single anvil technique (6,7). For sampling with the aperture, the slices were first pressed flat with a roller.

For the spectra presented in this paper, all of the sampling was done using the aperture, and topcoat slices were prepared so that their strongest absorptions had transmittance values between 5% and 10%. For some spectra not meeting this criterion, the absorption intensities were adjusted using spectral expansion (performed in the absorbance mode), and most of the baselines were adjusted to have their highest values near 100%. All of the spectral collections, calculations, and manipulations, including spectral additions and subtractions, were performed using Spectra Calc™ software.

Because of their strong infrared absorptions, all of the inorganic pigments were diluted with CsI prior to sampling. Dilution ratios of 1:2 to 1:10 were used and the pigment and CsI were ground together to form a uniformly dispersed and finely powdered mixture. This usually produced a static electricity charge which would cause the powder to be repelled from the sampling surface of the DAC. To prevent this, the powder and the anvils were treated for a few seconds with a Staticmaster® ionizing unit (8). The mixture was then pressed and sampled between both anvils of the DAC.

Elemental Analyses

Elemental analyses of some Reference Collection topcoats were conducted using X-ray fluorescence (XRF) spectrometry. A Kevex 0700 XRF spectrometer, equipped with a rhodium primary target and upgraded with an IXRF data system, was used. All analyses were performed using secondary target excitation, primarily with the titanium, tin, and gadolinium targets. For sampling, several slices of topcoat material were mounted onto the adhesive side of a thin strip of Scotch™ brand Magic® Tape suspended across the well of a plastic tray used to hold sampling cups. The adhesive side of the tape was face down so that no substrate was present between sample and detector. A tape strip without any sample was used to collect a background spectrum. For most analyses the sample chamber was not evacuated, but when analyzing for silicon or other low atomic number elements, a vacuum was used.

Results and Discussion

For metallic topcoats, the metal flakes usually provide most of the hiding power of the finish and the binder matrix itself must be transparent or semi-transparent to allow the flakes to be seen and produce their visual effect. With nonmetallic topcoats, pigments are required to produce both opacity and color, and these finishes generally contain significantly higher pigment concentrations than metallic ones. Prominent pigment absorptions thus occur predominantly in the spectra of nonmetallic topcoats and they comprise most of the examples which are discussed, although a few metallic topcoats are also included. Because most metallic topcoat spectra are relatively free of pigment absorptions, the contributions of the binder components alone can be observed and such spectra will be used for comparative purposes.

The descriptions of topcoat color used in this work are those from

the Reference Collection topcoat designation codes (2). Topcoats added to the Reference Collection after 1982 were not given color designations, but these were assigned colors based on comparisons to previously classified panels. Reference Collection colors are generic (for example, red, blue, yellow) and in some cases, it is useful to give more specific descriptions such as *gold* or *orange-brown*. These particular colors will be given in italics to differentiate them from those used in the Reference Collection.

The frequencies with which a given pigment occurs for a particular Reference Collection nonmetallic color are usually noted. Because inorganic pigments are less common in metallic finishes, extensive far-infrared data were not collected for these and usage frequencies are not usually cited. Complete data regarding pigment occurrence in Reference Collection topcoats will be presented in later papers in this series.

Inorganic pigment absorptions are often broad and their peak frequencies may vary by several wavenumbers or more between different spectra. When referring to specific absorptions, the peak frequencies will normally be rounded to the nearest 5 or 10 wavenumbers, although for the sharper absorptions, more precise values are given. For most of the spectra which are presented, the more prominent pigment absorptions are labeled with their frequencies; a complete listing of pigment absorption frequencies is given in Table 1.

Color-Imparting Pigments

Ferric Oxide—Ferric oxide (Fe_2O_3, hematite, Red Iron Oxide) is the primary ingredient in a number of pigments which range in color from orange to red to dark brown (9,10). Ferric oxide itself is red (rust-colored) but the source of the oxide, as well as the presence of other substances and pigments, leads to the color variations. The Fe_2O_3 pigments have usually been associated with automobile undercoats. Rodgers et al., for example, identified absorptions of this pigment in the spectra of a number of red, taupe, and brown automobile undercoats (1,3,11,12). They also reported its possible presence in the spectrum of a brown topcoat (3). The results of the present study indicate that ferric oxide is, in fact, a common pigment in red and brown nonmetallic topcoats: the spectra of well over one-third of Reference Collection red nonmetallic topcoats and approximately one-fourth of brown nonmetallic topcoats contain Fe_2O_3 absorptions. These absorptions are particularly prevalent for nonmetallic *maroon* shades, and they have also been observed in spectra of orange nonmetallic, and red, orange, brown, *gold*, and green[2] metallic topcoats as well.

Ferric oxide has a characteristic triplet of absorptions near 550 cm^{-1}, 470 cm^{-1}, and 330 cm^{-1} (Fig. 1c). These absorptions may be seen in the spectra of a *red-maroon* nonmetallic topcoat, FN86 1055 (Fig. 1d), a dark brown nonmetallic topcoat, KN83 0946 (Fig. 2a), and a brown metallic topcoat, NN78F0483 (Fig. 1b). All three of these topcoats have acrylic melamine enamel binders and as a comparison, Fig. 1a depicts the spectrum of this type of binder essentially free of pigment absorptions. This spectrum is that of a green metallic topcoat, NN78K0487; note its similarity to that of NN78F0483 (Fig. 1b). The lack of significant acrylic

melamine enamel binder absorptions below 700 cm^{-1} (Fig. 1a) indicates its usefulness as a "window" region.

Figure 3b depicts the spectrum of a red nonmetallic acrylic lacquer, DA80E0685, which contains ferric oxide. As a comparison, the spectrum of a similar metallic topcoat (DA80H0690) lacking significant pigment absorptions is shown in Fig. 3a. Acrylic lacquers have weak absorptions in the region below 700 cm^{-1} (Fig. 3a) and the strongest peak, at 365 cm^{-1}, may overlap the 330 cm^{-1} ferric oxide absorption. The result is a peak that may appear stronger and higher in frequency than expected for this pigment (Fig. 3b). (It is clear that the 365 cm^{-1} peak itself is not due to a pigment since it occurs in spectra of all acrylic lacquers and is also observed in the spectrum of poly[methyl methacrylate]—the main constituent of an acrylic lacquer.)

The absorption frequencies of ferric oxide observed in the spectra of a large number of topcoats and different Fe_2O_3 pigments, including published spectra of several such pigments (13), vary over a fairly wide range (Table 1). The shapes of the bands also vary somewhat (compare Figs. 1b, 1c, 1d, and 2a). These differences may reflect the different crystal forms of ferric oxide (14) that result from the various processes used to produce this compound, and this variability should be kept in mind when identifying this pigment.

Hydrous Ferric Oxide—Hydrous ferric oxide (FeO(OH), Yellow Iron Oxide) is another oxide of iron that is commonly used in automobile paints. This yellow pigment was identified for a wider range of topcoat colors than any of the other pigments discussed. For Reference Collection nonmetallic colors, hydrous ferric oxide absorptions occur in the spectra of a few red and orange topcoats, 15 to 20% of yellow topcoats, 20 to 25% of green topcoats, and 45 to 50% of brown topcoats. For metallic finishes, FeO(OH) absorptions were observed in spectra of yellow, orange, brown, *gold*, olive, and green topcoats; these absorptions are very common for olive metallic enamels (none of the Reference Collection nonmetallic colors are classified as olive). As in the case of Fe_2O_3, the colors of the FeO(OH)-based pigments may vary somewhat, but the very wide range of topcoat colors for which this pigment occurs clearly reflects its use with other colored pigments (discussed later).

The absorptions of hydrous ferric oxide, shown in Fig. 4c, consist of a 405/275 cm^{-1} low frequency pair together with some weaker peaks. Figures 4b and 4d are spectra of two FeO(OH)-containing yellow nonmetallic topcoats which have, respectively, acrylic melamine enamel and acrylic lacquer binders. The FeO(OH) absorptions in the two spectra are particularly strong and all of the pigment peaks (labeled by their frequencies) can be seen for both binder types. For most FeO(OH)-containing topcoats, however, the FeO(OH) absorptions are weaker and in many cases, only the low frequency 405/275 cm^{-1} pair is observed. An example of this is shown in Fig. 4a, which is the spectrum of a green metallic topcoat, NC76K0125.

Chrome Yellow—Another yellow pigment used in automobile topcoats is Chrome Yellow, which consists primarily of lead chromate ($PbCrO_4$) along with some lead sulfate ($PbSO_4$). The designation $PbCrO_4 \cdot xPbSO_4$ is sometimes used for Chrome Yellow since a mixed salt having a somewhat variable composition is involved. Although Rodgers et al. (1) did not present data for this pigment (which is not common in undercoats), they did note the possible

[2]According to DuPont Automotive Products, ferric oxide pigments—including red varieties—are used together with green organic pigments in certain green metallic finishes where they contribute to the production of olive, *yellow-green* or *green-brown* shades (personal communication, May 1995).

TABLE 1—*Infrared absorption frequencies of inorganic pigments identified in U.S. automobile original topcoats (1974–1989).*

Pigment*	Color	Topcoat Colors†	Absorption Frequencies‡
Ferric oxide§ Figs. 1c, 14a	Red to brown	NM: Red, orange, brown Met: Red, orange, brown, green	560–530 b, s 480–440 mb, s 350–310 b, s
Hydrous ferric oxide Figs. 4c, 14d	Yellow	NM: Yellow, orange, red, brown, green Met: Yellow, orange, brown, green, olive	3130 b, m 900 mb, m 795 mb, m 605 b, w 405 mb, s 275 n, s
Chrome Yellow Fig. 5a	Yellow	NM: Yellow, orange	853 b, s 832 n, vw, sh 399 n, vw 388 n, w 376 n, vw
Molybdate Orange Fig. 6a	Red-orange	NM: Orange, red, brown Met: Orange‖	860 b, s
Silica-encapsulated chromates Fig. 7d	Yellow to red-orange	NM: Yellow, orange	1090 b, s 855 b, s 465 b, m
Talc Fig. 10c	Not colored	NM: Semigloss black	3677 n, w 1020 mb, s 669 n, m 534 n, vw, sh 467 n, s 452 n, s 425 n, w, sh 345 n, vw
Diatomaceous silica Fig. 11a	Not colored	NM: Semigloss black	1090 b, s 795 mb, w 617 mb, w 475 b, m 386 mb, vw 301 n, vw
Synthetic silica Fig. 11c	Not colored	NM: Semigloss black	1100 b, s 800 b, w 470 b, m

*The figure number of the infrared spectrum of the pigment is indicated below each pigment in italics.

