

# 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\*

**REFERENCE:** 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(3): 514–542.

**ABSTRACT:** A previous study in this series demonstrated the feasibility of identifying organic pigments *in situ* based on their absorptions in infrared spectra of automobile topcoats. To isolate pigment peaks, spectra of closely matched topcoats lacking pigment features are subtracted from spectra of topcoats containing the pigment of interest. Once identified by this means, these pigments can often be determined based on the more limited number of pigment peaks observed between the broader binder absorptions, or superimposed on them. Spectra of closely related pigments are used to provide some indications of how distinct a particular set of pigment absorptions is. Using these techniques, several different quinacridone pigments have been identified in single-layer U.S. automobile original topcoats (1974–1989) from the Reference Collection of Automotive Paints. Two of these pigments, Quinacridone Red Y and Quinacridone Violet, were found to be common in red nonmetallic topcoats. Quinacridones were also identified in brown nonmetallic and red and brown metallic finishes. A number of different pigment combinations of quinacridones with both inorganic and organic pigments have been identified, and examples of these are presented. As a prerequisite to the analysis of pigments using this *in situ* method, analysts should be very familiar with the absorptions of automotive topcoat binders.

**KEYWORDS:** forensic science, criminalistics, paint analysis, infrared spectroscopy, pigment identification, quinacridones, Quinacridone Red Y, Quinacridone Violet, Quinacridone Magenta, Quinacridone Magenta B

The pigment or pigments used in an automobile topcoat may differ for finishes having similar colors, especially for topcoats of certain colors (1–3). Along with binder data, pigment compositions can thus serve in these cases as a means to discriminate further between those finishes which cannot be differentiated by color. Determination of specific pigments can also serve as a basis for the classification and identification of topcoats, and information about pigment frequency of use for different topcoat colors can be helpful in evaluating the significance of data collected. For those topcoats containing a pigment or pigment combination that is not

common (3), for example, the value of this information for comparative analyses or identification purposes is evident. Because some pigments are no longer used in automobile original equipment manufacturers (OEM) finishes (2), whereas others have been introduced recently (3), identification of one of these pigments in an unknown *original finish* can provide limits to the possible model years of vehicles which could have been the source of such a finish.

In previous studies of this series, several inorganic (1,2) and organic (3) pigments used in U.S. automobile original topcoats (1974–1989) were identified *in situ* using infrared spectroscopy. The topcoats consisted of single-layer finishes (monocoats) from the Reference Collection of Automotive Paints, and information regarding frequencies of occurrence for particular colors and beginning or ending usage dates (if applicable) were also presented for some of the pigments. The organic pigments identified were members of the benzimidazolone family, and Benzimidazolone Orange (Pigment Orange 36) in particular was found to be a common pigment in Reference Collection orange and red nonmetallic monocoats.

This paper describes the analysis of another group of organic pigments, the quinacridones, which were identified in a number of Reference Collection red nonmetallic monocoats, and in some brown nonmetallic and red and brown metallic ones as well. Because of their brilliant shades (mostly in reds and violets) and excellent light, heat, chemical, and bleed-resistant qualities (4–6), quinacridones find use in a number of applications besides automotive finishes. These include industrial, architectural, and decorative finishes, especially for outdoor uses, and plastics, furniture stains, printing inks, and artist's paints (6,7).

## Experimental

### *Instrumentation and Sampling*

Infrared spectra (4000 to 220  $\text{cm}^{-1}$ ) were acquired at a resolution of 4  $\text{cm}^{-1}$  on a Digilab FTS-7 Fourier transform infrared (FT-IR) spectrometer equipped with cesium iodide (CsI) optics and a deuterated triglycine sulfate (DTGS) detector. For the spectra depicted in this work, topcoats were sampled as thin slices held over a 1 mm circular aperture in a metal disk, mounted in a Digilab 5 $\times$  beam condenser. Pigments were sampled as powders diluted with CsI using a Digilab diffuse reflectance (DRIFTS) accessory. A total of 1000 scans were averaged when using the beam condenser, and 200 were averaged with the DRIFTS accessory. The spectrometer, sampling accessories, acquisition parameters used

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for data collection, and sample preparation methods have been described in more detail elsewhere (2,3).

### Topcoats and Pigments

Except for one sample, all of the topcoats discussed in this work are from the Reference Collection of Automotive Paints (Collaborative Testing Services, Inc., Herndon, VA). Topcoats will be referred to by their nine-character Reference Collection identification codes, which have been described previously (1). One red nonmetallic topcoat which was not available in the Reference Collection, PA79E0471, was obtained from the FBI Laboratory National Automotive Paint File (1).

The following pigments were used (pigment *Colour Index* (8) designations are given in parentheses since the cited common names are not universally used, and trade names are given in italics): Quinacridone Red Y (Pigment Violet 19, *gamma* crystal form), Hoechst Celanese *Hostaperm*<sup>®</sup> *Red E3B* and Bayer *Quindo*<sup>®</sup> *Red R-6700*; Quinacridone Violet (Pigment Violet 19, *beta* crystal form), Hoechst Celanese *Hostaperm Red Violet ER-02* and Bayer *Quindo Violet RV-6911*; Quinacridone Red Y/Quinacridone Violet mix, Sun Chemical Corp. *Sunfast*<sup>®</sup> *Red 19* (Sun Chemical Corp. refers to this pigment as Quinacridone Red B); Quinacridone Magenta (Pigment Red 122), Sun Chemical Corp. *Sunfast Magenta 122* and Hoechst Celanese *Hostaperm Pink E*; Quinacridone Magenta B (Pigment Red 202), Sun Chemical Corp. *Sunfast Magenta 202*; and Quinacridone Red Y 209 (Pigment Red 209), Sun Chemical Corp. *Sunfast Magenta 209* (Sun Chemical Corp. refers to this pigment as "Quinacridone Red Y," but "Quinacridone Red Y 209" is used here to distinguish it from Pigment Violet 19, *gamma* crystal form). Spectra of Benzimidazolone Orange (Pigment Orange 36) and some inorganic pigments are also discussed in this work, and these pigments have been described previously (2,3).

### Pigment Identification Procedures

The procedures used to identify organic pigments have been described in detail in the previous paper in this series (3), and only a brief summary is given here. Spectral subtraction was used to help visualize and clarify pigment absorptions and distinguish them from those of binders. For a topcoat containing a pigment of interest, another topcoat having a very similar composition, but lacking this pigment, was used to produce a subtrahend spectrum. For a given pigment, subtractions involving a number of different topcoat spectra and subtrahend spectra were conducted, and the difference spectrum which is depicted represents the best possible results for illustrative purposes. These difference spectra are therefore *not* typical and this type of analysis is not usually applicable to case samples, for which closely matched binder compositions are not normally readily accessible.

Since fewer pigment absorptions are actually observed in topcoat spectra themselves, it is useful to have some indication of just how different spectra of other automotive pigments are from those which were identified, especially for absorptions occurring in certain spectral regions. Spectra of the identified pigments were therefore compared with those of a number of other automotive organic pigments, including the benzimidazolones (3) and others that have been identified to date in Reference Collection monocoats. The absorptions were also compared with organic pigment absorptions of Reference Collection topcoat spectra that have yet to be identified. Most importantly, they were compared with absorptions of

other similar pigments in the same family, including all of the ones known to have been used in automotive paint, since they are the ones which have spectra most like those of the identified pigments.

### Spectral Calculations

Spectral calculations were performed using Spectra Calc<sup>™</sup> software. Topcoat spectral absorption intensities were adjusted so that the strongest peak had a transmittance value of between 2% and 7%, and the baselines were set to have their highest values near 100% (baselines were not flattened, however). For spectral subtraction, a subtrahend factor was chosen which produced minimal residual binder features and the baseline of the difference spectrum was adjusted, but not flattened; difference spectra absorption intensities were not adjusted. Reflectance spectra of pigments obtained using the DRIFTS accessory were converted to a transmittance format (9).

### Elemental Analyses

Elemental analyses were conducted using X-ray fluorescence (XRF) spectrometry. A Kevex 0700 XRF spectrometer equipped with a rhodium primary target, various secondary targets, and an IXRF Systems Inc. operating unit was used. Topcoats were sampled as thin slices mounted under a strip of adhesive tape, and data collected for a blank strip of tape were subtracted from each spectrum. For the spectra depicted in this work, X-rays from tin and titanium secondary targets were used for excitation, produced with X-ray tube voltages of 45 and 25 kV, respectively, and currents of 2.0 mA. The instrument chamber was evacuated and data were collected for 50,000 s (total live time). A few topcoats were sampled using a scanning electron microscope/energy dispersive X-ray analysis (SEM/EDX) system which has been described previously (3).

### Results and Discussion

The molecular structures of the quinacridone pigments discussed in this work are shown in Fig. 1. Structure I, the unsubstituted prototype of the translinear quinacridone ring system, is polymorphic and can exist in four different crystal forms (5,6). Two of

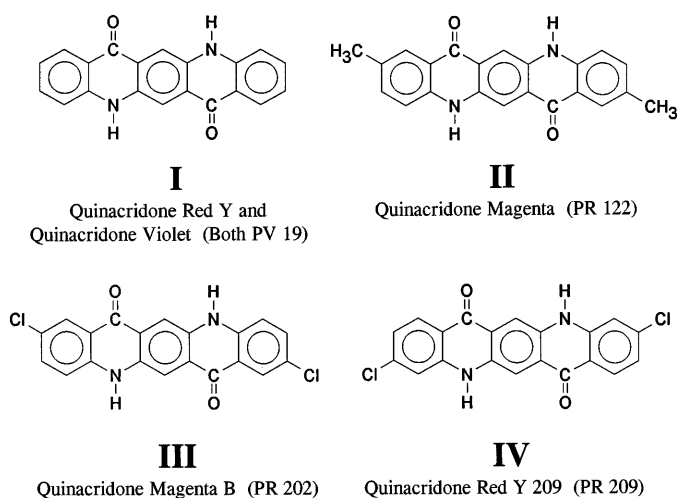


FIG. 1—Structures of the quinacridone pigments discussed in this work. The Colour Index abbreviations are: PV = Pigment Violet and PR = Pigment Red.

these, the *beta* and *gamma* polymorphs, are used as the pigments Quinacridone Violet and Quinacridone Red Y, respectively. Although nominally they have the same chromophore, the two have decidedly different colors: Quinacridone Violet has a deep purple-violet shade and Quinacridone Red Y is red-pink. The infrared spectra of the two, depicted in Fig. 2*a,b*, are very similar but they do have distinguishing features. Spectra of the other quinacridones discussed in this work are also depicted in Fig. 2 and their absorption frequencies are listed in Table 1.

All of the quinacridones were analyzed using DRIFTS, rather than a diamond anvil cell (DAC) accessory (1–3), since DRIFTS spectra more closely matched the pigment absorptions observed in topcoat spectra. As was found to be the case for most of the benzimidazolones (3), application of pressure caused spectral changes to occur for some of the quinacridones, although these were far less pronounced than those observed for the benzimidazolones. Pigment powders were therefore diluted with finely powdered CsI and they were mixed without grinding.

The crystal lattice arrangements of the quinacridones involve considerable intermolecular hydrogen bonding between C=O and N—H groups of adjacent molecules (Fig. 1), and this is believed to contribute to the superior durability of these pigments (5,6). It is thus possible that pressure-induced changes in this bonding pattern are the cause of the observed spectral changes for the pigments themselves. As present in topcoats, however, the quinacridones appear to be unaffected when low to moderate pressures are applied, since use of a low-pressure DAC for the analysis of such topcoats did not produce spectra noticeably different from those acquired without applied pressure.

Topcoat colors will be described by the generic colors used in the Reference Collection of Automotive Paints. Topcoats added to the Reference Collection after 1982 were not given such color designations, but these were assigned to a color category based on comparisons with previous panels. If a more specific color description (for example, *maroon*) is used, it is written in italics.

Whenever possible, topcoats that contain primarily only the pigment of interest were chosen for subtraction. The quinacridones, however, are usually used with other pigments, and for topcoats of the Reference Collection period these were mostly inorganic pigments; broad absorptions of inorganic pigments are therefore also observed in some subtraction results. Spectra of topcoats with both acrylic lacquer and acrylic melamine enamel binders, the two main types used in Reference Collection finishes, are presented since the spectral window regions differ for these.

### Quinacridone Red Y

The spectrum of a red nonmetallic enamel topcoat, NC76E0245, that contains Quinacridone Red Y (1) is shown in Fig. 3*b*, together with the spectrum (Fig. 3*a*) of a similar brown metallic topcoat, NC76F0127, which lacks observable pigment absorptions. Subtraction results for NC76E0245 minus NC76F0127 are shown in Fig. 3*c*, and the spectrum of Quinacridone Red Y is depicted below (Fig. 3*d*). All of the absorptions of Quinacridone Red Y may be seen in the difference spectrum, and their frequency values are all within  $2\text{ cm}^{-1}$  of those of the pigment reference spectrum. The relative absorption intensities are also consistent, and the close correlations for both frequencies and intensities can be compared to the differences which occur for the quinacridone absorptions depicted in Fig. 2 and listed in Table 1.

The spectrum of a red nonmetallic lacquer, NA77E0342, that contains Quinacridone Red Y is shown in Fig. 4*b*, along with the

spectrum of a green metallic lacquer, NA77K0337 (Fig. 4*a*), the subtraction results for NA77E0342 minus NA77K0337 (Fig. 4*c*), and the pigment reference spectrum (Fig. 4*d*). All of the Quinacridone Red Y absorptions are also observed in this difference spectrum, which additionally contains weak absorptions (2) of ferric oxide (Fig. 4*e*). The corresponding Quinacridone Red Y absorption frequencies for the difference and reference spectra are all within  $2\text{ cm}^{-1}$  of each other.

The pigment absorptions, relative to binder features, are weaker for the lacquer (Fig. 4*b*) compared with those of the enamel (Fig. 3*b*). The range of transmittance values for the two subtraction results therefore differ (compare the ordinate scales of Figs. 3*c* and 4*c*), and since a nonlinear scale is involved, the pigment reference spectra are depicted with transmittance values similar to those of the respective difference spectra to provide a better comparison of relative peak intensities.

### Quinacridone Violet

The spectrum of a red (*red-maroon*) nonmetallic enamel (PN76E0095) that contains Quinacridone Violet (1) is shown in Fig. 5*b*, along with data (Fig. 5*a*) for a brown (*olive-gold*) metallic enamel (PN76F0142), the subtraction results for PN76E0095 minus PN76F0142 (Fig. 5*c*), and a reference spectrum of Quinacridone Violet (Fig. 5*d*). The difference spectrum (Fig. 5*c*) contains a broad absorption at  $855\text{ cm}^{-1}$  of (2) Molybdate Orange<sup>2</sup> (Fig. 5*e*), along with absorptions of Quinacridone Violet. All of the Quinacridone Violet absorptions, except for a few weak ones that occur in the region where Molybdate Orange absorbs, can be seen in the subtraction results and their frequencies are all within  $2\text{ cm}^{-1}$  of their counterparts in the reference spectrum. The *olive-gold* subtrahend topcoat contains a small amount of hydrous ferric oxide (2), as evidenced by a pair of very weak absorptions at 401 and  $272\text{ cm}^{-1}$  (Fig. 5*a*, see also Fig. 6*a*; small amounts of hydrous ferric oxide appear to be very common in many yellow and brown nonmetallic and metallic finishes (2,3)). This produces the two weak inverse features at these same frequencies in the difference spectrum of Fig. 5*c*.