†The Reference Collection topcoat colors for which this pigment was identified are listed. Extensive far-infrared data were not collected for metallic finishes and it is possible that the iron oxide pigments were used for colors other than those listed. NM = a nonmetallic finish, Met = a metallic finish.

‡The frequencies are given in wavenumbers. The first symbol listed after the frequency value indicates the breadth of the absorption band (b = broad, mb = medium broad, and n = narrow), and the second represents the relative intensities (s = strong, m = medium, w = weak, vw = very weak, sh = a shoulder peak; the strongest absorption of a particular pigment is assigned a "strong" intensity). The variation of the absorption frequencies between samples for the narrow absorptions is usually a few wavenumbers, and may be larger for broad peaks.

§Ferric oxide is polymorphic and this is probably the reason its absorption frequencies vary so much. Generally, the ferric oxide frequencies observed for nonmetallic topcoats were higher than those observed for metallic ones.

‖These are not common and they may be topcoats from the mid 1970s or earlier having translucent appearances.

presence of lead chromate absorptions in the spectra of a both an orange and a red nonmetallic topcoat (3).

The spectrum of Chrome Yellow, shown in Fig. 5a, consists of a strong absorption at 855 cm⁻¹ with a low frequency shoulder peak at 832 cm⁻¹, and a weak triplet centered at 388 cm⁻¹ (see Table 1). Figure 5b depicts the spectrum of a yellow nonmetallic acrylic melamine enamel, NN78H0476, which has very strong absorptions of this pigment. Both the 832 cm⁻¹ shoulder peak and the low frequency triplet absorptions can be seen in this example, but for many topcoats, the triplet is too weak to be observed. For acrylic melamine enamels there are usually two very weak absorptions on the low frequency shoulder of the main chromate peak; the lower frequency member at 815 cm⁻¹ is due to melamine (1). The spectrum of a green nonmetallic acrylic lacquer,

DB75K0210, which contains a weak Chrome Yellow absorption is shown in Fig. 3c.

Chrome Yellow absorptions have been observed in the spectra of approximately 15% of Reference Collection yellow nonmetallic topcoats, and also in spectra of some orange and green nonmetallic finishes. They have not been detected in spectra of any metallic finishes.

Molybdate Orange—A red-orange pigment related to Chrome Yellow is Molybdate Orange. The name is somewhat misleading since this pigment actually consists of a mixed salt of mostly lead chromate with lesser amounts of lead molybdate and lead sulfate (9,10); it is sometimes referred to as lead chromate molybdate. The relative amounts of the two minor components are variable
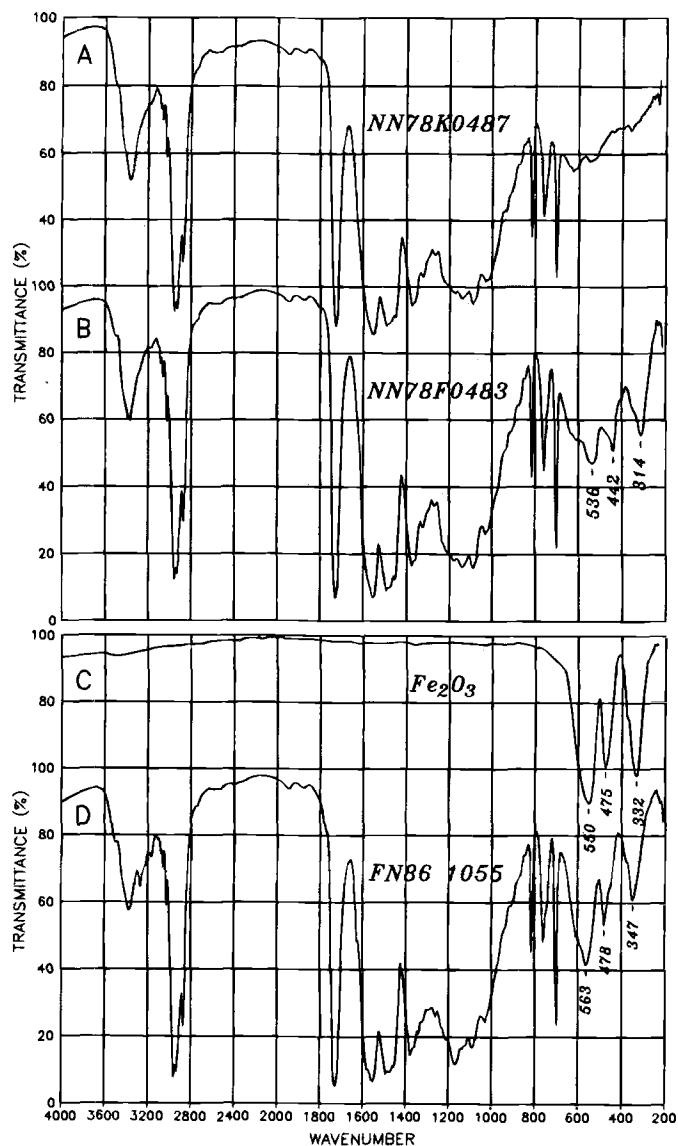
FIG. 1—*Spectra of:* (a) *a green metallic enamel topcoat, NN78K0487, which has no significant pigment absorptions;* (b) *a brown metallic enamel topcoat, NN78F0483, which contains ferric oxide;* (c) *ferric oxide; and* (d) *a red-maroon nonmetallic enamel topcoat, FN86 1055, which contains ferric oxide.*

FIG. 2—*Spectra of two nonmetallic brown enamel topcoats having the same color:* (a) *KN83 0946, which contains ferric oxide; and* (b) *FN83 0946, which contains ferric oxide and hydrous ferric oxide.*

Although they occur in similar spectral regions, Chrome Yellow and Molybdate Orange absorptions can often be distinguished from each other when their absorption intensities are high. In addition to the weak 832 cm^{-1} shoulder peak and the low frequency triplet, the ends of the Chrome Yellow 855 cm^{-1} absorptions usually have a less symmetrical shape, being somewhat more rounded on the high frequency side (compare these absorptions in Figs. 5 and 6a and 6b). These differences may be useful for classification and identification purposes (the absorption previously identified (3) in the spectrum of a red nonmetallic topcoat as possibly arising from lead chromate is more consistent with Molybdate Orange than Chrome Yellow). For comparative purposes, they are often not particularly significant since the topcoat colors themselves are usually noticeably different in such cases—when intense absorptions of a particular pigment occur in topcoat spectra, the topcoat colors are often quite similar to those of the pigment itself.

For the spectra of some topcoats having *yellow-orange* shades where both pigments may be used together, or for cases where the absorptions are weak, overlapped, or otherwise ill-defined, a clear distinction between the two chromate pigments is usually not possible. Also, other varieties of lead chromate pigments involving mixtures with alumina or lead hydroxide are possible (9,10). Should more information be required, other techniques such as microscopy or elemental analyses may provide useful complementary data.

Absorptions of Molybdate Orange have been observed in spectra of red, orange, and brown nonmetallic topcoats. This pigment is quite common for red colors: over one-third of Reference Collection red nonmetallic topcoats contain Molybdate Orange peaks in their spectra. For most of the red topcoats, the absorptions are consistent with Molybdate Orange, and as might be expected, Chrome Yellow does not appear to be used much for this color. For orange colors, absorptions of Molybdate Orange or Chrome Yellow (or both) occur in the spectra of over two-thirds of the

(hence the designation PbCrO$_4$·xPbMoO$_4$·yPbSO$_4$), but the chromate to molybdate molar ratio is typically[3] around 1:0.15.

As might be expected, the spectrum of Molybdate Orange (Fig. 6a) is quite similar to that of Chrome Yellow, with one main absorption[4] near 860 cm^{-1}. The fine structures—the shoulder peak and the low frequency weak triplet—observed for Chrome Yellow (Fig. 5a) are absent, however. The spectrum of a red nonmetallic acrylic melamine enamel, 74E0003, which contains Molybdate Orange is shown in Fig. 6b. Note that the sharp peak at 815 cm^{-1} on the low frequency shoulder of the pigment peak is due to melamine and not the pigment.

[3]Wayne Pigment Corp., personal communication, Aug. 1994.

[4]Lead molybdate itself (which has a very pale yellow color) has a strong broad absorption at 780 cm^{-1}. The lower absorption frequency of the molybdate anion compared to the chromate anion is probably the reason the 860 cm^{-1} Molybdate Orange peak is skewed to the right (Fig. 6a). This feature, however, may not be apparent in spectra of acrylic melamine enamels due to the presence of melamine and styrene absorptions.
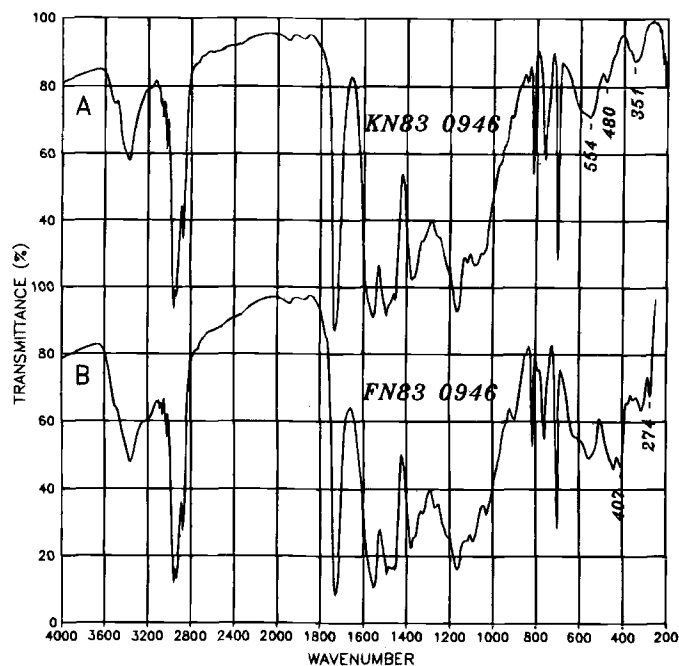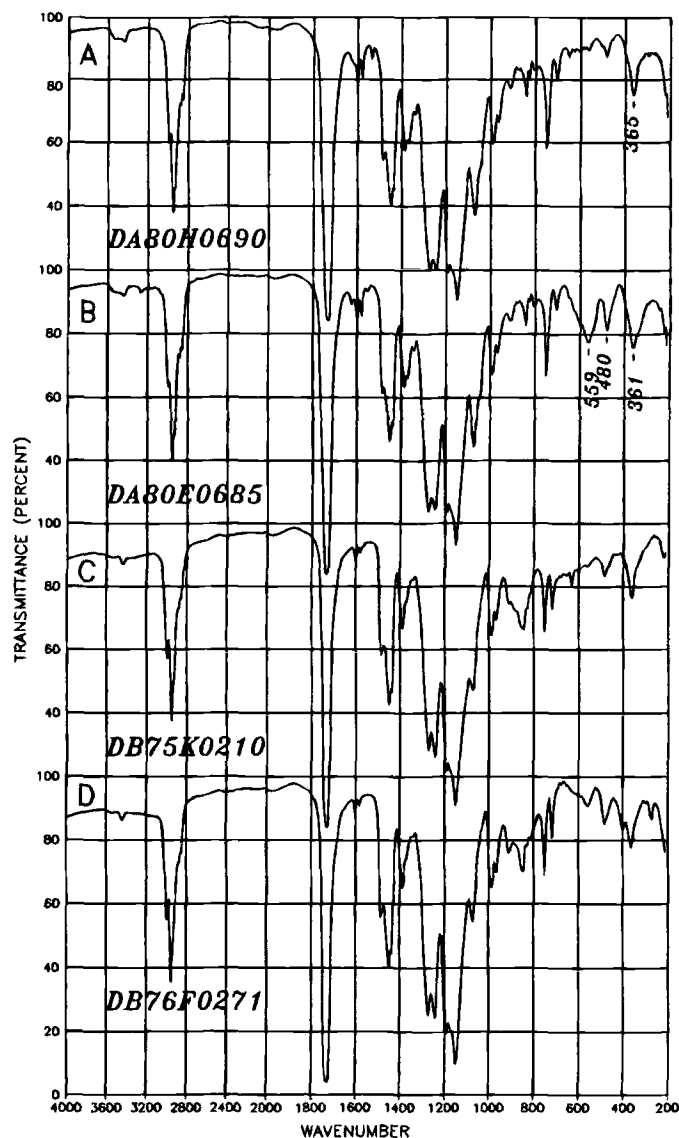
FIG. 3—*Spectra of four acrylic lacquer topcoats:* (a) *DA80H0690, yellow metallic, which has no significant pigment absorptions;* (b) *DA80E0685, red nonmetallic, which contains ferric oxide;* (c) *DB75K0210, green nonmetallic, which contains a chromate pigment; and* (d) *DB76F0271, orange-brown nonmetallic, which contains ferric oxide, hydrous ferric oxide, and a chromate pigment.*

FIG. 4—*Spectra of:* (a) *a green metallic enamel topcoat, NC76K0125, which contains hydrous ferric oxide;* (b) *a yellow nonmetallic enamel topcoat, 74H0117, which contains hydrous ferric oxide;* (c) *Yellow Iron Oxide (hydrous ferric oxide); and* (d) *a yellow nonmetallic acrylic lacquer, DB75H0211, which contains hydrous ferric oxide.*

Reference Collection nonmetallic topcoats. A weak absorption of Molybdate Orange was observed in the spectrum of an orange metallic topcoat,[5] but use of this pigment in metallic finishes appears to be quite uncommon.

Silica-Encapsulated Lead Chromate Pigments—To minimize the possibility that lead chromate, an oxidant, will react with the paint binder, a few manufacturers coat the chromate pigment particles with a layer of silica. Use of these silica-encapsulated

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[5]This topcoat, 74G0056, has a turbid or translucent appearance unlike most metallic finishes. The weak Molybdate Orange peak is inconspicuous, but elemental analysis confirmed the presence of lead, molybdenum and chromium in this topcoat. A personal communication with DuPont Automotive Products (May 1995) confirmed that Molybdate Orange was used in some orange metallic finishes approximately 20 years ago, and that such topcoats did have translucent appearances.
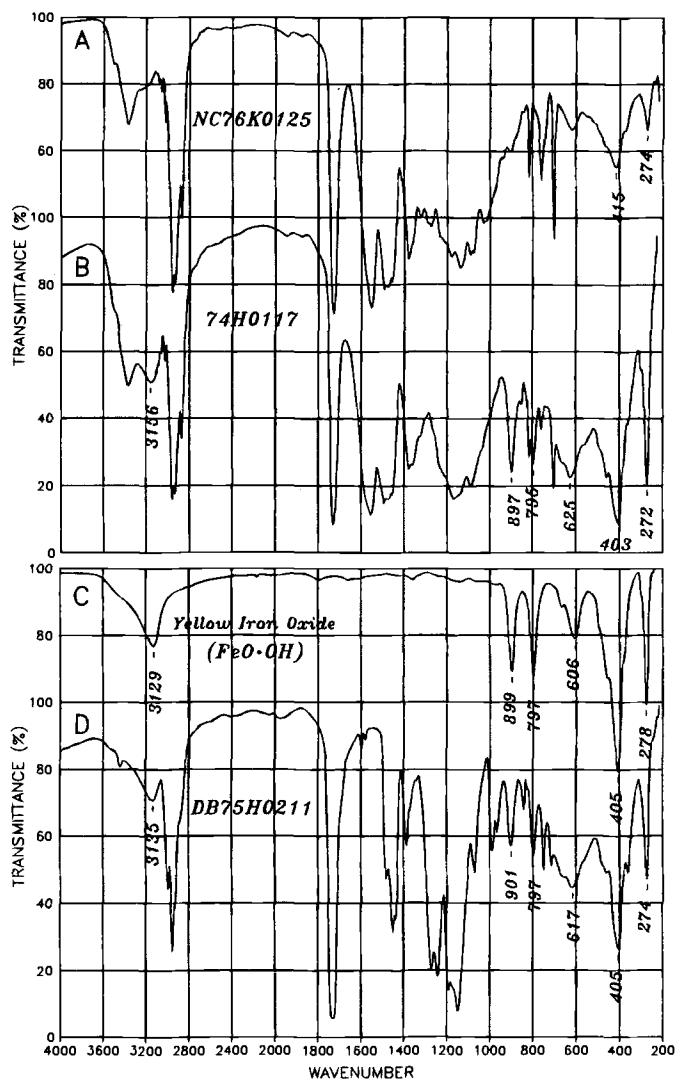
pigments in Reference Collection topcoats is considerably less than that of the conventional chromates, presumably due to economic factors since encapsulated pigments are more expensive to produce. Absorptions of encapsulated pigments have been detected in the spectra of approximately one dozen orange nonmetallic topcoats and a few yellow nonmetallic topcoats; most of these are acrylic lacquers produced by DuPont.

The spectrum of an orange nonmetallic acrylic lacquer, 74G0070, which contains strong encapsulated Molybdate Orange absorptions is shown in Fig. 7b. Comparison to a comparable lacquer binder spectrum (Fig. 7a) indicates that in addition to the chromate feature near 860 cm^{-1}, there is a weaker broad absorption between 500 and 400 cm^{-1} and what appears to be a broad absorption on the low frequency shoulder of the strong acrylic lacquer binder peak at 1150 cm^{-1}. To better delineate these extra absorptions, spectral subtractions were performed for most topcoats having such spectral features. Spectra of metallic topcoats lacking pigment absorptions were chosen as subtrahends, and these were
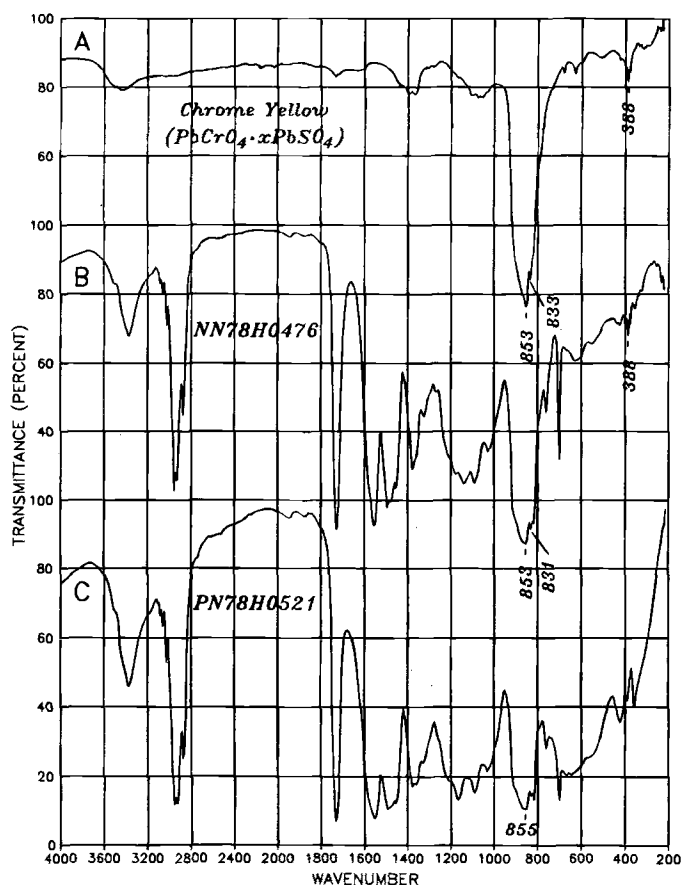
FIG. 5—*Spectra of:* (a) *Chrome Yellow (PbCrO₄·xPbSO₄);* (b) *a yellow nonmetallic enamel topcoat, NN78H0476, which contains Chrome Yellow; and* (c) *a yellow nonmetallic enamel topcoat, PN78H0521, which contains Chrome Yellow and rutile.*