Subtraction data for PA75E0202 (Fig. 7*b*), a red (*maroon*) nonmetallic lacquer that contains Quinacridone Violet, and PA75F0184 (Fig. 7*a*), a brown metallic lacquer, are shown in Fig. 7*c*. PA75E0202 also contains a small amount of silica-encapsulated Molybdate Orange (discussed in more detail later), but essentially all of the significant Quinacridone Violet absorptions are observed in this difference spectrum, and their frequencies are all within  $2\text{ cm}^{-1}$  of those of the reference spectrum (Fig. 7*d*).

As previously noted, Quinacridone Violet and Quinacridone Red Y differ only in their crystal lattice structures and although their spectra are very similar (Fig. 2*a* and 2*b*), they can be distinguished. The differences in the region below  $2000\text{ cm}^{-1}$  are minor, but they

<sup>2</sup>Molybdate Orange (a solid solution of lead chromate with lesser amounts of lead molybdate and lead sulfate), Chrome Yellow (a solid solution of lead chromate with lead sulfate), and other chromate pigments all produce strong absorptions in this region, and it is not always possible to determine which of these pigments is present based on infrared data alone (2). The absorption of Fig. 5*b* appears to be more consistent with that of Molybdate Orange, however, and an elemental analysis of this topcoat confirmed the presence of molybdenum, lead, and chromium. These elements were detected in all of the topcoats discussed in this work for which this chromate absorption was observed, so the pigments responsible will be referred to as Molybdate Orange.

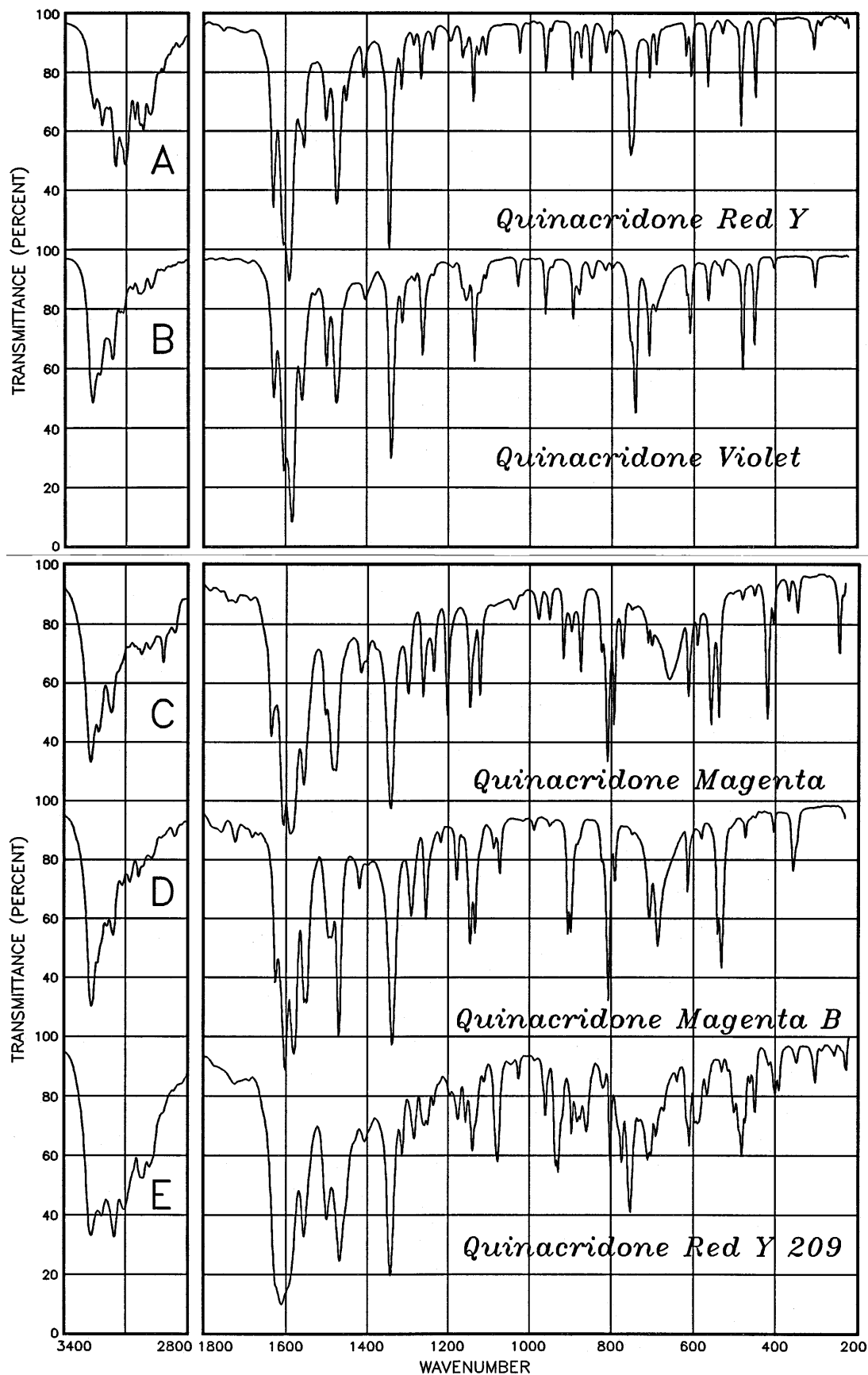


FIG. 2—Spectra in the 3400–2800  $\text{cm}^{-1}$  and 1800–200  $\text{cm}^{-1}$  regions of: (a) Quinacridone Red Y; (b) Quinacridone Violet; (c) Quinacridone Magenta; (d) Quinacridone Magenta B; and (e) Quinacridone Red Y 209.

TABLE 1—Infrared absorption frequencies of quinacridone automotive paint pigments.

Pigment*	Color	Infrared Absorption Frequencies†	Comments
Quinacridone Red Y <i>Figs. 2a, 4d</i>	Pink Red	3258m, 3219m, 3152m, 3106m, 3057m, 3032m, 3017m, 2980m, 2920vw, 2841vw, 2785vw, 2722vw, 1628s, 1603sh, 1589vs, 1553m, 1499w, 1474s, 1451w, 1406w, 1343vs, 1314w, 1283vw, 1265w, 1236w, 1192vw, 1163w, 1138m, 1125vw, 1107w, 1024w, 961w, 947vw, 895w, 874w, 853w, 814w, 799vw, 754m, 708w, 691w, 619w, 608w, 565w, 529vw, 484m, 448m, 401vm, 305w, 287vw	<i>Gamma</i> crystal form of unsubstituted quinacridone. Identified in approximately 40% of red nonmetallic Reference Collection monocoats; also identified in some metallic finishes.
Quinacridone Violet <i>Figs. 2b, 7d</i>	Dark Purple Violet	3266m, 3229sh, 3167m, 3131w, 3115w, 3069vw, 3027w, 2978w, 1626s, 1603sh, 1588vs, 1559m, 1528vw, 1499m, 1474m, 1402w, 1339s, 1312w, 1281vw, 1262m, 1235vw, 1188vw, 1155w, 1134m, 1107vw, 1028w, 961w, 893w, 878w, 847w, 814vw, 799vw, 743s, 708m, 692w, 617sh, 610w, 563w, 529w, 478m, 499m, 401w, 301w	<i>Beta</i> crystal form of unsubstituted quinacridone. Identified in approximately 20% of red nonmetallic Reference Collection monocoats and approximately one dozen brown nonmetallic monocoats; also identified in some metallic finishes.
Quinacridone Magenta <i>Figs. 2c, 8d</i>	Maroon Violet	3271s, 3231s, 3169m, 3021m, 2982m, 2915m, 2859w, 2724vw, 2610vw, 2575m, 1902vw, 1846vw, 1784vw, 1740vw, 1723vw, 1626s, 1603vs, 1588vs, 1555s, 1483s, 1478s, 1414w, 1341vs, 1298m, 1262m, 1235w, 1202m, 1144m, 1121m, 1038vw, 976w, 949w, 916m, 895w, 872m, 822sh, 808s, 793m, 772m, 748vw, 710w, 700w, 658m, 611m, 590w, 556m, 536m, 480vw, 449vw, 419m, 405w, 366w, 345w, 243m	Methyl substitution of quinacridone. Identified in a couple of red nonmetallic Reference Collection monocoats.
Quinacridone Magenta B <i>Figs. 2d, 10d</i>	Red Violet	3268s, 3239sh, 3192w, 3162m, 3115w, 3079w, 3036w, 2972w, 2861vw, 2708vw, 2674vw, 2583vw, 1896vw, 1757vw, 1723vw, 1682vw, 1626s, 1601vs, 1580vs, 1555s, 1549s, 1495m, 1487m, 1470vs, 1420w, 1339vs, 1290m, 1254m, 1217vw, 1177w, 1144m, 1132m, 1086w, 1071w, 988vw, 949vw, 905m, 897m, 806s, 791w, 708m, 687m, 613w, 579vw, 540m, 530s, 473w, 403w, 355w	Chlorine substitution of quinacridone. Identified in approximately one dozen red nonmetallic Reference Collection monocoats; also identified in some metallic finishes.
Quinacridone Red Y 209 <i>Fig. 2e</i>	Yellow Red	3270s, 3217s, 3156s, 3108s, 3013m, 2984m, 2716vw, 2612vw, 1927vw, 1724vw, 1611vs, 1555s, 1499s, 1468vs, 1406w, 1343vs, 1314w, 1283w, 1258w, 1250w, 1235vw, 1194vw, 1175w, 1155w, 1138m, 1109vw, 1076m, 1024m, 961w, 934m, 928m, 895m, 882m, 874m, 858m, 818w, 801m, 774m, 752s, 710m, 702m, 691w, 671sh, 638vw, 610m, 594w, 588w, 565w, 530vw, 500w, 480m, 473sh, 461vw, 448w, 415vw, 399w, 390w, 347vw, 301w, 255vw, 226w	Chlorine substitution of quinacridone. Not identified in any Reference Collection monocoats. Not a common automotive paint pigment; more likely to be used in plastics.

\*The figure number in which the infrared spectrum of this pigment appears is listed in italics.

†Given in wavenumbers. The relative intensity of each absorption is given after its frequency. The abbreviations are: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, and sh = a shoulder peak.

are seen clearly in the subtraction results. Compare, for example, the absorptions in the 1550–1450  $\text{cm}^{-1}$  and 900–800  $\text{cm}^{-1}$  spectral regions of Fig. 3c and 3d with those of Fig. 7c and 7d. The most pronounced differences between the spectra of the two pigments, however, occur in the C-H stretching region (3300–2800  $\text{cm}^{-1}$ ), and these differences are also evident in the various subtraction results (Figs. 3c, 4c, 5c, and 7c).

#### Quinacridone Magenta

The spectrum of a red (*maroon*) nonmetallic lacquer (NA75E0202) that contains Quinacridone Magenta (II) and ferric oxide (Fig. 5e) is depicted in Fig. 8b, along with that (Fig. 8a) of a similar blue metallic lacquer (NA75L0180). Subtraction results for NA75E0202 minus NA75L0180 and the Quinacridone Magenta reference spectrum are shown below (Fig. 8c and 8d, respectively). The pigment absorptions of NA75E0202 are weak compared with those of the binder, and the residual binder features of Fig. 8c are fairly strong; note also the interference fringes, which originate from Fig. 8b. Except for a couple of weak peaks, however, all of the absorptions of Quinacridone Magenta can be observed in the difference spectrum and all the corresponding frequencies agree within 2  $\text{cm}^{-1}$ .

The spectrum of a red nonmetallic enamel, NN79E0561, that contains Molybdate Orange and a small amount of Quinacridone Magenta B is shown in Fig. 9b. Only a few pigment absorptions

can be seen clearly in this topcoat spectrum, and these are labeled with their frequencies. Most of the Quinacridone Magenta absorptions in the 1700–1100  $\text{cm}^{-1}$  region, however, can be seen in the difference spectrum of Fig. 9e. This was obtained by subtracting from Fig. 9b the spectrum of NN78F0482, a brown nonmetallic topcoat (the spectrum of NN78F0482 is not depicted). The weaker pigment peaks below 1300  $\text{cm}^{-1}$  are indicated with asterisks in Fig. 9e to distinguish them from residual binder features, which are prominent. Although not shown, a few other weak Quinacridone Magenta absorptions between 1000 and 800  $\text{cm}^{-1}$  were also observed in difference spectra. The frequencies of the difference spectra peaks and the corresponding pigment reference values are within 2  $\text{cm}^{-1}$  of each other, except for a couple which differ by 4  $\text{cm}^{-1}$ .

#### Quinacridone Magenta B

Spectra of a red (*plum*) metallic lacquer (74E0085) that contains Quinacridone Magenta B (III) and a green metallic lacquer (74K0087) used for subtraction are shown in Fig. 10b and 10a, respectively. The difference and pigment reference spectra are shown in Fig. 10c and 10d, respectively. All of the pigment absorptions are observed in the subtraction result, and with the exception of two absorptions (which differ by 3  $\text{cm}^{-1}$  and 4  $\text{cm}^{-1}$ ), the corresponding frequencies agree within 2  $\text{cm}^{-1}$ .

The spectrum of a red nonmetallic enamel (KN79E0561) that contains a small amount of Quinacridone Magenta B and Molyb-

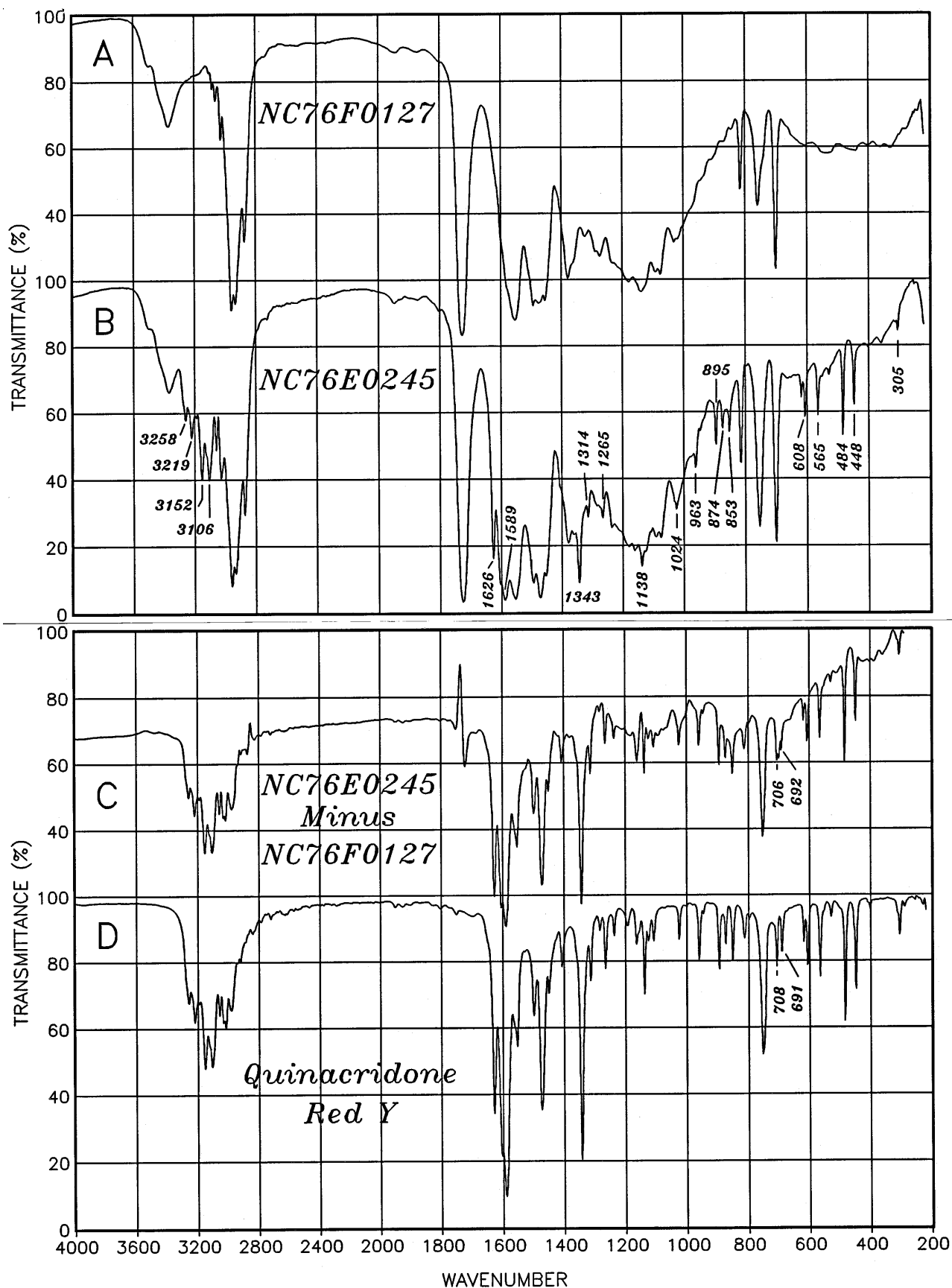


FIG. 3—Spectra of: (a) a brown metallic enamel topcoat, NC76F0127; (b) a red nonmetallic enamel topcoat, NC76E0245, that contains Quinacridone Red Y; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Quinacridone Red Y.