FIG. 6—*Spectra of:* (a) *Molybdate Orange (PbCrO₄·xPbMoO₄· yPbSO₄);* (b) *a red nonmetallic enamel topcoat, 74E0003, which contains Molybdate Orange;* (c) *an orange-brown nonmetallic enamel topcoat, 74G0019, which contains ferric oxide and Molybdate Orange; and* (d) *a red-brown nonmetallic enamel topcoat, NN78F0482, which contains ferric oxide and Molybdate Orange.*

chosen based on their similarities, both visually and also on chemical compositions indicated by Reference Collection designation codes, to the topcoats of interest. Following each subtraction, three broad absorptions resulted along with (usually) weaker uncompensated binder absorptions—either as positive or negative peaks. Subtraction results for 74G0070 (Fig. 7b) minus DB76L0195 (Fig. 7a) are shown in Fig. 7c; the three broad absorptions match those of silica-encapsulated Molybdate Orange (Fig. 7d). In addition to the chromate pigment absorption near 855 cm⁻¹, the other two absorptions (1092 cm⁻¹ and 465 cm⁻¹) are consistent with those of silica.

The spectrum of an orange nonmetallic acrylic melamine enamel, PN78G0393, which contains an encapsulated chromate pigment is shown in Fig. 8a. In this case, the encapsulated chromate appears to be Chrome Yellow based on the low frequency shoulder peak at 833 cm⁻¹, the shape of the 853 cm⁻¹ absorption, and the very weak features near 390 cm⁻¹. For an acrylic melamine enamel binder, the 1092 cm⁻¹ silica absorption may not be as conspicuous as it is for a lacquer, since acrylic enamels have strong C-O stretching fundamentals in this region and their pattern may vary due to differences in the acrylic monomers used (1).

Noncolored Pigments

Titanium Dioxide—This pigment is by far the most common used in nonmetallic topcoats. It is particularly prevalent among the lighter colors and is found in all Reference Collection white
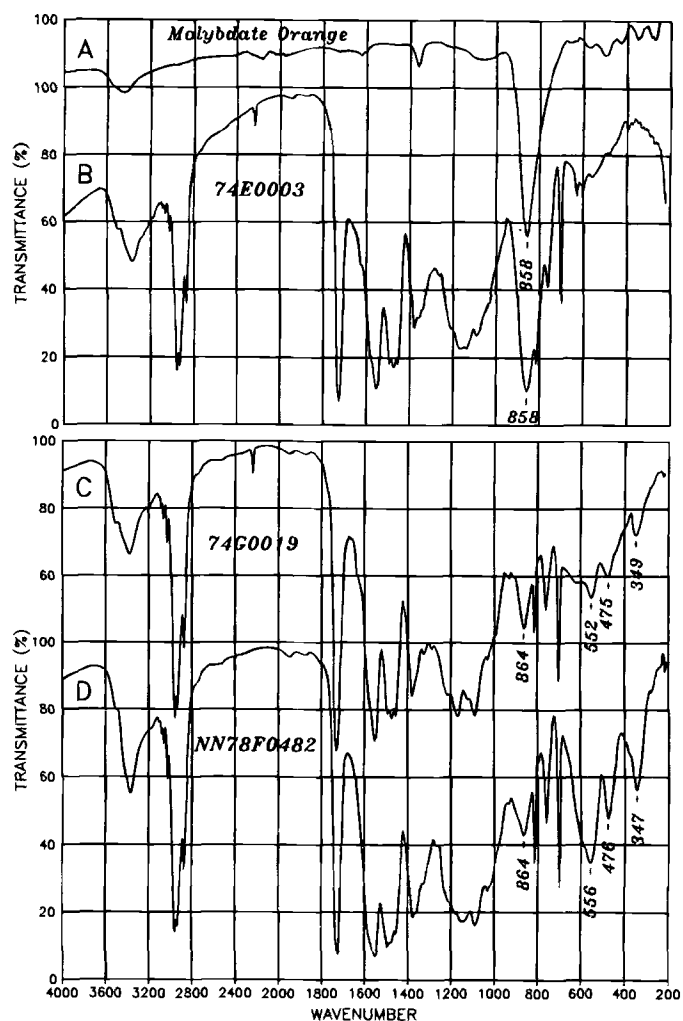
topcoats and in many yellow topcoats—especially in the *off-white* and *beige* shades. Although less common for dark colors, the lighter shades of some of these, such as light blue, gray, and pink, usually also contain significant amounts of titanium dioxide (these lighter shades usually have a "creamy" appearance).

Spectra of anatase and rutile, the two crystal forms of titanium dioxide used in paints, are shown in Figs. 9a and 9b, respectively. While the two forms may sometimes be used together, rutile, the more refractive polymorph, is clearly the dominant form used in topcoats as evidenced from numerous spectra. Conspicuous rutile absorptions may be seen, for example, in the spectra (Figs. 9c and 9d) of two yellow nonmetallic enamels.

Talc—Strong absorptions of three pigments normally associated with undercoats were identified in the spectra of some black nonmetallic topcoats. The three, talc, diatomaceous silica, and synthetic silica, are extender pigments. Significantly, while the majority of black nonmetallic topcoats have glossy finishes, the particular topcoats containing these extender pigments all had noticeably flatter finishes best described as semigloss or eggshell. Since black topcoats are naturally opaque, additional noncolored
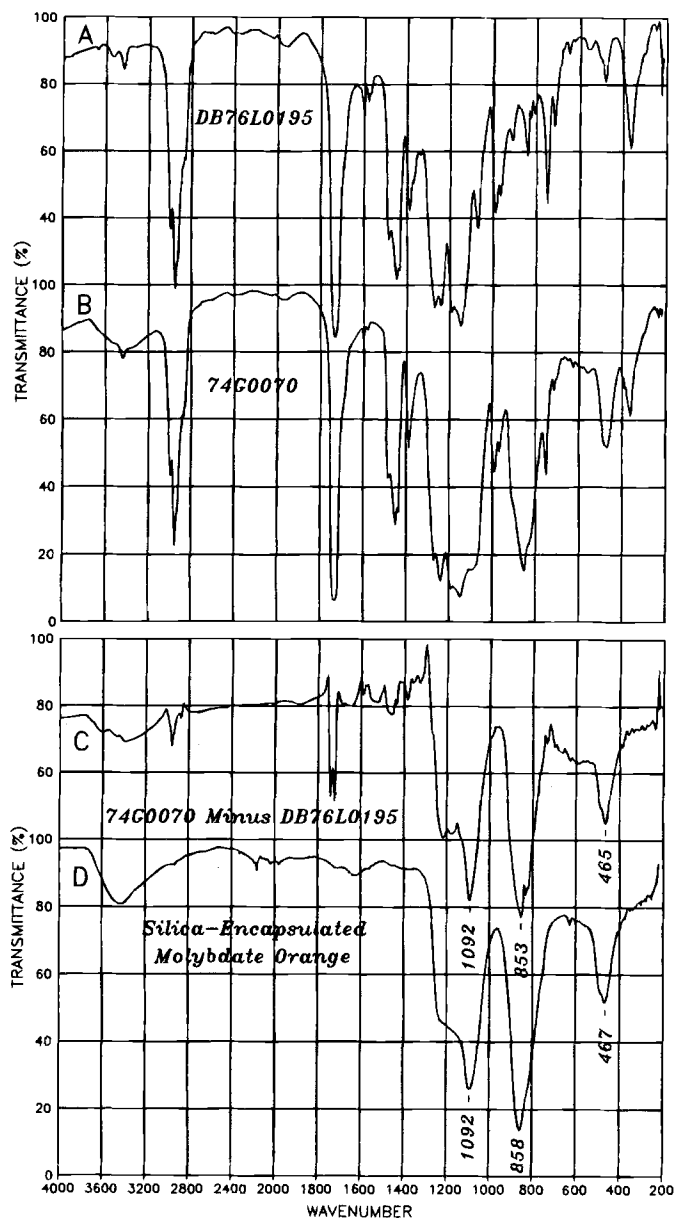
FIG. 7—*Spectra of:* (a) *a blue metallic acrylic lacquer topcoat, DB76L0195;* (b) *an orange nonmetallic acrylic lacquer topcoat, 74G0070, which contains an encapsulated chromate pigment;* (c) *subtraction results—spectrum* (b) *minus 0.80 times spectrum* (a)*; an absorbance value of 0.10 was added to the difference spectrum to adust its baseline; all spectral calculations were performed in absorbance and the final result was converted to transmittance; and* (d) *silica-encapsulated Molybdate Orange.*

FIG. 8—*Spectra of two nonmetallic orange enamel topcoats having the same color:* (a) *PN78G0393, which contains an encapsulated chromate pigment; and* (b) *NN78G0393, which contains hydrous ferric oxide and a chromate pigment.*

FIG. 9—*Spectra of:* (a) *titanium dioxide - anatase;* (b) *titanium dioxide—rutile;* (c) *a yellow nonmetallic enamel topcoat, LC81H0506, which contains rutile; and* (d) *a yellow nonmetallic enamel topcoat, KC81H0506, having the same color, which contains hydrous ferric oxide and rutile.*

pigments are not required and titanium dioxide absorptions were not detected in any of their spectra. These extender pigments are thus clearly serving as flatting agents. Absorptions of the three occur in spectra of approximately 10% of Reference Collection black nonmetallic topcoats.