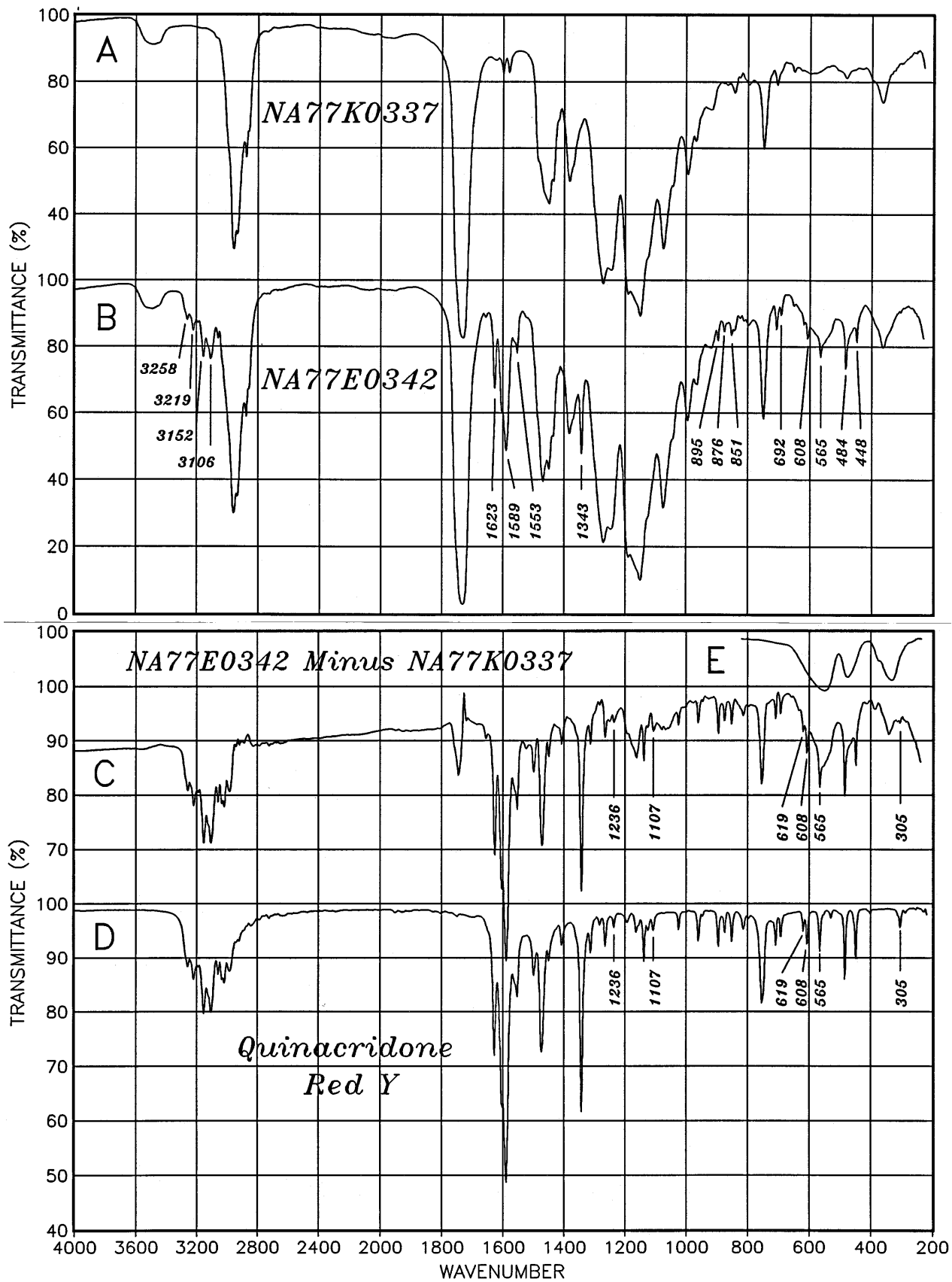


FIG. 4—Spectra of: (a) a green metallic lacquer topcoat, NA77K0337; (b) a red nonmetallic lacquer topcoat, NA77E0342, that contains Quinacridone Red Y and ferric oxide; (c) subtraction results—spectrum (b) minus spectrum (a); (d) Quinacridone Red Y; and (e) ferric oxide.

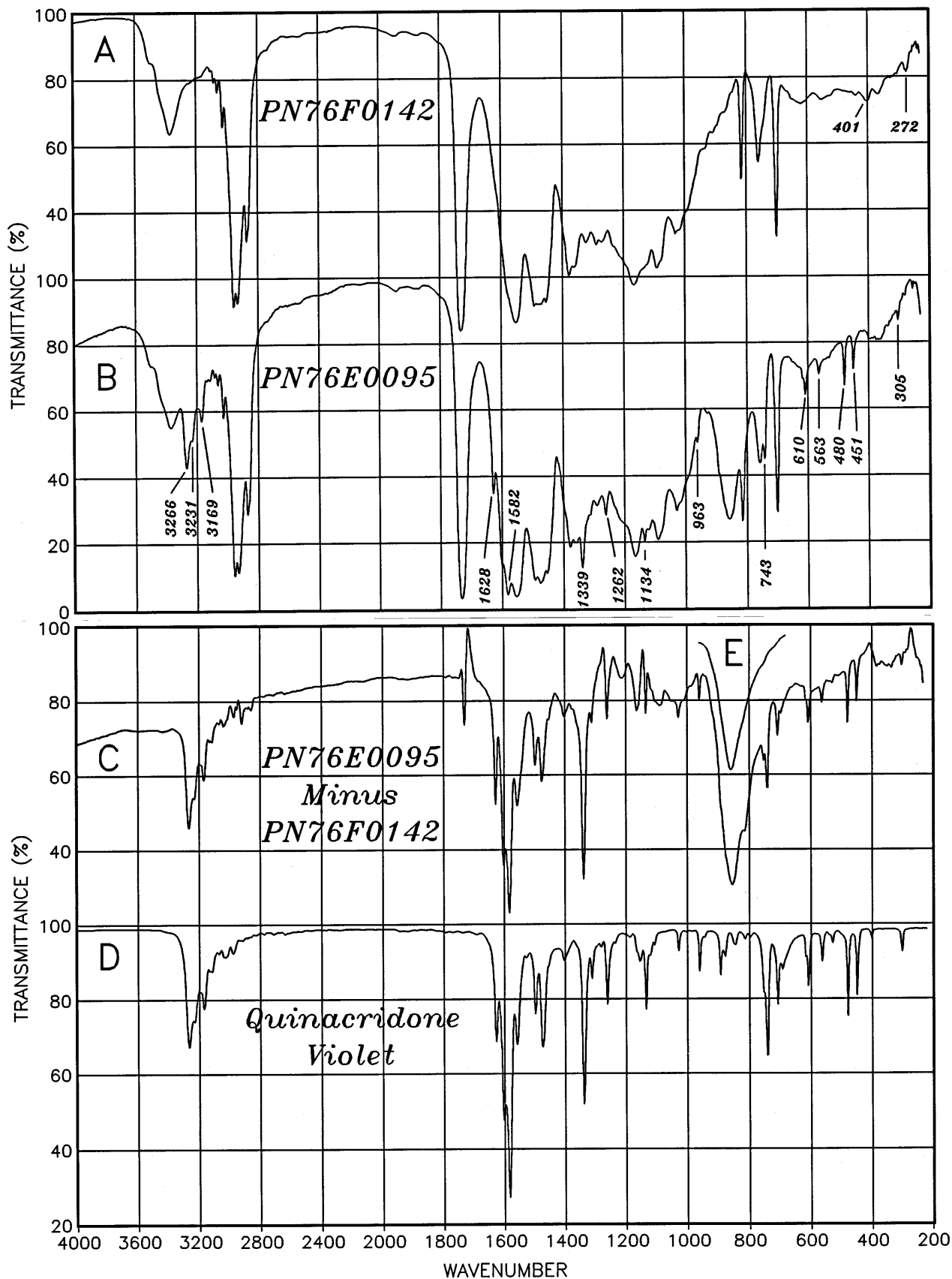


FIG. 5—Spectra of: (a) a brown metallic enamel topcoat, PN76F0142; (b) a red nonmetallic enamel topcoat, PN76E0095, that contains Quinacridone Violet and Molybdate Orange; (c) subtraction results—spectrum (b) minus spectrum (a); (d) Quinacridone Violet; and (e) Molybdate Orange.



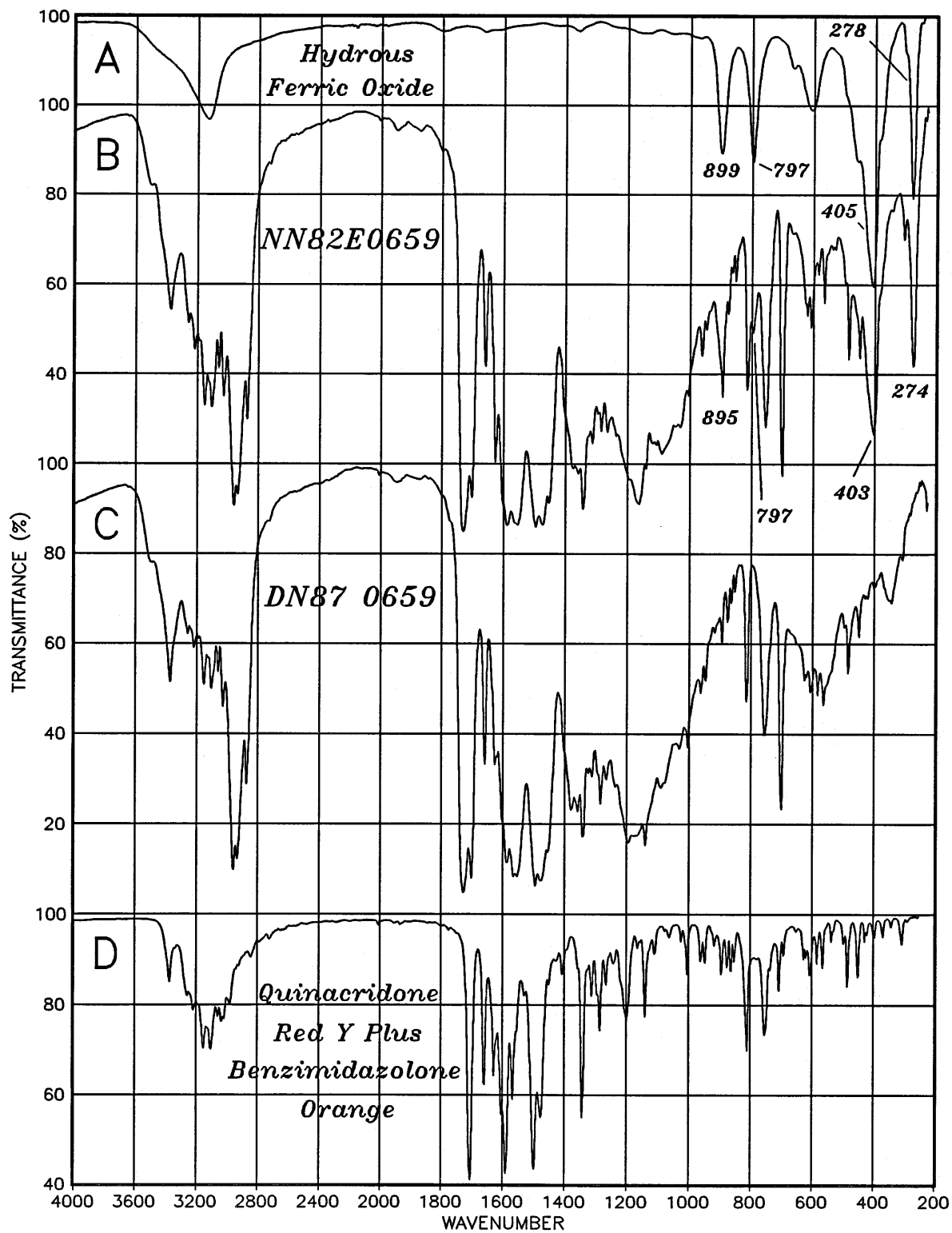


FIG. 6—Spectra of: (a) hydrous ferric oxide; (b) a red nonmetallic enamel topcoat, NN82E0659, that contains Quinacridone Red Y, Benzimidazolone Orange, and hydrous ferric oxide; (c) a red nonmetallic enamel topcoat, DN87 0659, that contains Quinacridone Red Y, Benzimidazolone Orange, ferric oxide, and rutile; and (d) an addition of the absorptions of Quinacridone Red Y and Benzimidazolone Orange.

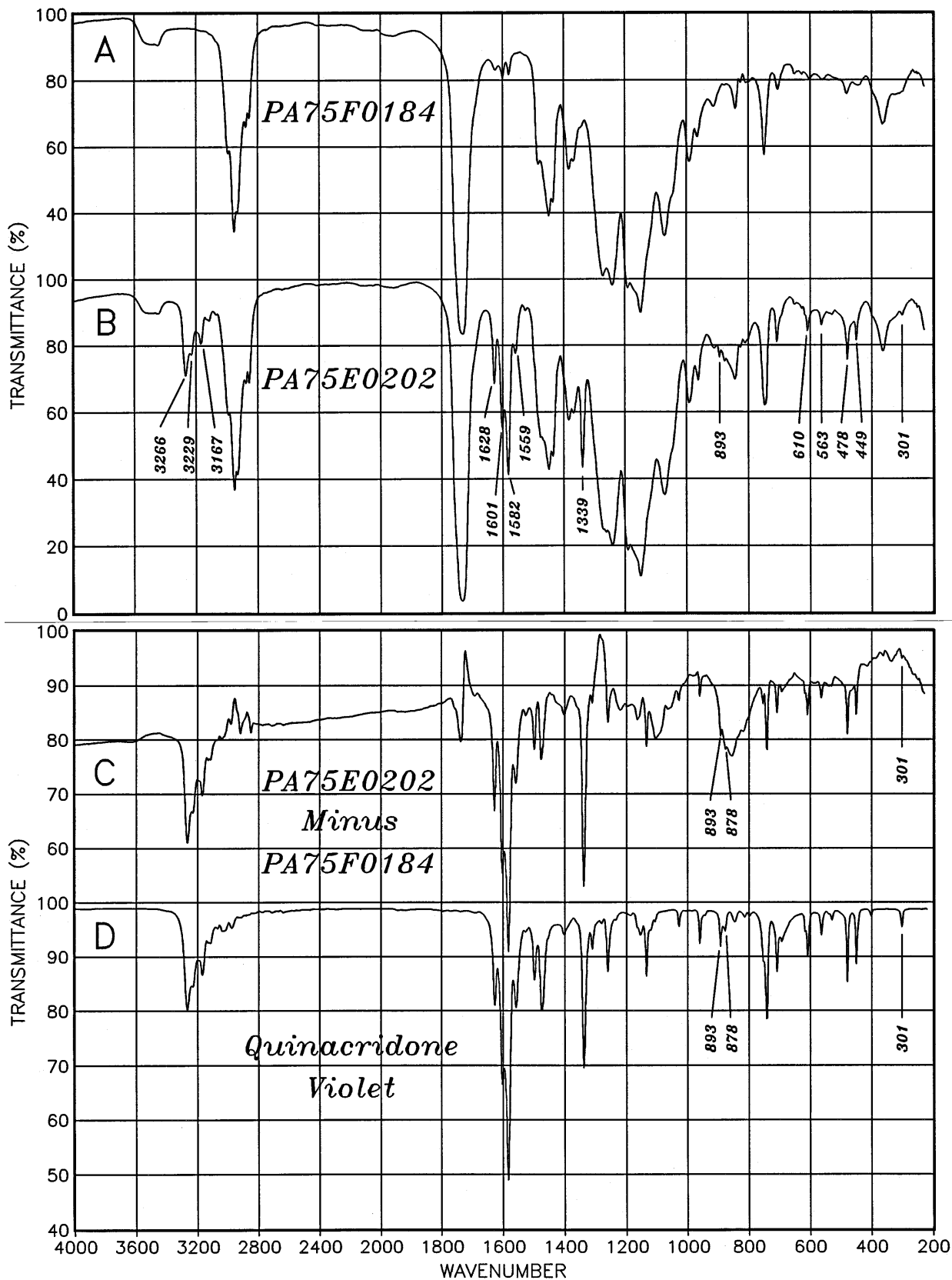


FIG. 7—Spectra of: (a) a brown metallic lacquer topcoat, PA75F0184; (b) a red nonmetallic lacquer topcoat, PA75E0202, that contains Quinacridone Violet and silica-encapsulated Molybdate Orange; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Quinacridone Violet.

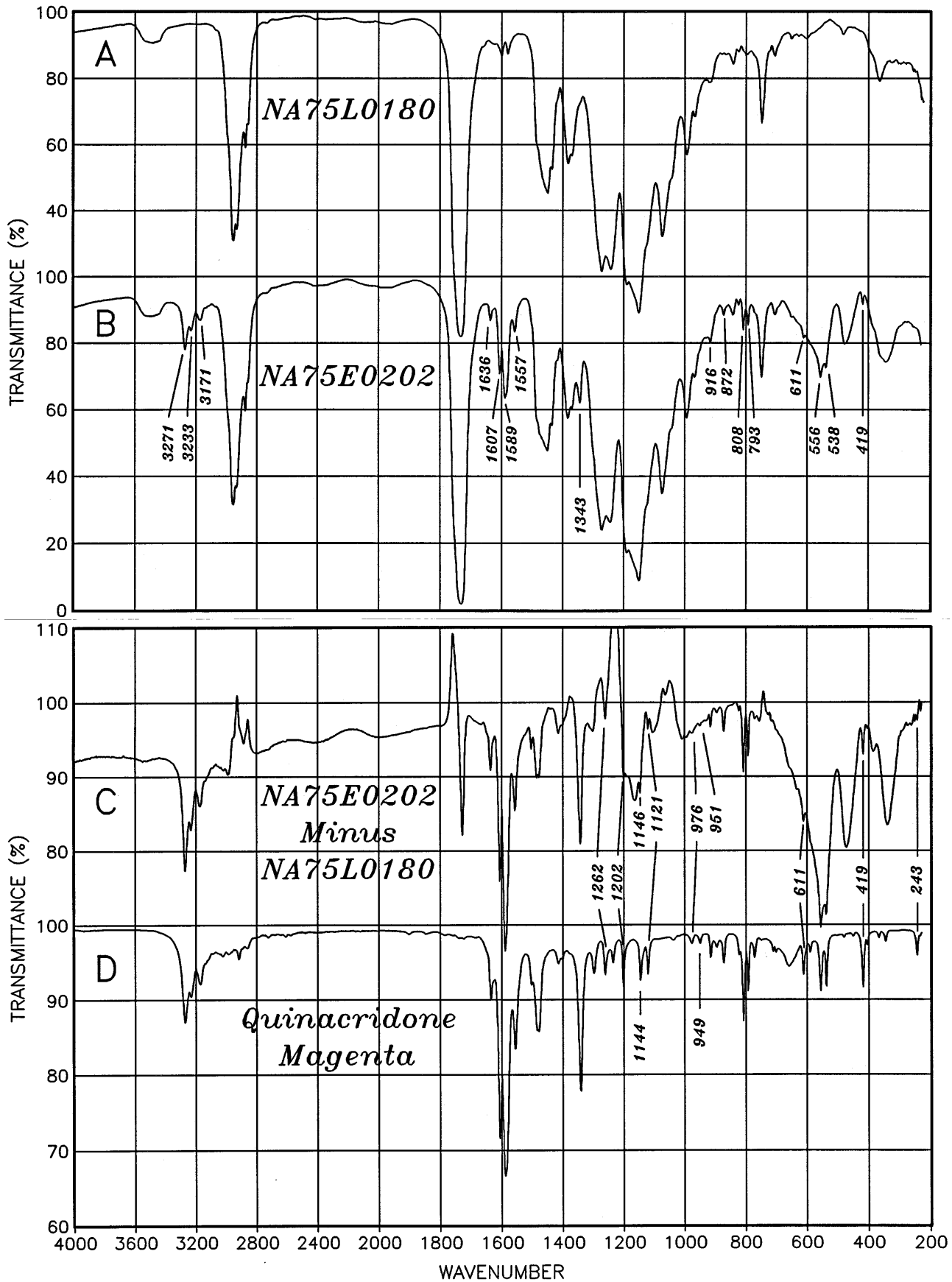


FIG. 8—Spectra of: (a) a blue metallic lacquer topcoat, NA75L0180; (b) a red nonmetallic lacquer topcoat, NA75E0202, that contains Quinacridone Magenta and ferric oxide; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Quinacridone Magenta.

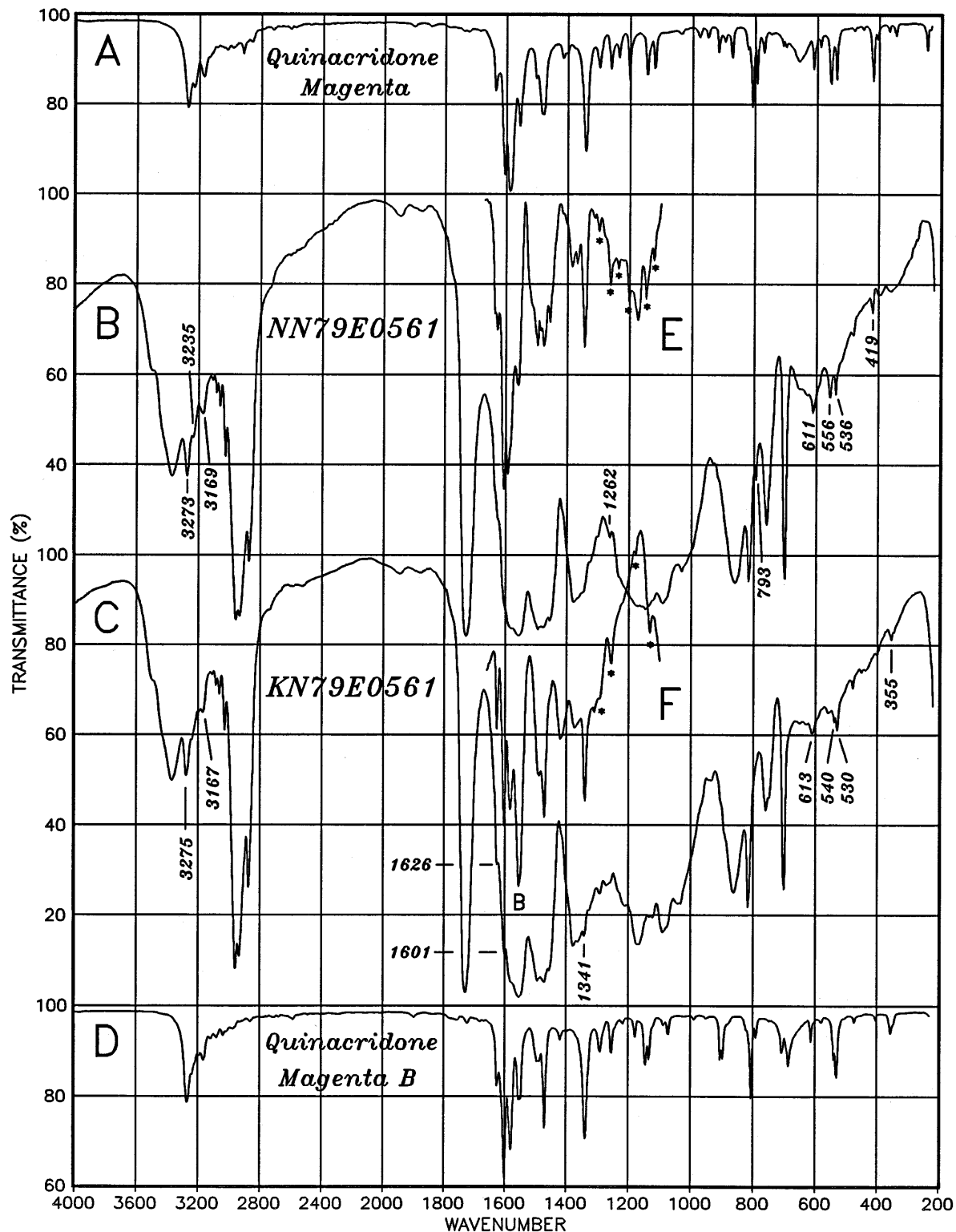


FIG. 9—Spectra of: (a) Quinacridone Magenta; (b) a red nonmetallic enamel topcoat, NN79E0561, that contains Quinacridone Magenta and Molybdate Orange; (c) a red nonmetallic enamel topcoat, KN79E0561, that contains Quinacridone Magenta B and Molybdate Orange; (d) Quinacridone Magenta B; (e) subtraction results—spectrum (b) minus the spectrum of NN78F0482 (not shown); and (f) subtraction results—spectrum (c) minus the spectrum of KN79H0566 (not shown). Some pigment absorptions are marked with asterisks, and a residual binder feature is labeled "B."

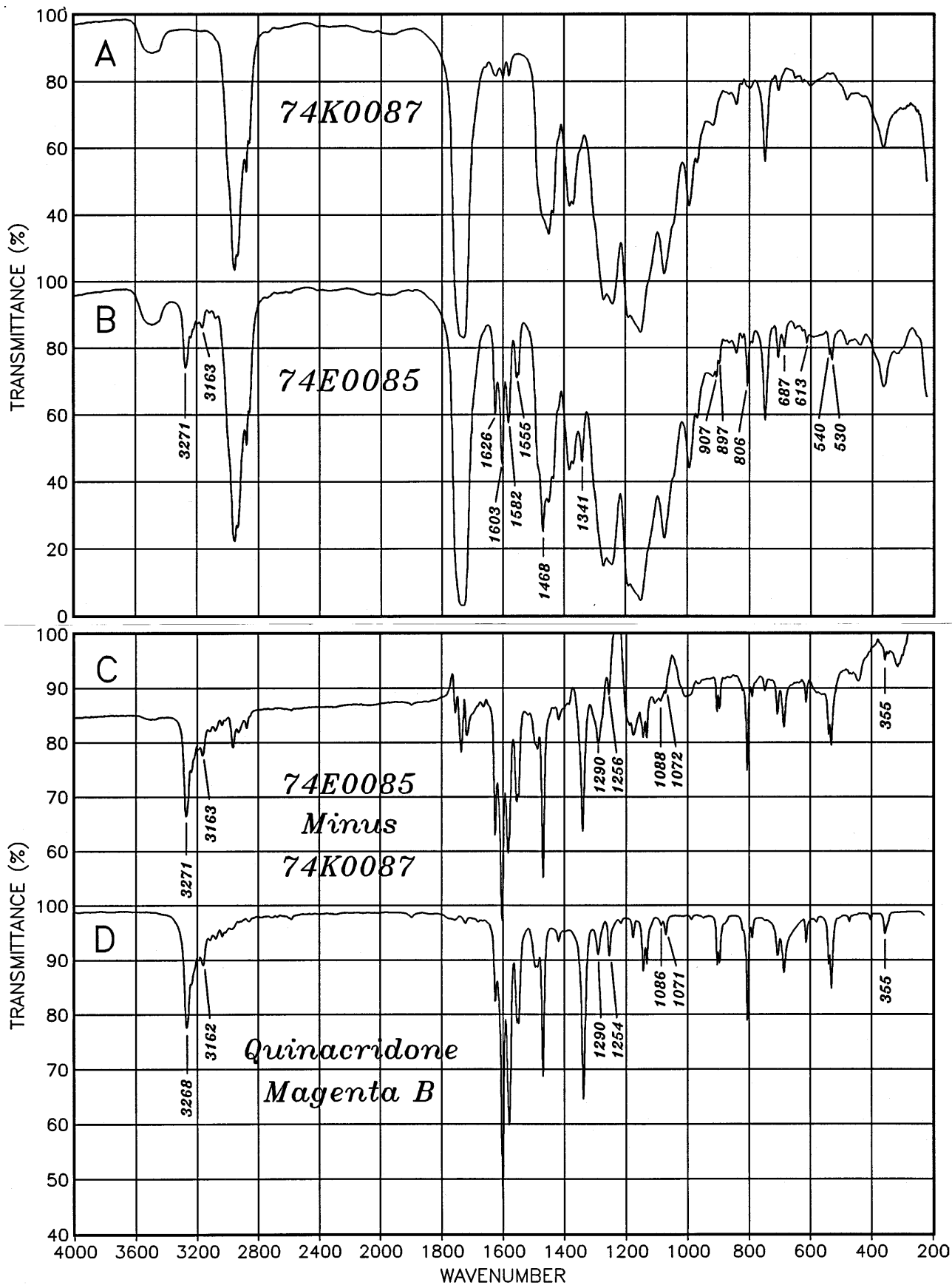


FIG. 10—Spectra of: (a) a green metallic lacquer topcoat, 74K0087; (b) a red metallic lacquer topcoat, 74E0085, that contains Quinacridone Magenta B; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Quinacridone Magenta B.

date Orange is shown in Fig. 9c. As in the case of NN79E0561 (Fig. 9b), only a few pigment absorptions are observed in the topcoat spectrum itself (Fig. 9c); these are labeled with their frequencies. Most of the other Quinacridone Magenta B absorptions in the 1700–1100  $\text{cm}^{-1}$  region can be seen in the difference spectrum (Fig. 9f) obtained by subtracting from Fig. 9c the spectrum of KN79H0566, a yellow nonmetallic enamel. Note that the strongest absorption of Fig. 9f (labeled with a "B") is due to a residual binder feature; it occurs in some difference spectra but not in others, whereas the pigment triplet observed just to the left of it is seen in all of the difference spectra. A few of the weak pigment absorptions of Fig. 9f are labeled with asterisks, and the frequencies of most of the pigment absorptions of Fig. 9c and 9f are within 2  $\text{cm}^{-1}$  of those of the reference spectrum.