Spectra of two such topcoats containing talc, PN80C0630 and NW78C0407, are shown in Figs. 10a and 10b, respectively. All of the absorptions of talc (Fig. 10c) can be identified in the two spectra. Both of these topcoats have acrylic melamine enamel binders, but the strong pigment absorptions may make binder identification more difficult. This is more likely the case for
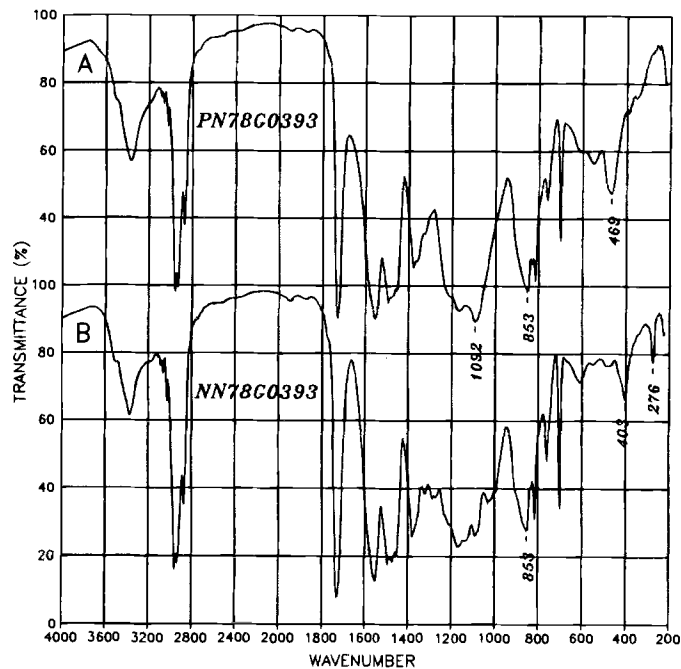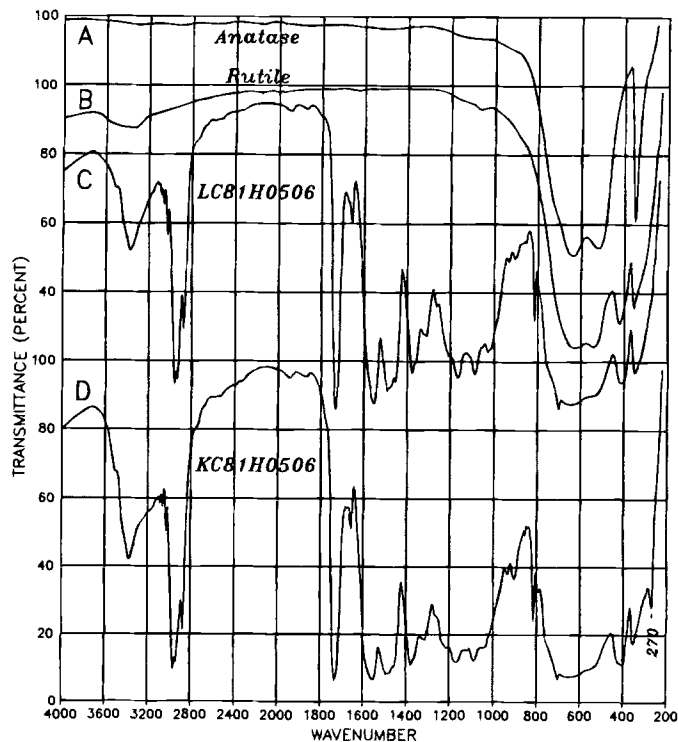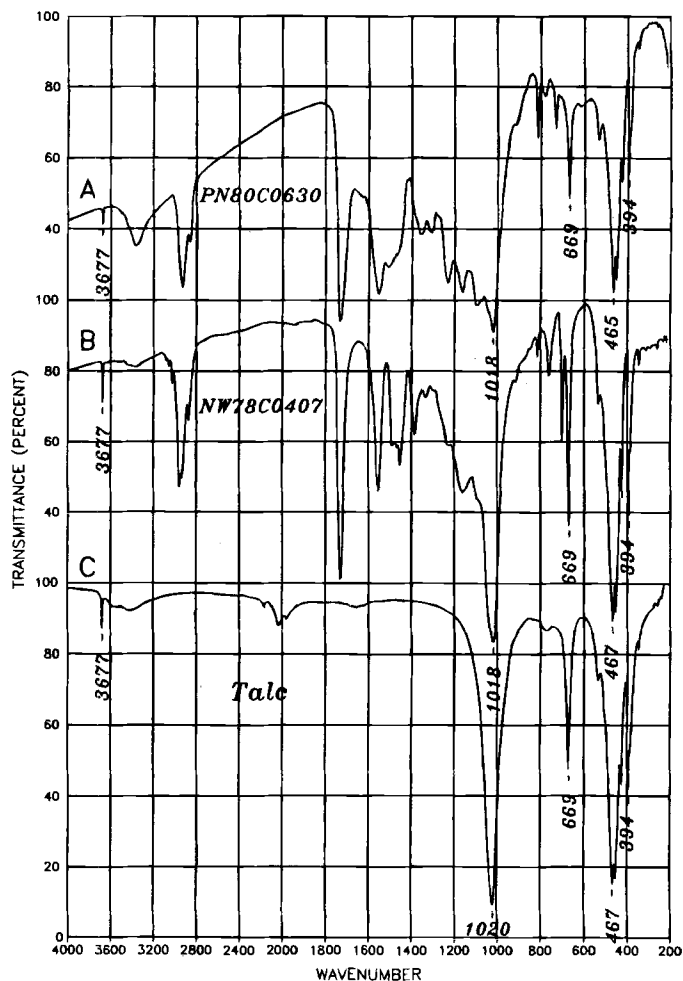
FIG. 10—*Spectra of:* (a) *a semigloss black nonmetallic enamel topcoat, PN80C0630, which contains talc and possibly a carbonate pigment;* (b) *a semigloss black nonmetallic enamel topcoat, NW78C0407, which contains talc; and* (c) *talc; the weak absorptions near 2000 cm⁻¹ are DAC sampling artifacts (2).*
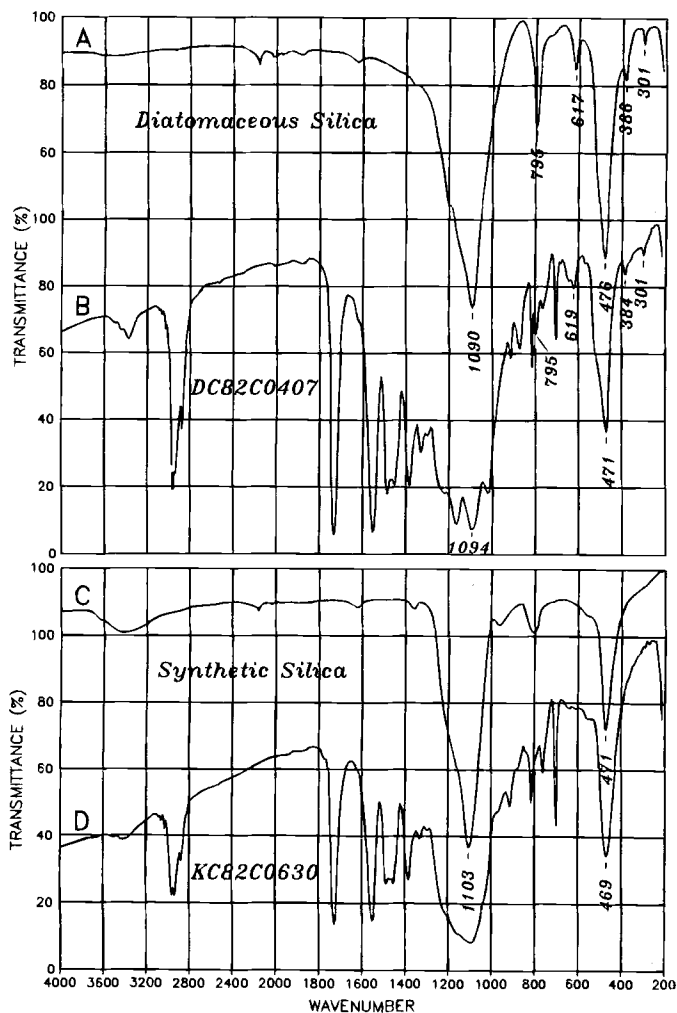

FIG. 11—*Spectra of:* (a) *diatomaceous silica;* (b) *a semigloss black nonmetallic enamel topcoat, DC82C0407, which contains diatomaceous silica;* (c) *synthetic silica; and* (d) *a semigloss black nonmetallic enamel topcoat, KC82C0630, which contains synthetic silica.*

PN80C0630 (Fig. 10*a*), since the characteristic strong broad melamine absorption at 1550 cm⁻¹ (1) appears to have coalesced with the adjacent lower frequency absorption. This may reflect the additional presence of a carbonate, since the various types of carbonate extender pigments all have strong broad absorptions between 1500 and 1400 cm⁻¹ (1,13). Note also the pronounced slope of the baseline of this spectrum, caused by strong pigment (presumably carbon) scattering.

Diatomaceous Silica and Synthetic Silica—Various forms of silica, including crystalline silica, diatomaceous silica, amorphous silica, and synthetic silica, may be used as extender pigments (10). As noted earlier, the first two types were identified in automobile undercoats (1). Diatomaceous silica and synthetic silica have been identified in a few black nonmetallic topcoats similar to those discussed previously, where they are used as flatting agents. As examples, spectra of DC82C0407 (Fig. 11*b*), which contains diatomaceous silica (Fig. 11*a*), and KC82C0630 (Fig. 11*d*), which contains synthetic silica (Fig. 11*c*), are presented.

The spectrum of crystalline silica (1,13) is easily distinguished from that of the diatomaceous and synthetic forms. The spectrum of diatomaceous silica (Fig. 11*a*) has three weak peaks below 700 cm⁻¹ that do not occur for the synthetic form (Fig. 11*c*), and the

795 cm⁻¹ absorption is sharper and stronger for the former. These four peaks may be seen in the spectrum of DC82C0407 (Fig. 11*b*), but they do not occur in the spectrum of KC82C0630 (Fig. 11*d*). As was the case for silica-encapsulated chromate pigments, the strongest silica absorptions near 1100 cm⁻¹ may not be as conspicuous as expected for the spectra of acrylic melamine enamels, but the 470 cm⁻¹ absorptions usually stand out.

Multiple Pigment Absorptions

The color-imparting pigments that have been described are often used in combination with each other and with organic pigments to produce a variety of different colors. Because most of the inorganic pigments absorb in different spectral regions, their combinations can often be readily identified. In some cases, the pigment combinations which are detected are consistent with the observed colors, as when a yellow pigment and a red pigment are identified for an orange topcoat. In other cases, organic pigments having infrared absorptions too weak to be observed are used with the pigments that are identified. Blue organic pigments, for example, are undoubtedly used with the yellow inorganic pigments in the green topcoats whose spectra are shown in Figs. 3*c* and 4*a*.

Iron Oxide Combinations—Absorptions consistent with mixtures involving ferric oxide and hydrous ferric oxide have been observed in the spectra of some brown nonmetallic topcoats. These absorptions all occur below 1000 cm^{-1}, and they may be better observed in the expanded views shown in Fig. 12. The expected absorption pattern for a roughly 1:1 mix (by weight) of the two oxides is shown in Fig. 12a. For this, spectra of the two pigments (Figs. 1c and 4c) were added using different ratios; to verify the relative amounts of pigments involved, these results were then compared to spectra obtained for actual mixtures of the two oxides. Spectra of two brown (*orange-brown*) nonmetallic enamels,
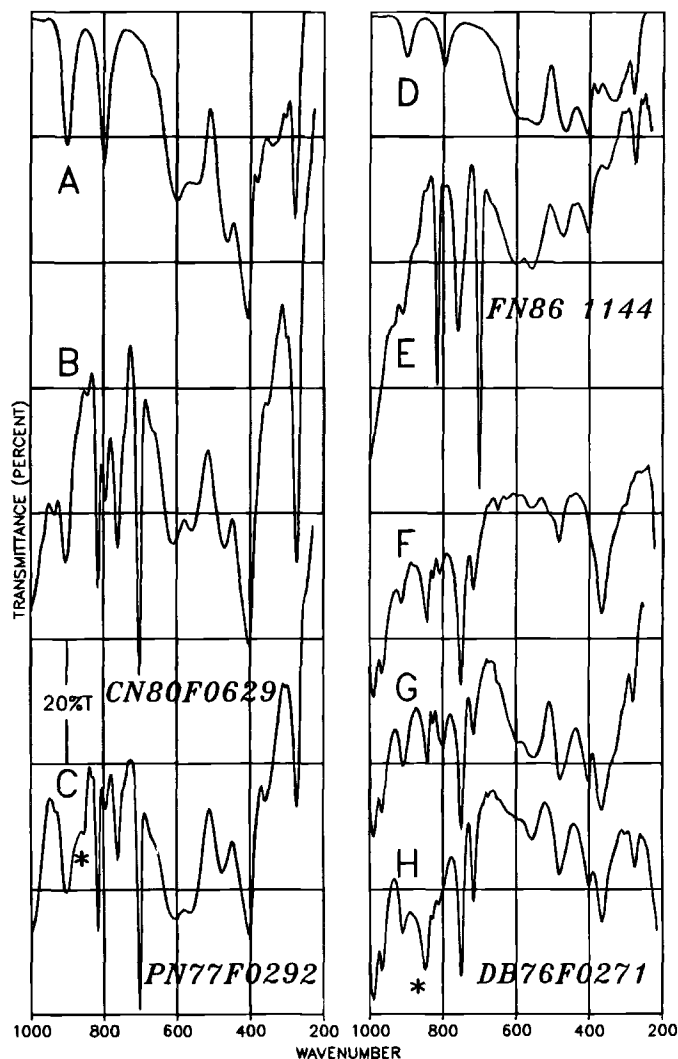

FIG. 12—*Spectra in the 1000 cm^{-1} to 200 cm^{-1} region of: (a) an addition of the absorptions of ferric oxide and hydrous ferric oxide representing an approximate 1:1 mixture by weight; (b) an orange-brown nonmetallic enamel topcoat, CN80F0629, which contains ferric oxide and hydrous ferric oxide; (c) an orange-brown nonmetallic enamel topcoat, PN77F0292, which contains ferric oxide, hydrous ferric oxide, and a chromate pigment; the weak chromate absorption is marked with an asterisk; (d) an addition of the absorptions of ferric oxide and hydrous ferric oxide; (e) a brown nonmetallic enamel topcoat, FN86 1144, which contains ferric oxide and hydrous ferric oxide; (f) DB76L0195 (see Fig. 7a); (g) an addition of the absorptions of ferric oxide and hydrous ferric oxide to the spectrum of DB76L0195 (above); and (h) an orange-brown nonmetallic acrylic lacquer topcoat, DB76F0271, which contains ferric oxide, hydrous ferric oxide, and a chromate pigment; the weak chromate absorption is marked with an asterisk (see also Fig. 3d, which depicts this entire spectrum).*

CN80F0629 and PN77F0292, which contain Fe_2O_3/FeO(OH) pigment ratios similar to this 1:1 mix are shown in Figs. 12b and 12c, respectively. The observed and expected absorption profiles are consistent and the minor differences probably reflect variations in the Fe_2O_3 absorptions due to polymorphism. Figure 12e is the spectrum of a brown nonmetallic topcoat, FN86 1144, which also contains a Fe_2O_3-FeO(OH) mixture, but it has more Fe_2O_3 than the 1:1 mix; a pigment addition spectrum with a similar pattern is shown above (Fig. 12d). The spectrum of another topcoat (FN83 0946, dark brown nonmetallic) which also has more of the Fe_2O_3 is shown in Fig. 2b. Note that for both of the latter two spectra, the relative intensity of the 405/275 cm^{-1} FeO(OH) pair (Fig. 4c) in the overall pattern is weaker compared to Fig. 12a.

The spectrum of a brown (*orange-brown*) nonmetallic acrylic lacquer, DB76F0271, which contains a Fe_2O_3-FeO(OH) mixture is depicted in Fig. 3d; an expanded view is given in Fig. 12h. Also shown is essentially the spectrum of the binder itself (Fig. 12f—this is an expanded view of Fig. 7a), and the results of an addition of Fe_2O_3-FeO(OH) absorptions to this binder spectrum (Fig. 12g). Lacquer binder absorptions occur in this low frequency region, but the observed spectrum (Fig. 12h) is consistent with the results expected (Fig. 12g) for an iron oxide mixture.

Iron Oxide and Lead Chromate Combinations—A closer examination of the spectrum of DB76F0271 in the 1000-800 cm^{-1} region (Figs. 3d and 12h—compare to Figs. 3a and 12f, respectively) indicates that an additional weak broad absorption near 860 cm^{-1} is probably also present. The same appears to be the case for the enamel (PN77F0292) spectrum of Fig. 12c when compared to Fig. 12b. These features (marked by asterisks in Fig. 12) suggest that a chromate pigment is present, and elemental analyses confirmed the presence of lead, chromium, molybdenum and iron in both topcoats. These particular *orange-brown* topcoats thus contain (at least) *three* different colored pigments: two iron oxides and a lead chromate.

Spectra of two nonmetallic enamels that contain absorptions of both ferric oxide and a chromate pigment are shown in Fig. 6c (74G0019, orange or *orange-brown*) and Fig. 6d (NN78F0482, brown or *red-orange-brown*). It may be helpful to compare the two spectra to Fig. 1d, which is the spectrum of an enamel with just ferric oxide. The weak broad 864 cm^{-1} absorptions of Figs. 6c and 6d appear to be more indicative of lead chromate molybdate than lead chromate, and elemental analyses confirmed the presence of molybdenum in both topcoats (along with lead, chromium, and iron).

Figure 8b depicts the spectrum of an orange nonmetallic enamel, NN78G0393, which contains absorptions of both hydrous ferric oxide and a chromate pigment (as a comparison, spectra of enamels which contain the individual pigments are shown in Figs. 4a and 6b). An elemental analysis of NN78G0393 indicated the presence of lead, chromium, molybdenum and iron.

Rutile Combinations—Because of their relatively high opacities (10), colored inorganic pigments are frequently used alone or with other colored pigments with little or no titanium dioxide. As noted previously, this may not be true for the lighter colors, and of the color-imparting pigments discussed, the yellow ones (hydrous ferric oxide and Chrome Yellow) in particular are more frequently used with rutile. Figure 9d depicts the spectrum of a yellow nonmetallic enamel, KC81H0506, which contains hydrous ferric oxide together with a large amount of rutile. The lower frequency member of the FeO(OH) 405/275 cm^{-1} pair is visible but the 405 cm^{-1}

peak is obscured by the rutile absorption (Fig. 9b). The presence of the 405 cm^{-1} FeO(OH) peak appears to be manifested as a small but noticeable shift in the rutile peak to a lower frequency (compare these features in Figs. 9c and 9d—the vertical grid line of the latter figure, however, may make this feature more difficult to see). Titanium and iron were detected for KC81H0506, while LC81H0506, which lacks an observable FeO(OH) peak (Fig. 9c), contains mainly titanium and only a small amount of iron.

The spectrum of a yellow nonmetallic enamel, which contains significant amounts of both Chrome Yellow and rutile is shown in Fig. 5c, while the spectrum of DA76H0208, a yellow nonmetallic acrylic lacquer, which contains an encapsulated chromate pigment and rutile, is shown in Fig. 13a. An elemental analysis of the latter topcoat indicated the presence of lead, chromium, silicon, titanium, and a small amount of iron.

For many topcoats, less noticeable amounts of titanium dioxide may be used with the colored pigments. The titanium dioxide infrared absorptions may not be apparent or they may be manifested as weak broad dips in the baselines of the spectra centered near 600 cm^{-1}. Titanium (among other elements) was detected for 74H0117 (Fig. 4b), DB75H0211 (Fig. 4d), and 74G0019 (Fig. 6c) and this dip may be seen to varying degrees in the three spectra.