#### Other Quinacridone Automotive Paint Pigments

The four pigments discussed above, plus one other quinacridone and some quinacridone solid solution mixtures, are currently marketed for use in automotive paints. The four identified pigments can be used in both metallic and nonmetallic finishes, but Quinacridone Red Y is used<sup>3</sup> primarily in nonmetallic paints because of its opacity. Quinacridone Red Y 209 (IV) may be used for automobiles, but it is not a common automotive pigment and is more likely to be used in plastics.<sup>4</sup> The spectrum of Quinacridone Red Y 209 is depicted in Fig. 2e.

Ciba-Geigy markets several solid solution mixtures of quinacridones "dissolved" in a host matrix. The quinacridone may be a minor component and the spectra of these mixtures are readily distinguishable from those of the pigments described in the present study. These solid solution automotive pigments are intended primarily for use in metallic finishes, and they will be discussed in a subsequent paper.

#### Recognition and Differentiation of Quinacridone Pigment Absorptions in Topcoat Spectra

For spectra of topcoats with acrylic lacquer or acrylic melamine enamel binders, the observation of characteristic pigment absorptions occurring in three spectral regions provides very strong indications of the presence of one of the four quinacridones. These features include absorptions in the 3300–3000  $\text{cm}^{-1}$  region, a multiplet structure (1640–1570  $\text{cm}^{-1}$ ), and a peak near 1340  $\text{cm}^{-1}$ . Since most of the absorptions of the quinacridones are quite sharp, the frequencies which are observed should normally be within 3  $\text{cm}^{-1}$  of those cited here. Except for Quinacridone Red Y, the other three identified pigments have quite similar absorptions in the hydrogen stretching region (Fig. 2b, 2c, and 2d) with a main peak between 3275 and 3265  $\text{cm}^{-1}$ , and a weaker one between 3173 and 3163  $\text{cm}^{-1}$ ; a very weak shoulder peak may sometimes be resolved between the two. In contrast, Quinacridone Red Y has several peaks from 3300 to 3000  $\text{cm}^{-1}$  (Fig. 2a), and four of these (3258, 3219, 3152, and 3106  $\text{cm}^{-1}$ ) are usually observed in most topcoat spectra (Figs. 3b and 4b). All four pigments have a very characteristic multiplet of absorptions between 1640 and 1570  $\text{cm}^{-1}$  that superficially look similar (Fig. 2); there are, however, minor but significant differences in their specific patterns. The four quinacridones also have a strong absorption near 1340  $\text{cm}^{-1}$  (Fig. 2).

<sup>3</sup>Personal communications: Sun Chemical Corp., Jan. 1997, and DuPont Automotive Products, June 1997.

<sup>4</sup>Personal communications: Sun Chemical Corp., Hoechst Celanese Corp., and DuPont Automotive Products, Jan. 1997.

Due to conjugation, the stretching frequencies of the quinacridone pyridone carbonyl groups (Fig. 1) are quite low (Fig. 2). The spectra of both lacquers and enamels that contain one of the four quinacridones—and no other organic pigments—therefore exhibit a gap (1720–1640  $\text{cm}^{-1}$ ) between the binder acrylic ester carbonyl and pigment carbonyl absorptions. The absence of peaks in this narrow region is very significant since most topcoat organic pigments, including the benzimidazolones (3), have prominent carbonyl absorptions there.<sup>5</sup> It is thus another characteristic feature to consider when examining spectra, and this region can also be useful when interpreting spectra of topcoats containing some quinacridone pigment combinations (discussed later).

In most cases where appreciable amounts of pigments were used, the three characteristic spectral features indicative of the four identified quinacridones can be observed. Other weaker absorptions, most of which occur below 1000  $\text{cm}^{-1}$ , may then be used to narrow further the list of possibilities, provide additional indications about likely pigment identities, or help identify the specific quinacridone involved.

*Acrylic Lacquers*—Quinacridone absorptions are usually much easier to recognize in the spectra of lacquers since the entire multiplet feature can be observed (Figs. 4b, 7b, 8b, 10b, and 11b). Lacquer binders have only very weak peaks in this region (Figs. 4a, 7a, 8a, and 10a), so little or no distortion of this very characteristic quinacridone feature occurs. Quinacridone Red Y and Quinacridone Violet have multiplet absorptions at 1626, 1603 (which is a shoulder or a partially resolved peak), 1589, and 1553  $\text{cm}^{-1}$  (Fig. 4b) and 1628, 1601, 1582, and 1559  $\text{cm}^{-1}$  (Fig. 7b), respectively. As noted, the most pronounced difference occurs in the hydrogen stretching region (compare Figs. 4b and 7b). The peaks at 1343  $\text{cm}^{-1}$  for Quinacridone Red B (Fig. 4b) and 1339  $\text{cm}^{-1}$  for Quinacridone Violet (Fig. 7b) occur in a narrow lacquer window and are almost always easily observed.

Most of the spectral region below 1000  $\text{cm}^{-1}$  is free of significant binder features for lacquers, and several quinacridone pigment absorptions, although weak, can usually be observed. For Quinacridone Red Y and Quinacridone Violet, four low-frequency absorptions in particular are useful indicators since they can be observed in many lacquer spectra and they differ from those of the two magenta pigments. The values of these for the two polymorphs occur at (Quinacridone Violet frequencies are given in parentheses): 619/608—a doublet (610 with a high-frequency shoulder), 565 (563), 484 (478), and 448  $\text{cm}^{-1}$  (449  $\text{cm}^{-1}$ ). All four may be seen in the lacquer spectra of Figs. 4b and 7b, and they are usually observed even when ferric oxide absorptions are present (Fig. 4b). Some of the other weak peaks that can be observed in lacquer spectra for these two pigments are labeled with their frequencies in Figs. 4b and 7b. As noted earlier, weak absorptions in the 900–800  $\text{cm}^{-1}$  region, if observed, may further help to distinguish between the two polymorphs.

The absorptions of Quinacridone Magenta and Quinacridone Magenta B in topcoat spectra are usually weaker than those observed for Quinacridone Red Y and Quinacridone Violet. If the spectrum of a lacquer has the multiplet feature together with the Quinacridone Violet-type hydrogen stretching pattern and the 1340  $\text{cm}^{-1}$  peak, the four low-frequency absorptions of Quinacridone

<sup>5</sup>A good example of this is presented in Fig. 14 of the previous paper in this series (3). The spectrum of an enamel which contains Quinacridone Violet is depicted (Fig. 14d) together with spectra of six other enamels and a lacquer, each of which contains a different organic pigment.

Red Y/Quinacridone Violet should be sought. Lack of these absorptions should prompt a search for other weak absorptions below  $1000\text{ cm}^{-1}$ , and a closer examination of the multiplet structure. Spectra of lacquers which contain Quinacridone Magenta have a doublet at  $808/793\text{ cm}^{-1}$ ; additional peaks at 916, 872, 611, 556, 538, and  $419\text{ cm}^{-1}$  may be observed (Fig. 8b), depending on the amount of pigment used and the presence of other pigment absorptions. Spectra of lacquers with Quinacridone Magenta B have a single peak at  $806\text{ cm}^{-1}$ , with additional peaks at  $907/897$ , 687, 613, and  $540/530\text{ cm}^{-1}$  (Fig. 10b). The multiplet absorptions for Quinacridone Magenta and Quinacridone Magenta B occur at 1636, 1607, 1589, and  $1557\text{ cm}^{-1}$  (Fig. 8b) and 1626, 1602, 1582, and  $1555\text{ cm}^{-1}$  (Fig. 10b), respectively. The four peaks have different relative intensities, and although they are subtle features, the  $1589\text{ cm}^{-1}$  peak of Quinacridone Magenta is relatively broad and the weak  $1555\text{ cm}^{-1}$  peak of Quinacridone Magenta B is usually a doublet; these minor details can be seen in Figs. 8b and 10b.

Figure 11 presents a comparison of the absorptions of two different quinacridones as observed in spectra of lacquers. PA79E0471 (Fig. 11b) contains Quinacridone Violet and ferric oxide, and NA75E0202 (Fig. 11c, also shown in Fig. 8b) contains Quinacridone Magenta and ferric oxide. The intensities of the quinacridone absorptions, relative to binder features, are similar for both spectra, as are those of ferric oxide. The two lacquers also have very similar colors, so this is a particularly useful and relevant comparison. The pigment absorption intensities are weak, but the differences between the absorptions of the two quinacridones may be seen clearly.

In general, pigment absorption intensities are weaker for metallic finishes. Spectra of two red (*orange-red rust*) metallic lacquers of color 0214 that have weak quinacridone absorptions are depicted in Fig. 12a and 12b. PA76E0214 (Fig. 12a) has a weak hydrogen stretching absorption at  $3271\text{ cm}^{-1}$ , multiplet peaks at 1626, 1597, 1582, and  $1557\text{ cm}^{-1}$  (this peak is actually a doublet), and two doublets at  $808/795\text{ cm}^{-1}$  and  $540/530\text{ cm}^{-1}$  (these weak features are seen more clearly when the display of data are expanded). The frequencies and relative intensities of all of these absorptions are consistent with those of Quinacridone Magenta B. Although the other absorptions of this quinacridone are not seen, they either occur in obscured regions or else there are indications of their presence, such as a minor protrusion on the side of a strong absorption.

The quinacridone pigment absorptions of DB76E0214 (Fig. 12b) appear to be comparable in intensity to those of Fig. 12a, but they are less distinct (possibly due to the presence of a second organic pigment). The main hydrogen stretching absorption occurs at  $3279\text{ cm}^{-1}$  and the multiplet consists of peaks at 1626, 1597, and  $1559\text{ cm}^{-1}$ ; the  $1582\text{ cm}^{-1}$  absorption is unresolved and it is not clear if the  $1559\text{ cm}^{-1}$  peak is a doublet. The 1343, 808, and  $795\text{ cm}^{-1}$  peaks are observed and the intensity ratio of the latter two are consistent with those of Quinacridone Magenta B. None of the other pigment peaks are seen clearly, however, although there are hints of their presence in a few cases.

*Acrylic Melamine Enamels*—For enamels, the complete multiplet structure cannot be observed and the individual multiplet peaks are superimposed on the side of the strong broad melamine absorption at  $1550\text{ cm}^{-1}$  (Figs. 3b and 5b); when small amounts of pigments are used, these may appear as shoulders or they may be completely obscured. The hydrogen stretches, the  $1340\text{ cm}^{-1}$  peak, and the lower frequency absorptions can often be seen, however,

as can some other weak absorptions (between  $1300$  and  $1000\text{ cm}^{-1}$ ) not observed for lacquers.

Enamels often have no significant binder features below  $700\text{ cm}^{-1}$  and the four characteristic low-frequency absorptions of Quinacridone Red Y/Quinacridone Violet can usually be readily observed in their spectra (Figs. 3b, 5b, 12c, 13c, and 13d); a weaker absorption at  $305\text{ cm}^{-1}$  is also frequently observed for both pigments. Some of the other absorptions of the two polymorphs which can be seen in enamel spectra are labeled with their frequencies in Figs. 3b and 5b.

A comparison of the absorptions of Quinacridone Red Y and Quinacridone Violet as observed in enamel spectra is shown in Fig. 13. NW77E0054 (nonmetallic *orange-red*) contains Quinacridone Red Y and Molybdate Orange (Fig. 13c), whereas LC77E0235 (nonmetallic *red-maroon*) contains Quinacridone Violet, Molybdate Orange, and ferric oxide (Fig. 13d). The hydrogen stretching absorptions provide a very clear distinction between the two polymorphs, but minor differences in the absorptions below  $2000\text{ cm}^{-1}$  are also observable.

As described previously, spectra of two enamels that contain small amounts of the magenta pigments are depicted in Fig. 9. Manifestations of the quinacridone multiplet are hardly noticeable for NN79E0561 (Fig. 9b), but two very weak shoulder peaks are resolved for KN79E0561 (Fig. 9c). Quinacridone Magenta peaks are also observed in the spectrum of NN79E0561 at 3273, 3235, 3169, 1262, 793, 611, 556, 536, and  $419\text{ cm}^{-1}$  (Fig. 9b), whereas Quinacridone Magenta B peaks of KN79E0561 occur at 3275, 3167, 1341, 613, 540, 530, and  $355\text{ cm}^{-1}$  (Fig. 9c).

#### *Use of Quinacridones in U.S. Automobile Original Monocoats (1974–1989)*

For this survey of quinacridone use in U.S. automobile original finishes (1974–1989), spectra of all available nonmetallic monocoats in the Reference Collection of Automotive Paints were acquired between  $4000$  and  $220\text{ cm}^{-1}$  (3). Although metallic monocoats of all colors were not analyzed, most of the red and orange ones and many of the brown finishes were sampled. The percentages which are cited for red nonmetallic monocoats are based on the total number of samples tested (234); these included all of the available panels in the Reference Collection, plus a few more obtained from the FBI Laboratory (1). A total of 174 brown nonmetallic monocoats were analyzed.

Quinacridone Red Y and Quinacridone Violet were identified in approximately 40% and 20% of red nonmetallic monocoats, respectively, and at least a dozen more contain a Quinacridone Red Y/Quinacridone Violet pigment combination (discussed later). Quinacridone Magenta B was identified in approximately one dozen such finishes, but Quinacridone Magenta was found in only a couple. Together, the four quinacridones were used in two-thirds of red nonmetallic monocoats.

Quinacridone Violet was identified in approximately one dozen brown nonmetallic monocoats and, as might be expected, all of these have red-brown (*maroon*) shades. For all of the nonmetallic finishes except for a few red ones which contain Quinacridone Red Y, the quinacridones were used together with other pigments as evidenced by the spectral absorptions of these other pigments. A fairly wide range in the amounts of pigments used was observed for Quinacridone Red Y and Quinacridone Violet but, as noted earlier, only small quantities of the magenta pigments were indicated. These observations probably reflect economic factors<sup>6</sup> since

<sup>6</sup>Personal communications: Sun Chemical Corp. and DuPont Automotive Products, Jan. 1997.

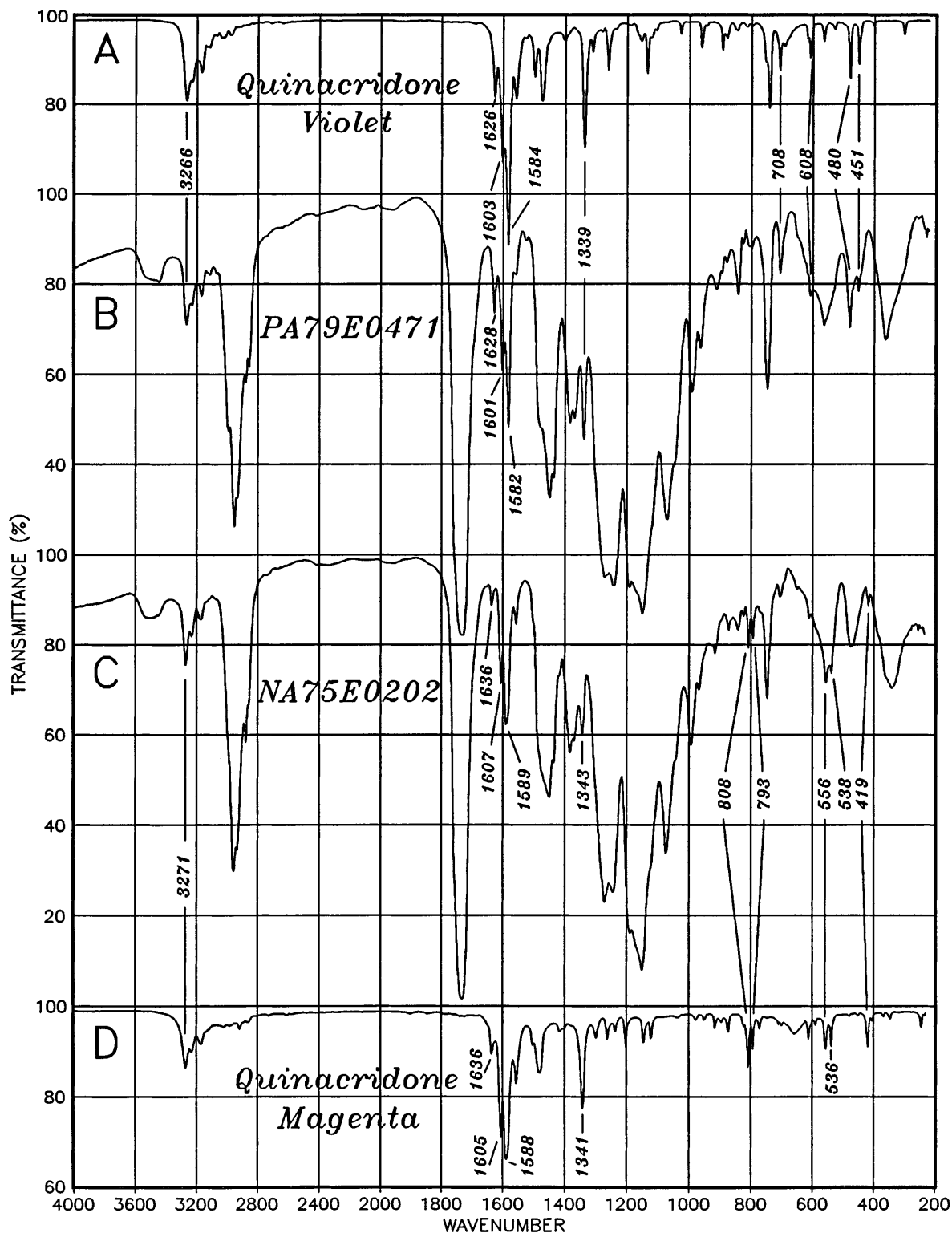


FIG. 11—Spectra of: (a) Quinacridone Violet; (b) a red nonmetallic lacquer topcoat, PA79E0471, that contains Quinacridone Violet and ferric oxide; (c) a red nonmetallic lacquer topcoat, NA75E0202, that contains Quinacridone Magenta and ferric oxide; and (d) Quinacridone Magenta.

the quinacridone magentas are more expensive, and similar shades can often be produced using Quinacridone Violet instead.

Quinacridone Red Y, Quinacridone Violet, and Quinacridone Magenta B were also identified in some red and brown metallic monocoats, although they are not as common for these. As

expected, heavy pigment loads were not usually used for metallic finishes and the pigment absorptions are generally weak.

Quinacridones were first synthesized in 1955, and Quinacridone Red Y was first introduced commercially in 1958 (5). Use of quinacridones in Reference Collection finishes span the entire time



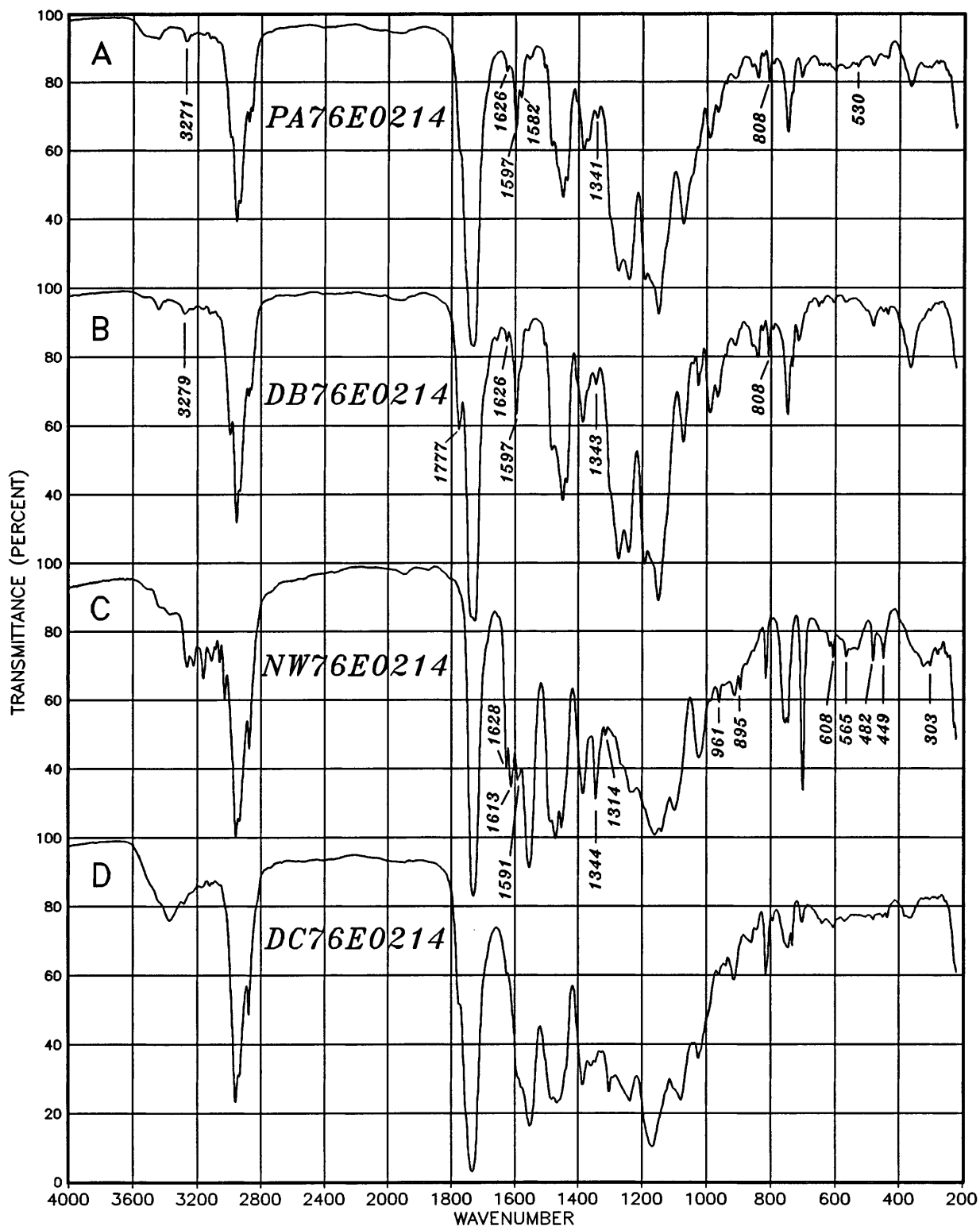


FIG. 12—Spectra of four red metallic topcoats of color 0214: (a) PA76E0214, a lacquer that has weak absorptions of Quinacridone Magenta B; (b) DB76E0214, a lacquer that has weak absorptions of Quinacridone Magenta B and a second unidentified organic pigment; (c) NW76E0214, an enamel that contains Quinacridone Red Y and a second unidentified organic pigment; and (d) DC76E0214, an enamel that does not have any significant pigment absorptions.

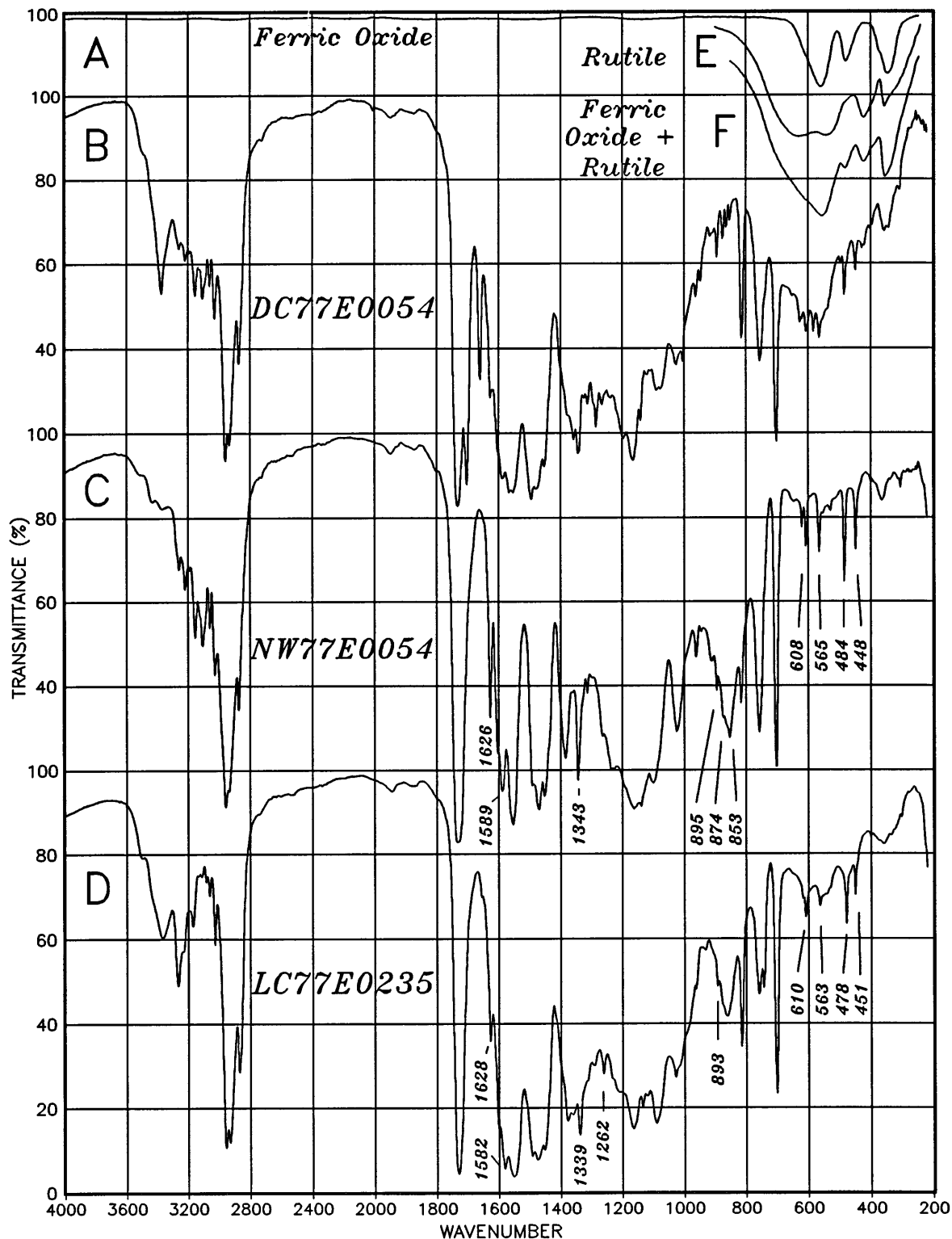


FIG. 13—Spectra of: (a) ferric oxide; (b) a red nonmetallic enamel topcoat, DC77E0054, that contains Quinacridone Red Y, Benzimidazolone Orange, rutile, and ferric oxide; (c) a red nonmetallic enamel topcoat, NW77E0054, that contains Quinacridone Red Y and Molybdate Orange; (d) a red nonmetallic enamel topcoat, LC77E0235, that contains Quinacridone Violet, Molybdate Orange, and ferric oxide; (e) rutile; and (f) an addition of the absorptions of rutile and ferric oxide.

period covered (1974–1989), hence their presence cannot be used to indicate possible vehicle model years, as was found to be the case for the benzimidazolones (3), which were introduced later.

### Pigment Combinations

**Quinacridones and Inorganic Pigments**—Inorganic pigments are usually more opaque than organic ones and they are also considerably less expensive. Organic/inorganic pigment combinations are frequently used not only to produce a particular desired shade, but also to reduce costs and provide greater hiding power, especially for nonmetallic finishes. Organic/inorganic pigment combinations are generally much easier to recognize than organic/organic ones, since organic pigment absorptions are narrow and occur over the entire spectral range, whereas most inorganic pigment absorptions are broad and occur mostly in the lower frequency regions.

Two inorganic pigments in particular, ferric oxide (red-brown) and Molybdate Orange (orange-red), occur often in Reference Collection red nonmetallic monocoats (2). As the previous discussions may have indicated, combinations of quinacridones with ferric oxide (Figs. 4*b*, 11*b*, 11*c*, and 13*d*) and Molybdate Orange (Figs. 5*b*, 7*b*, 9*b*, 9*c*, 13*c*, and 13*d*) are thus quite common in such finishes. Ferric oxide is especially prevalent in nonmetallic *maroon* topcoats (2), and this is also true of Quinacridone Violet; not surprisingly, many of the topcoats containing Quinacridone Violet/ferric oxide combinations are *maroon*.

The spectrum of a *red-maroon* enamel (LC77E0235) that contains Quinacridone Violet, Molybdate Orange, and a small amount of ferric oxide is shown in Fig. 13*d*, and that of a red lacquer (NA76E0076) that contains Quinacridone Red Y, Molybdate Orange, and a small amount of ferric oxide is depicted in Fig. 14*c*. The absorptions of small quantities of ferric oxide used with Quinacridone Red Y or Quinacridone Violet are not always readily apparent since the ferric oxide absorptions are broad, and the quinacridone 480  $\text{cm}^{-1}$  peak overlaps the middle ferric oxide absorption (compare Fig. 13*a* and 13*d*); for lacquers, the acrylate 350  $\text{cm}^{-1}$  binder absorption (2) occurs in the same region as the lowest frequency ferric oxide absorption (compare Fig. 4*a*, 4*b*, and 4*e*). For the spectrum of the enamel LC77E0235 (Fig. 13*d*), which has weak ferric oxide absorptions, it is useful to compare the low-frequency region with that of NW77E0054 (Fig. 13*c*), an enamel that does not contain ferric oxide (iron was detected by elemental analysis for LC77E0235 but not for NW77E0054).

Silica-encapsulated lead chromate pigments were used in some Reference Collection yellow, orange, and red nonmetallic monocoats (2), primarily in certain lacquers produced by DuPont (which patented the encapsulation process) and PPG. For finishes containing heavy pigment loads of the encapsulated lead chromates, the encapsulated nature is usually quite apparent from the silica absorptions, which serve to distinguish these pigments from their non-encapsulated counterparts (2). When smaller quantities of these chromates are used, as may occur when they are combined with organic pigments, determination of the encapsulated nature becomes much more difficult.