Topcoats with Similar Colors: Pigment Differences

The colored pigments that have been described in this work were used primarily in red, orange, brown and yellow nonmetallic topcoats. Within this group, it was not unusual for Reference Collection topcoats having similar colors to have different pigment compositions. As might be expected, topcoats of colors for which a larger number of different pigments were identified tended to exhibit greater diversity in their compositions and spectra. The spectra of red nonmetallic topcoats, in particular, were among the

most diverse due to use of a variety of different inorganic and organic pigments and various combinations thereof. Even for colors for which only a single inorganic pigment was identified, however, some diversity was observed because of use of organic pigments and pigment combinations.

Spectra of two nonmetallic yellow lacquers having similar colors are shown in Fig. 13. As noted earlier, DA76H0208 (Fig. 13a) contains an encapsulated chromate pigment and rutile, while DA77H0043 (Fig. 13b) contains noticeably more rutile (relative to binder absorptions), a few weak sharp absorptions between 1700 cm^{-1} and 1500 cm^{-1} which are probably due to an organic pigment, and indications of a small amount of a chromate pigment. An elemental analysis of DA77H0043 confirmed the presence of the latter pigment, since lead, chromium, and titanium were detected.

In a number of cases, topcoats having identical colors (as defined by their Reference Collection codes) also had different pigment compositions. Five examples of such colors are presented. All involve nonmetallic enamel topcoats and most of these have already been discussed. The colors, topcoat pairs, and pigments which were identified (given in parentheses) are: (1) brown, Fig. 2a—KN83 0946 (ferric oxide) and Fig. 2b—FN83 0946 (ferric oxide and hydrous ferric oxide); (2) orange, Fig. 8a—PN78G0393 (encapsulated chromate) and Fig. 8b—NN78G0393 (hydrous ferric oxide and a chromate pigment); (3) yellow, Fig. 9c—LC81H0506 (rutile and most likely an organic pigment with absorptions too weak to be observed) and Fig. 9d—KC81H0506 (rutile and hydrous ferric oxide); (4) semigloss black, Fig. 10a—PN80C0630 (talc and possibly a carbonate) and Fig. 11d—KC82C0630 (synthetic silica); and (5) semigloss black, Fig. 10b—NW78C0407 (talc) and Fig. 11b—DC82C0407 (diatomaceous silica). The latter two examples involve extender pigments that are used to modify luster rather than impart color.

Differences in the Spectra of Some Inorganic Pigments

Because of the simplicity of inorganic pigment spectra and the possibility of weak or overlapping peaks, it is not unusual to observe only one or two pigment absorptions in certain topcoat spectra (for example, Figs. 3c, 4a, and 9d). To assess better the degree of confidence with which such absorptions can be attributed to specific pigments, it is useful to examine the spectra of some closely related compounds.

Figure 14 depicts spectra of seven inorganic oxides from 1000 cm^{-1} to 200 cm^{-1}, together with ferric oxide (Fig. 14a) and hydrous ferric oxide (Fig. 14d) absorptions. These compounds were chosen because of the similarities of their spectra to those of the two iron oxides; they do not have any significant absorptions above 1000 cm^{-1}. The seven, all of which have been used as paint pigments (pigment colors—if not apparent—are given in parentheses), are: (1) zinc iron ferrite brown spinel ([Zn,Fe]Fe$_2$O$_4$:TiO$_2$), Fig. 14b; (2) cobalt aluminate blue spinel (CoAl$_2$O$_4$), Fig. 14c; (3) cobalt chromite blue-green spinel (Co[Al,Cr]$_2$O$_4$), Fig. 14e; (4) zinc iron chromite brown spinel ([Zn,Fe][Fe,Cr]$_2$O$_4$), Fig. 14f; (5) Black Iron Oxide (Fe$_3$O$_4$), Fig. 14g; (6) lead (III) oxide (Pb$_3$O$_4$, orange), Fig. 14h; and (7) chromium (III) oxide (Cr$_2$O$_3$, green), Fig. 14i. Of these, the spectrum of the brown spinel (Fig. 14b) resembles that of ferric oxide the most, but even considering the variation of frequencies exhibited by ferric oxide absorptions (Table 1), the middle absorption of the spinel triplet occurs at a lower frequency. Also, the shapes and relative intensities of the absorptions are different. The others are not likely to be confused with the two iron oxides, and except for chromium oxide, the seven have not
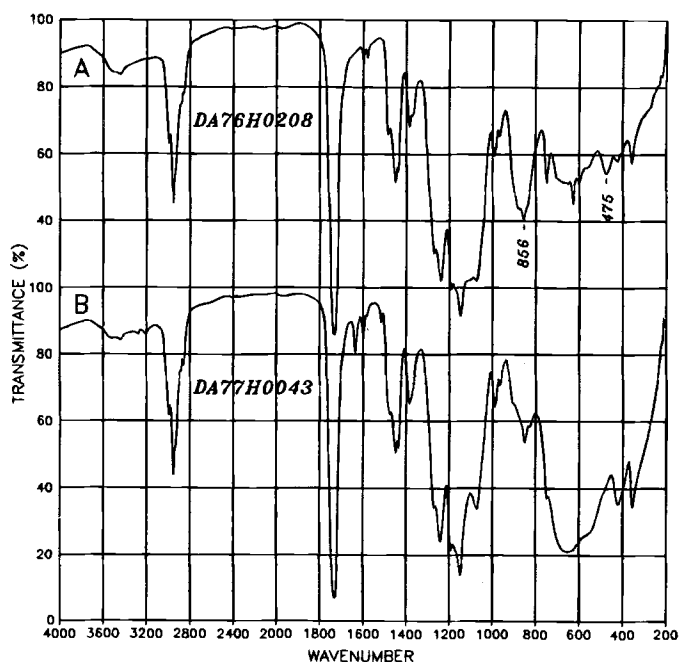

FIG. 13—*Spectra of:* (a) *a yellow nonmetallic acrylic lacquer topcoat, DA76H0208, which contains an encapsulated chromate pigment and rutile; and* (b) *a yellow nonmetallic acrylic lacquer topcoat, DA77H0043, which has a similar color and which contains rutile, a small amount of a chromate pigment, and probably an organic pigment which produces the weak sharp absorptions.*
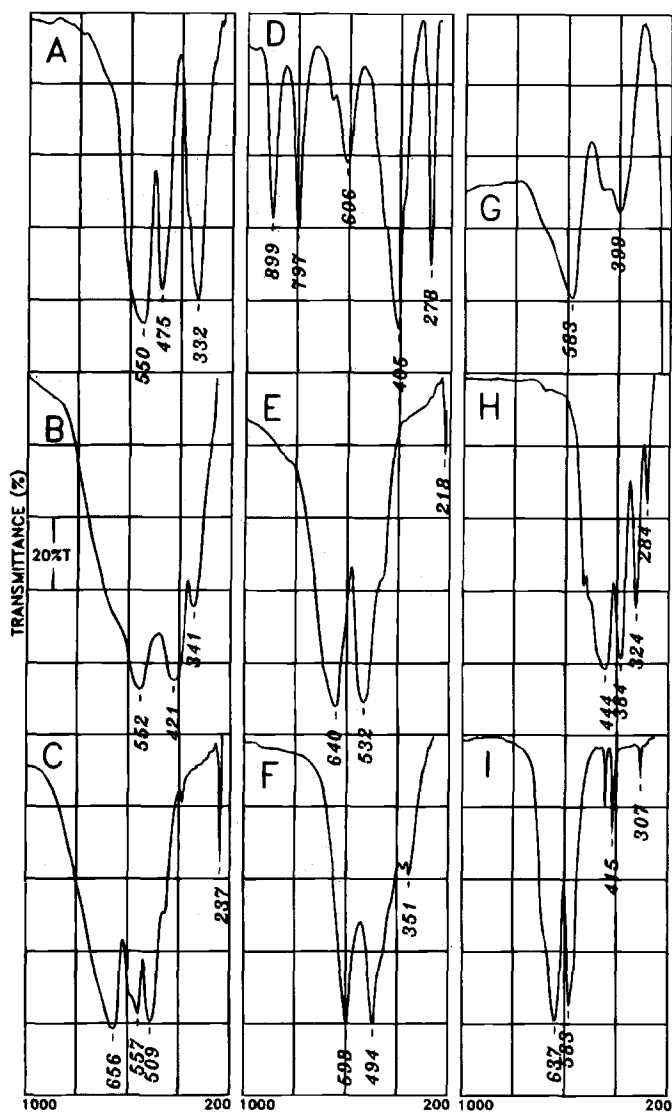
FIG. 14—*Spectra of nine inorganic oxide pigments in the 1000 cm⁻¹ to 200 cm⁻¹ region:* (a) *ferric oxide;* (b) *zinc iron ferrite brown spinel;* (c) *cobalt aluminate blue spinel;* (d) *Yellow Iron Oxide (hydrous ferric oxide);* (e) *cobalt chromite blue-green spinel;* (f) *zinc iron chromite brown spinel;* (g) *Black Iron Oxide;* (h) *lead* (III) *oxide; and* (i) *chromium* (III) *oxide.*

been associated with use (15,16) in automobile topcoats (to date, none, including chromium oxide, have been identified in Reference Collection topcoats).

Pigment Absorptions in the 700-220 cm⁻¹ Spectral Region

Except for Molybdate Orange (Fig. 6a), all of the other pigments that have been discussed have one or more absorptions in the spectral region below 700 cm⁻¹, and ferric oxide has all of its absorptions in this region. The value of low frequency absorptions for topcoat analysis thus varies depending on the pigment or pigments involved.

For Chrome Yellow (Fig. 5a), only the weak 388 cm⁻¹ triplet occurs below 700 cm⁻¹ and although it adds considerable weight to the confirmation of this pigment, the 855 cm⁻¹ chromate peak itself is usually quite distinct when the triplet is strong enough to be observed. A similar situation occurs for talc. While it has very distinct absorptions below 700 cm⁻¹ (Fig. 10c), the strong 1020

cm⁻¹ absorption—and especially the weak sharp 3677 cm⁻¹ peak—are together unmistakable indications of the presence of talc.