The spectrum of silica-encapsulated Molybdate Orange is depicted in Fig. 14*a*, and spectra of two red nonmetallic DuPont and PPG lacquers that contain this pigment and quinacridones are shown in Fig. 14*b* and 14*d*, respectively. The silica absorption near 1100  $\text{cm}^{-1}$  (Fig. 14*a*) is quite broad and in lacquer spectra it overlaps the strong acrylate 1150  $\text{cm}^{-1}$  binder feature. The primary indication that the Molybdate Orange is encapsulated is thus the weak broad 450  $\text{cm}^{-1}$  features of Fig. 14*b* and 14*d*, upon which

are superimposed two sharper absorptions of Quinacridone Red Y/Quinacridone Violet. The presence of this weak broad feature is more apparent when it is compared with the absorptions of binder alone, shown in Fig. 14*e* (this is a portion of the spectrum of PA76L0180, a blue metallic lacquer with a binder composition similar to that of PA76E0076—compare Fig. 14*e* and 14*d*). Note that the spectrum of NA76E0076 (Fig. 14*c*) also contains what appears to be this feature but, as discussed earlier, this is due to a small amount of ferric oxide; this spectrum also has a weak broad ferric oxide absorption near 570  $\text{cm}^{-1}$ . Silicon was detected by elemental analyses for DB76E0076 and PA76E0076, and the primary indications that an encapsulated chromate is present are detection of this element and a weak broad absorption at 450  $\text{cm}^{-1}$  (together with a chromate absorption).

The spectrum of another topcoat which contains a small amount of silica-encapsulated Molybdate Orange and quinacridone is shown in Fig. 7*b*. The chromate absorption of this topcoat is quite weak and the encapsulated nature of the pigment is not really evident from Fig. 7*b*, but the subtraction result (Fig. 7*c*) has a weak broad feature near 1100  $\text{cm}^{-1}$  (see Fig. 14*a*) and the Quinacridone Violet pair in the 500–400  $\text{cm}^{-1}$  region appears on a very weak broad background compared with Fig. 7*d*; silicon was also detected by elemental analysis.

**Quinacridones and Benzimidazolone Orange**—Benzimidazolone Orange, an orange pigment, was identified in nearly a third of Reference Collection red nonmetallic monocoats, and it is actually more common in red monocoats than in orange ones (3). For all of these red monocoats, prominent spectral absorptions of other pigments are also observed and in the vast majority of these cases, combinations of Benzimidazolone Orange with either Quinacridone Red Y or Quinacridone Violet are involved. For Reference Collection nonmetallic monocoats of all colors, these two pigment combinations are, by far, the most common that result in significant spectral absorptions of two or more organic pigments. The combination of Quinacridone Red Y with Benzimidazolone Orange may be used to produce an orange-red “*fire engine red*” shade (3). Quinacridone Red Y was used with Molybdate Orange to produce a similar shade before the use of lead pigments in U.S. automobile original finishes was discontinued (2), since Molybdate Orange and Benzimidazolone Orange have very similar colors.

Quinacridone Red Y/Benzimidazolone Orange combinations are observed for topcoat colors other than *fire engine red*, but this particular shade often involves heavy pigment loads for both components in order to produce the bright and vivid appearance characteristic of *fire engine red*. Since most of the pigment absorptions are quite sharp, numerous peaks of both Quinacridone Red Y and Benzimidazolone Orange can be observed in such spectra. The spectrum of one of these *orange-red* lacquers, DB78E0436, is depicted in Fig. 15*c*. Except where strong binder absorptions occur, all of the expected peaks for both pigments (Fig. 15*a* and 15*b*) can be observed, some labeled with their frequencies.

Figures 6*b*, 6*c*, and 13*b* depict spectra of three enamels that contain Quinacridone Red Y and Benzimidazolone Orange. A spectral addition of the absorptions of the two pigments is shown in Fig. 6*d*, and a detailed examination of the enamel spectrum of Fig. 6*c* indicates that all of the significant peaks of this composite result are observed, except in those regions where strong binder features occur.

Spectral absorptions of Quinacridone Red Y/Benzimidazolone

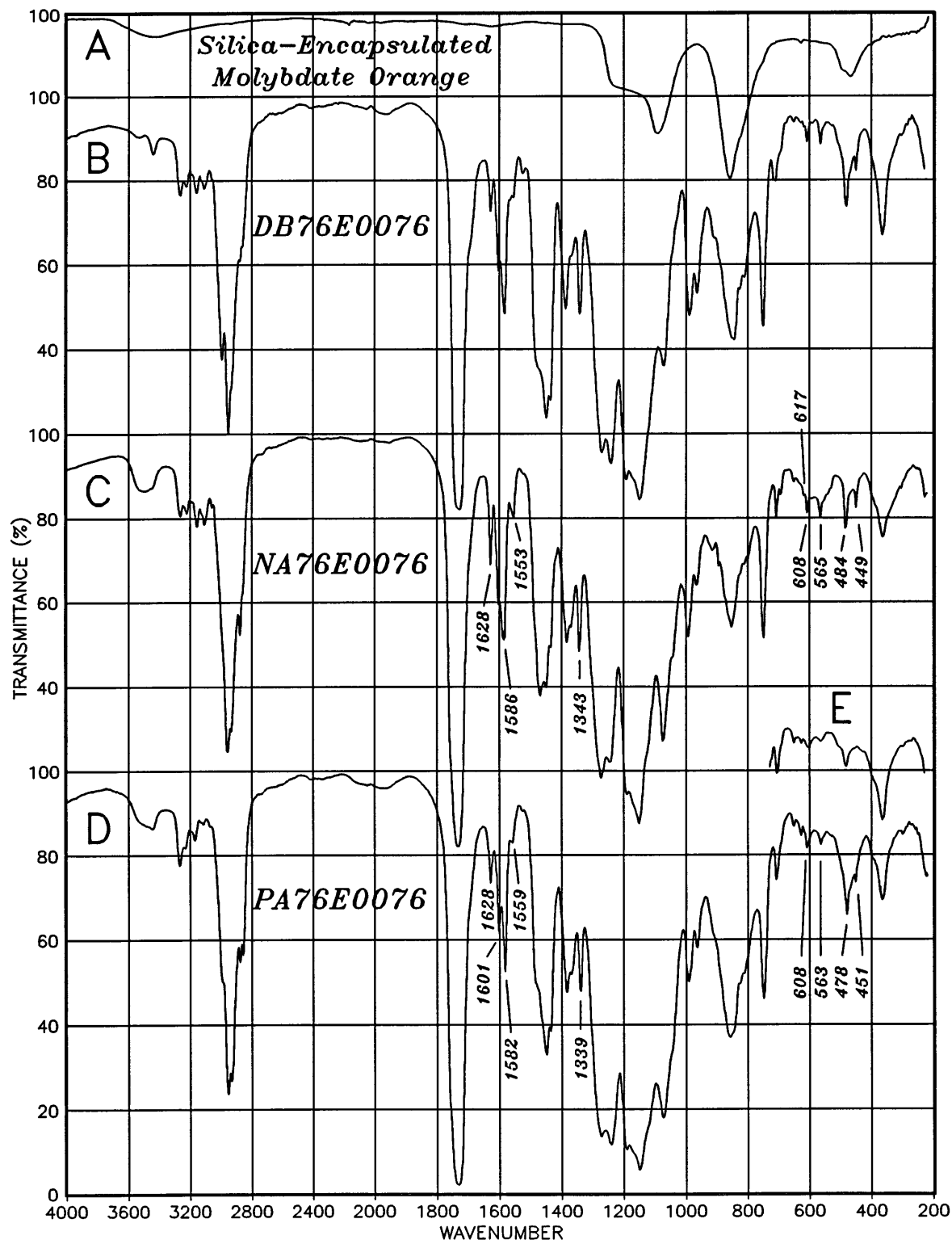


FIG. 14—(a) Spectrum of silica-encapsulated Molybdate Orange. Spectra of three red nonmetallic lacquer topcoats of color 0076: (b) DB76E0076, which contains Quinacridone Red Y, Quinacridone Violet, and silica-encapsulated Molybdate Orange; (c) NA76E0076, which contains Quinacridone Red Y, Quinacridone Violet, Molybdate Orange, and a small amount of ferric oxide; (d) PA76E0076, which contains Quinacridone Violet and silica-encapsulated Molybdate Orange; and (e) A portion of the spectrum of PA7620180, a blue metallic lacquer which has a binder composition similar to that of PA76E0076.

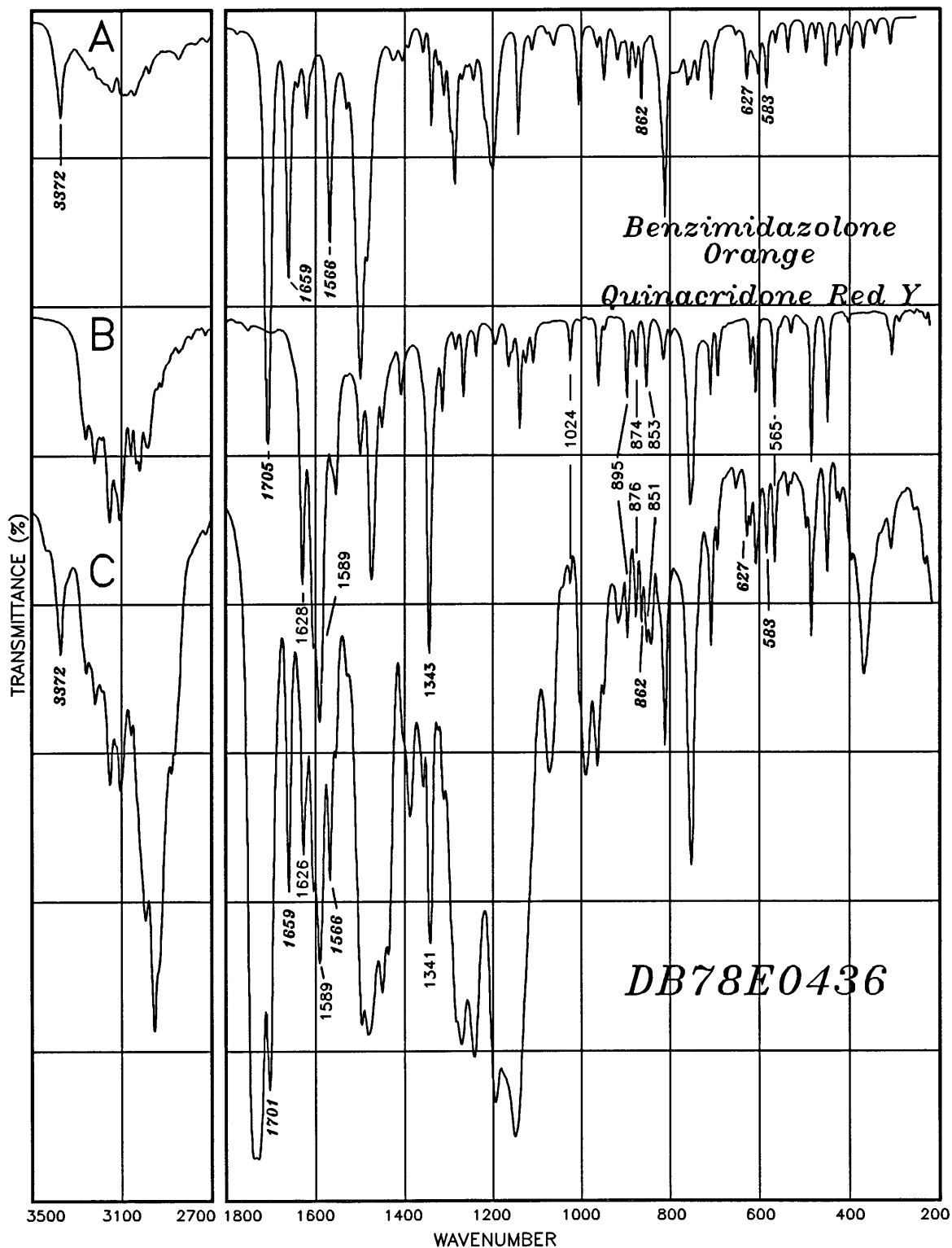


FIG. 15—Spectra in the 3500–2700  $\text{cm}^{-1}$  and 1800–200  $\text{cm}^{-1}$  regions of: (a) Benzimidazolone Orange; (b) Quinacridone Red Y; and (c) a red nonmetallic lacquer topcoat, DB78E0436, that contains these two pigments.

Orange or Quinacridone Violet/Benzimidazolone Orange combinations can usually be recognized from the conspicuous sharp Benzimidazolone Orange absorption at 3372  $\text{cm}^{-1}$  and two other Benzimidazolone Orange absorptions at 1701  $\text{cm}^{-1}$  (on the low-frequency side of the binder carbonyl absorption) and 1659  $\text{cm}^{-1}$ , along with those of the quinacridone (see Figs. 6b, 6c, 13b, and

15c; also compare Fig. 13b and 13c). Many other weaker Benzimidazolone Orange absorptions are also observed (compare Fig. 15a and 15c) and their frequencies have been listed previously (3).

In addition to Quinacridone Red Y and Benzimidazolone Orange, the three enamels discussed above contain inorganic pigments: NN82E0659 (Fig. 6b) also contains hydrous ferric oxide

(Fig. 6a), whereas DC77E0054 (Fig. 13b) also has low-frequency absorptions indicative of a mixture of ferric oxide (Fig. 13a) and rutile (Fig. 13e). A spectral addition of the absorptions of ferric oxide and rutile is shown in Fig. 13f. DN87 0659 (Fig. 6c) likewise contains ferric oxide and rutile. The spectra of the latter two enamels thus contain significant absorptions of four different pigments.<sup>7</sup>

Spectra of two *dark red* nonmetallic lacquers that contain Quinacridone Red Y/Benzimidazolone Orange combinations are shown in Fig. 16a and 16b. NB79E0599 (Fig. 16b) contains much less Benzimidazolone Orange than DB79E0599 (Fig. 16a), and also contains a small amount of ferric oxide.

*Quinacridone Red Y and Quinacridone Violet*—Pigment combinations involving two different quinacridones may be used in some finishes, the most common of these being the Quinacridone Red Y/Quinacridone Violet mixture. This combination may be sold premixed, or the two pigments can be combined by the finish formulators<sup>8</sup> themselves. The pigment that Sun Chemical Corp. markets as *Sunfast Red 19* (which is called Quinacridone Red B), for example, is a mix<sup>9</sup> of these two. This product has a shade which is intermediate between those of the two pure pigments, and an addition of the spectra of the two polymorphs depicted in Fig. 2a and 2b, each normalized with the strongest peak having an absorbance value of one, produced a spectrum essentially identical to that of *Sunfast Red 19*. Absorptions in the hydrogen stretching region for the addition result and *Sunfast Red 19* are shown in Fig. 17e and 17i, respectively, and as a comparison, similar data for the pure polymorphs are depicted in Fig. 17a and 17c. These results suggest that *Sunfast Red 19* has a composition close to an equimolar (or equal weight in this case) mixture.