For encapsulated pigments (Fig. 7d), the 465 cm⁻¹ silica peak is usually more important, especially for acrylic melamine enamels, to help establish the encapsulated nature of the chromate since the main silica absorption is partially obscured by binder peaks. This same low frequency peak is also important for silica itself, as are the weak features (Fig. 11a) that can serve to distinguish between the diatomaceous and synthetic forms. It should be remembered, however, that the number of Reference Collection topcoats which contain encapsulated pigments and silica is relatively small, so that the need for these particular far-infrared distinctions is not expected to occur often (as far as Reference Collection topcoats are concerned).

This is not true for topcoats containing the two iron oxide pigments, which are much more common. Hydrous ferric oxide has three absorptions above 700 cm⁻¹ (Fig. 4c), but they are not apparent in most spectra except for those of a few yellow nonmetallic, brown nonmetallic, or olive metallic topcoats which contain large amounts of this pigment. For most topcoats, only the FeO(OH) pair below 425 cm⁻¹ is observed.

For instruments equipped with narrowband MCT detectors, none of the ferric oxide absorptions can be observed, and with a few exceptions, the same is true for topcoats which contain hydrous ferric oxide. With broadband MCT detectors, the two ferric oxide absorptions above 450 cm⁻¹ can be observed but the hydrous ferric oxide pair below 425 cm⁻¹ cannot.

Lead Pigments in Topcoats: A Possible Usage Timeframe

As discussed, various types of lead chromate pigments were found in yellow, brown, and especially, in orange and red nonmetallic Reference Collection topcoats. Because of health concerns about the toxicity of lead (and to a lesser extent chromium) compounds, use of lead pigments in many types of paint has been discontinued. Lead chromates were phased out of use in U.S. automobile original topcoats during the 1980s (mostly in the mid 1980s), and there are few, if any, topcoats that contain these pigments on *regular production* American vehicles from the 1990s.[6] General Motors continued to use lead chromate pigments for certain special order automobiles, such as fleet vehicles, until 1994, when all use of this pigment was discontinued.[7] As was found to be the case for acrylonitrile (2), lead chromate pigments can thus serve as both a means to differentiate between topcoats and also provide some indication of when certain topcoats may have been produced. It should be stressed that the latter applies only to U.S. original finishes; imported vehicle original finishes and repaints may have different (or no) ending dates for lead pigment usage.

Of possible relevance to paint transfer cases or issues involving contamination, it is worth noting that lead chromate pigments continue[8] to be used in yellow traffic paints, such as traffic control striping used on highways and airports (17). They are also still used in safety identification paints on some buses, ambulances, and fire trucks.

Elemental Analyses

For inorganic pigment identification, elemental analyses provide information that is particularly appropriate to confirm, clarify, or

augment the infrared results. Elemental data are especially useful for cases where: (1) ambiguity about an identification occurs because the pigment infrared absorptions are weak, obscured, or unusual; (2) a chromate pigment is involved but the infrared data do not provide a clear distinction as to type, and this information is desired; or (3) an MCT detector is used to collect infrared data and one wishes to determine if an iron oxide pigment might be present in the topcoat. Even when there are no indications of the presence of an inorganic pigment based on infrared data, elemental results may detect low levels of certain pigment elements, as illustrated later.

For the third case mentioned where an MCT detector is used, elemental data may serve to determine if a far-infrared analysis is warranted—assuming this option exists—since detection of iron may not, by itself, be sufficient to determine which iron-containing pigment is involved. Detection of this element for a yellow topcoat or a *gold* metallic topcoat probably reflects use of hydrous ferric oxide, while its detection for a blue topcoat is likely due to iron ferrocyanide (2). For green nonmetallic topcoats, hydrous ferric oxide is a likely choice, but iron from ferrocyanide cannot be ruled out since it too may be used in green paints (although it does not appear to have been used (2) in Reference Collection green nonmetallic topcoats). For green or olive metallic topcoats, both hydrous ferric oxide and ferric oxide may be used, although the former is more common. Detection of iron in a red or *maroon* topcoat is most likely due to ferric oxide, although hydrous ferric oxide has been used for a few red colors. Likewise, for orange or brown topcoats it is possible that both iron oxides may have been used, either alone or in combination. It should be noted that small amounts of iron may also be present[9] in some paints as a residue transferred from the steel ball mills used to disperse pigments in the paint vehicle, or from other sources of contamination.

Elemental analyses using XRF spectrometry were conducted on most of the topcoats for which spectra have been presented, as well as on many others. To illustrate the differences in elemental composition that can occur between topcoats and how they correlate with infrared data, XRF spectra of four of the topcoats are shown in Fig. 15. The elements detected by XRF analysis and the pigments identified from infrared spectroscopy (given in parentheses with figure numbers) are: (1) Fig. 15a—DB75H0211, mostly iron, some titanium, and a small amount of lead (hydrous ferric oxide, Fig. 4d); (2) Fig. 15b—PN78H0521, lead, chromium, titanium, and a small amount of molybdenum (Chrome Yellow and titanium dioxide, Fig. 5c); (3) Fig. 15c—74E0003, lead, chromium, molybdenum, and a small amount of iron (Molybdate Orange, Fig. 6b); and (4) Fig. 15d—74G0019, iron, lead, chromium, molybdenum, titanium, and nickel (ferric oxide and a chromate pigment, Fig. 6c). The nickel detected for 74G0019, an orange topcoat, may reflect use of Nickel Azo Yellow, an organic pigment known to have been used in automobile topcoats (10,15,16). The K series lines of sulfur, an element which should be present (as lead sulfate) in all of the topcoats except for DB75H0211 (Fig. 15a), occur in the same region as the M lines of lead (the first peak on the left near 2 KeV) and therefore are not evident.

Summary

Five color-imparting inorganic pigments were identified from their infrared absorptions in spectra of some U.S. automobile original topcoats (1974–1989). They are ferric oxide (Fe_2O_3), hydrous
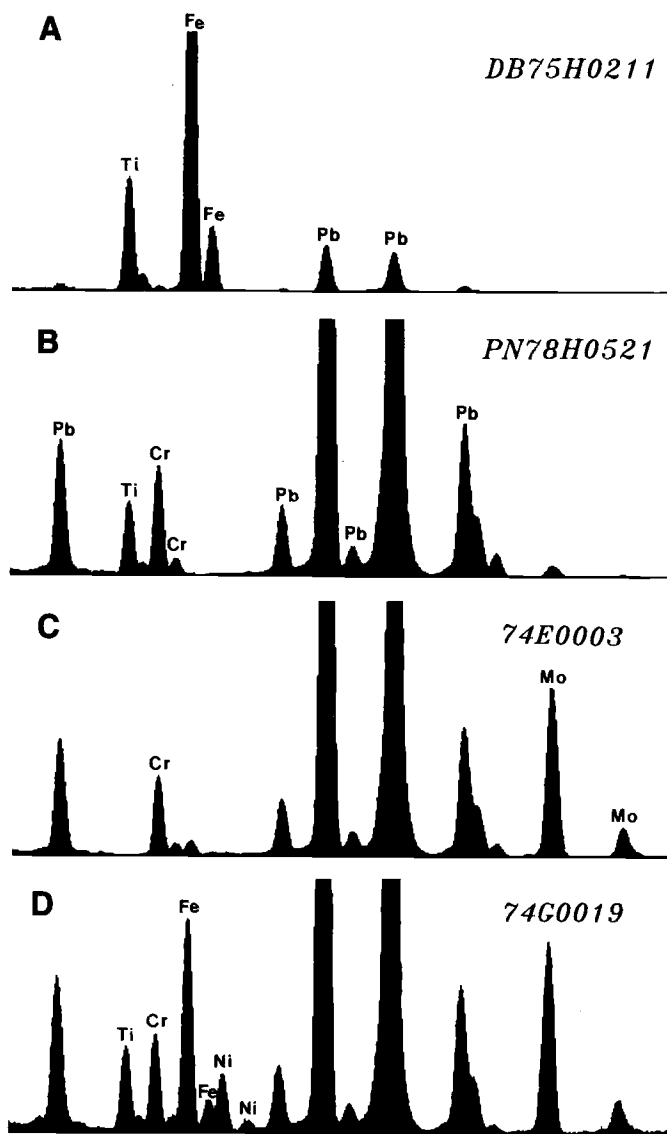
[9]See Footnote 7.

FIG. 15—*XRF spectra between 1 and 21 KeV of four nonmetallic topcoats sampled using a tin secondary target as the excitation source (topcoat colors are given in parentheses): (a) DB75H0211 (yellow); (b) PN78H0521 (yellow); (c) 74E0003 (red); and (d) 74G0019 (orange). Topcoat slices were sampled using a vacuum and data were collected for 50,000 seconds (total live time). A background spectrum, taken of a strip of tape without any sample, was subtracted from each of the four spectra.*

ferric oxide (FeO[OH]), Chrome Yellow ($PbCrO_4 \cdot xPbSO_4$), Molybdate Orange ($PbCrO_4 \cdot xPbMoO_4 \cdot yPbSO_4$), and silica-encapsulated lead chromate pigments. All are used in nonmetallic topcoats, and absorptions of the two iron oxides were also observed in spectra of some metallic finishes. Three extender pigments used as flatting agents, talc, diatomaceous silica, and synthetic silica, were identified in a few black semigloss nonmetallic topcoats. A list of the inorganic pigments which have been identified is given in Table 1, together with their infrared peak frequencies (or range of frequencies) and the types of topcoats in which they have been identified.

Various combinations of the five colored pigments with each other and with titanium dioxide (rutile) were identified in some topcoats. These combinations, as well as others involving organic pigments, contribute to the diversity of pigment compositions which were found to occur, especially for red, orange, yellow,

and brown nonmetallic topcoats. Many such topcoats with similar colors were found to have distinct infrared spectra, even when similar binders were used. The far-infrared region below 700 cm^{-1} may be important for the analysis of topcoats containing inorganic pigments, particularly if one of the iron oxides is involved. Lead chromate pigments, which occur in many yellow, orange, red and brown nonmetallic topcoats of the Reference Collection time period, are no longer used in U.S. automobile original finishes.

Acknowledgments

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