Due to the differences in the hydrogen stretching absorptions between Quinacridone Red Y (Fig. 17a) and Quinacridone Violet (Fig. 17c), mixtures of these two can often be identified in topcoat spectra based on the particular pattern which occurs; minor differences in quinacridone absorptions below 1800  $\text{cm}^{-1}$  may also be observed, but the hydrogen stretching absorptions usually provide the most definitive indications of such mixtures. Examples of topcoats with absorptions indicative of these mixtures are presented for three Reference Collection red nonmetallic colors; interestingly, differences in the ratios of the two polymorphs are observed for two or more topcoats of each of these colors.

Absorptions in the 3700–2700  $\text{cm}^{-1}$  region of NC76E0244, an enamel which contains primarily just Quinacridone Red Y, are depicted in Fig. 17b (compare with Fig. 17a). Another enamel of this same color, NN76E0244 (Fig. 17d), contains Quinacridone Violet and Quinacridone Red Y (and ferric oxide, although absorptions of this pigment are not observed in this region). Note that NN76E0244 contains more Quinacridone Violet than the approximate 1:1 mix (Fig. 17e), but Quinacridone Red Y absorptions can still be observed.

Absorptions (3500–3000  $\text{cm}^{-1}$ ) of three enamels of color 1351 that contain various Quinacridone Red Y/Quinacridone Violet mixtures are shown in Fig. 17f, 17g, and 17h, and similar data for

three lacquers of color 0076 are depicted in Fig. 17j, 17k, and 17l (the full spectra of the latter three are presented in Fig. 14). For both colors, increasing amounts of Quinacridone Violet are indicated for these sequences (from top to bottom), and PA76E0076 (Fig. 17l) appears to contain only Quinacridone Violet (compare with Fig. 17c). The hydrogen stretching absorption differences between PA76E0076 and DB76E0076, although minor, are significant since the absorptions below 2000  $\text{cm}^{-1}$  do not differ greatly (compare Fig. 14b and 14d).

The pigment hydrogen stretching absorptions of topcoats containing the two polymorphs and their mixtures are quite reproducible, so the differences that may occur can be significant and revealing features. Since either polymorph may be used as a tint to adjust the shade of a particular topcoat, the relative amounts of the two can vary continuously. When the polymorphs are used together and no significant amounts of other organic pigments are present, or when they are used with inorganic pigments, other pigment absorptions do not occur in this region. If significant amounts of other organic pigments are also present, however, this may not be the case and care should be exercised in interpreting data. The pigment hydrogen stretching absorptions of DB79E0599 (Fig. 16a), for example, suggest a polymorph mix, but Benzimidazolone Orange absorptions are also present. A comparison of the hydrogen stretching absorptions of the three spectra of Fig. 15 indicates that this pigment does not interfere. The unidentified organic pigment of NW76E0214 (Fig. 12c), on the other hand, does have absorptions in this region.

A few Reference Collection topcoats appear to contain a mixture of Quinacridone Red Y with one of the quinacridone magentas, but mixtures of the two magentas with each other and with Quinacridone Violet are less likely to occur<sup>10</sup> since the three have similar shades. Table 2 summarizes the various quinacridone pigment combinations that have been identified in this study. In addition to these combinations, for which the main pigment components have been identified, DB76E0214 (Fig. 12b) contains a quinacridone and an unidentified organic pigment. The latter produces the 1777  $\text{cm}^{-1}$  absorption, which also appears to be present, to a lesser extent, in the spectra of Fig. 12a and 12d. NW76E0214 (Fig. 12c) contains Quinacridone Red Y, an unidentified organic pigment that gives rise to the 1613  $\text{cm}^{-1}$  absorption (which is not part of the quinacridone multiplet), and what appears to be a small amount of ferric oxide.

#### *Pigment Compositional Differences for Some Topcoats Having Similar Colors*

In addition to the differences in the ratios of Quinacridone Red Y and Quinacridone Violet that were used for some topcoats having the same Reference Collection color, a few other colors also have topcoats containing different compositions of quinacridones. These colors include: (1) 0202 (nonmetallic *maroon*)—PA75E0202 (Fig. 7b) contains Quinacridone Violet and silica-encapsulated Molybdate Orange, whereas NA75E0202 (Fig. 8b) contains Quinacridone Magenta and ferric oxide; as noted earlier, color 0471 is similar to color 0202, and PA79E0471 (Fig. 11b) contains Quinacridone Violet and ferric oxide; colors 0202 and 0471 are also similar to color 1351, which has topcoats with various Quinacridone Red Y/Quinacridone Violet mixtures (Fig. 17f, 17g, and 17h), so separate formulations involving three different quinacridones were used to produce these similar shades of maroon. (2) 0561 (nonmetallic

<sup>7</sup>This composition appears to be similar to one cited (10) as a common pigment formulation for orange-red enamels which was used as a replacement for such finishes containing Molybdate Orange. This formulation is (values given in pounds of pigment per 100 gallons): Benzimidazolone Orange 35.2, Quinacridone Red Y 22.5, ferric oxide 17.2, and titanium dioxide 16.0. The cost of this pigment mixture was 3<sup>1</sup>/<sub>2</sub> times that of the Molybdate Orange formulation which it replaced.

<sup>8</sup>DuPont Automotive Products, personal communication, Jan. 1997.

<sup>9</sup>Sun Chemical Corp., personal communication, Jan. 1997.

<sup>10</sup>See Footnote 8.

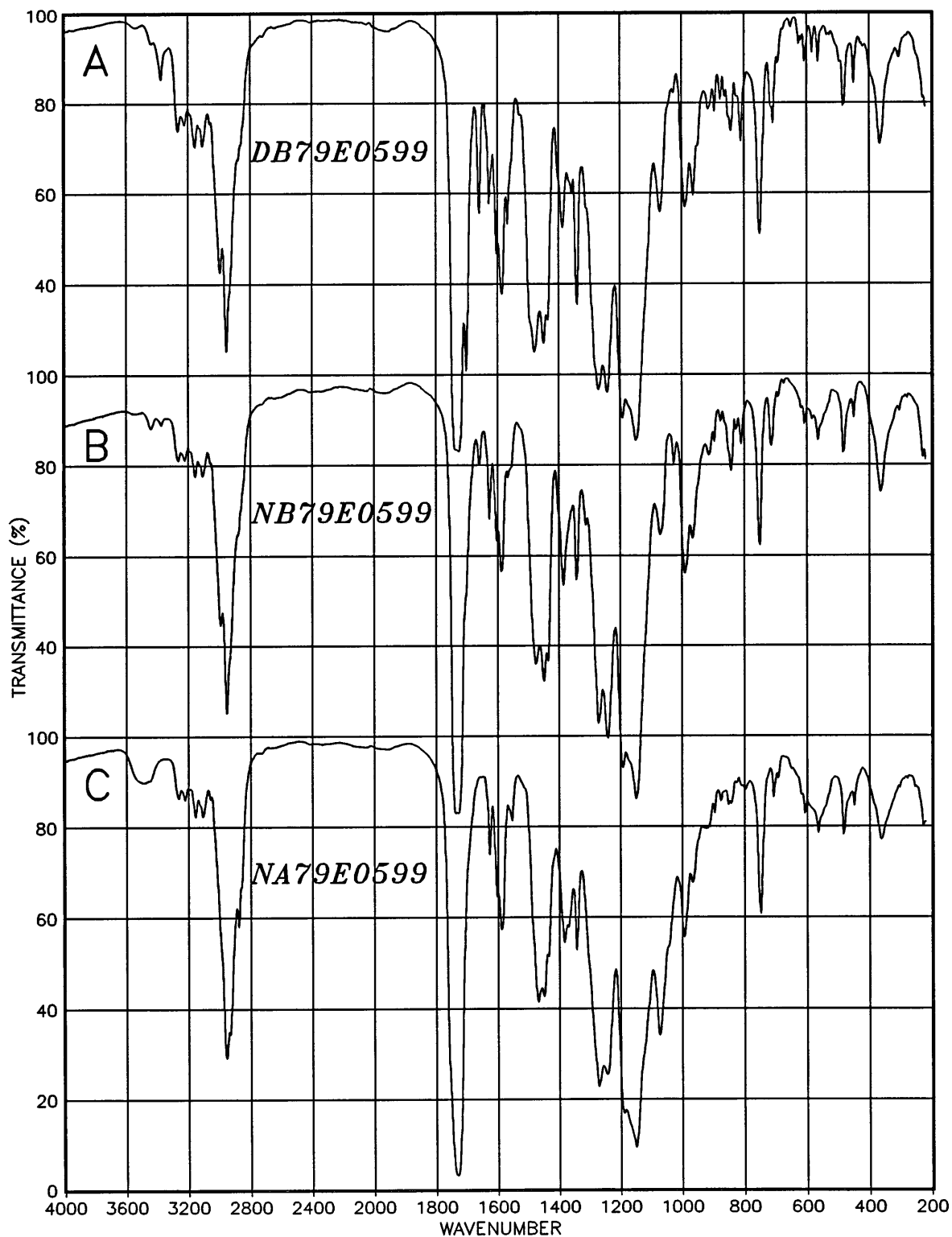


FIG. 16—Spectra of three red nonmetallic lacquer topcoats of color 0599: (a) DB79E0599, which contains Quinacridone Red Y, Quinacridone Violet and Benzimidazolone Orange; (b) NB79E0599, which contains Quinacridone Red Y, Benzimidazolone Orange, and ferric oxide; and (c) NA79E0599, which contains Quinacridone Red Y and ferric oxide.

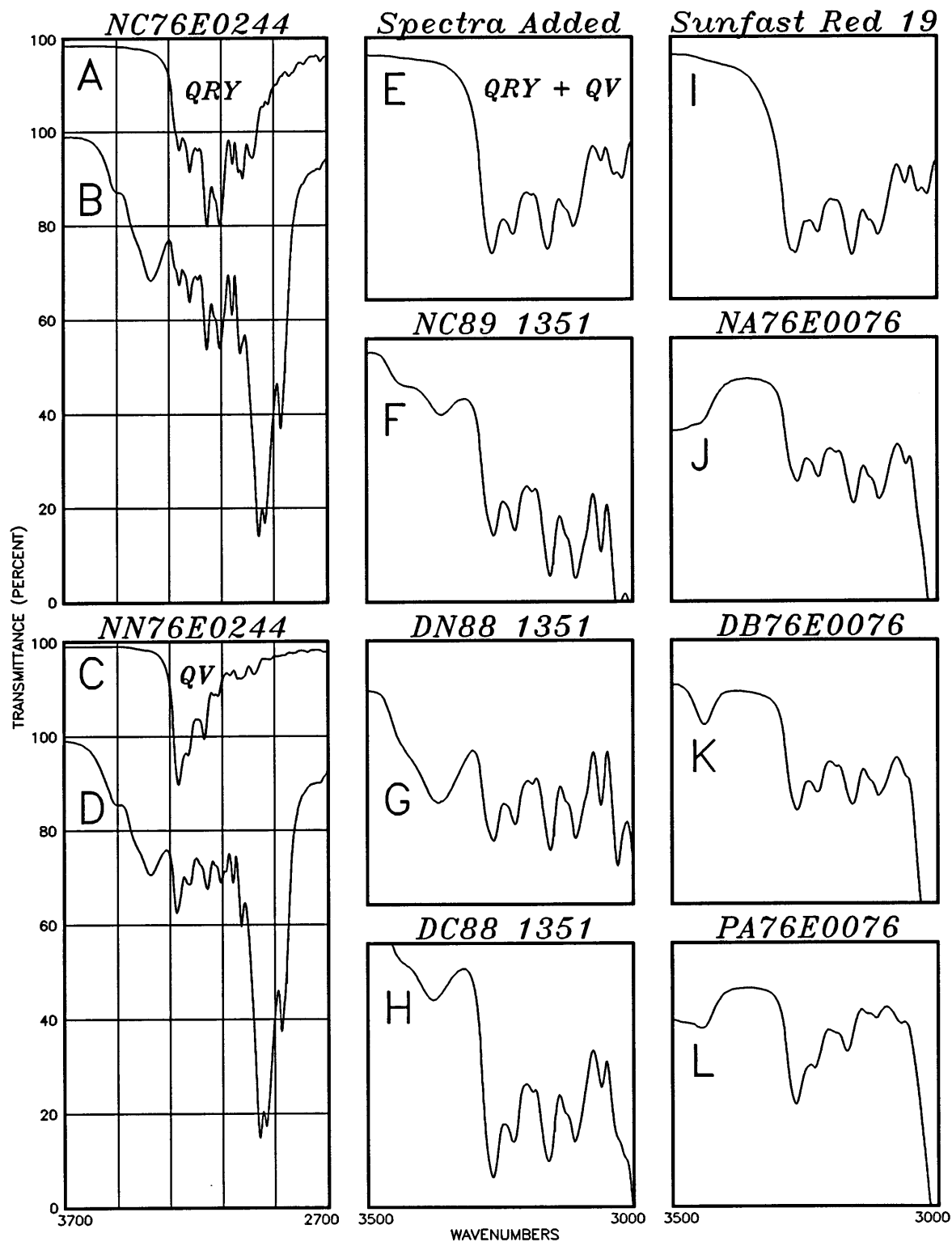


FIG. 17—Spectra in the hydrogen stretching region of: (a) Quinacridone Red Y; (b) a red nonmetallic enamel topcoat, NC76E0244, that contains Quinacridone Red Y; (c) Quinacridone Violet; (d) a red nonmetallic enamel topcoat, NN76E0244, that contains Quinacridone Red Y, Quinacridone Violet, and ferric oxide; (e) an addition of the absorptions of Quinacridone Red Y and Quinacridone Violet; (i) Sunfast Red 19, a pigment mixture of Quinacridone Red Y and Quinacridone Violet; and spectra of six topcoats—(f) NC89 1351, (g) DN88 1351, (h) DC88 1351, (j) NA76E0076, (k) DB76E0076, and (l) PA76E0076—which contain various Quinacridone Red Y/Quinacridone Violet mixtures; the ordinate range depicted for (e) through (l) is 30% transmittance.



TABLE 2—Quinacridone pigment combinations identified in red nonmetallic monocoats.

Topcoat	Shade	Binder	Pigments Identified	Fig.	Comments*
NA77E0342	Red	Acrylic lacquer	Quinacridone Red Y, Ferric oxide	4b	Ferric oxide spectrum—Fig. 4e
PN76E0095	Red-maroon	Acrylic melamine enamel	Quinacridone Violet, Molybdate Orange	5b	Molybdate Orange spectrum—Fig. 5e
NN82E0659	Orange-red	Acrylic melamine enamel	Quinacridone Red Y, Benzimidazolone Orange, Hydrrous ferric oxide	6b	Benzimidazolone Orange spectrum—Fig. 15a Hydrrous ferric oxide spectrum—Fig. 6a Quinacridone Red Y plus Benzimidazolone Orange spectrum—Fig. 6d
DN87 0659	Orange-red	Acrylic melamine enamel	Quinacridone Red Y, Benzimidazolone Orange, Ferric oxide, Rutile	6c	Rutile spectrum—Fig. 13e Ferric oxide plus rutile spectrum—Fig. 13f
PA75E0202	Maroon	Acrylic lacquer	Quinacridone Violet, Silica-encapsulated Molybdate Orange	7b	Silica-encapsulated Molybdate Orange spectrum—Fig. 14a EDX: Al, Si, Pb, Ti, Cr, Fe, Ni
NA75E0202	Maroon	Acrylic lacquer	Quinacridone Magenta, Ferric oxide	8b	EDX: Al, Si, Cl, Fe
NN79E0561	Red	Acrylic melamine enamel	Quinacridone Magenta, Molybdate Orange	9b	XRF spectrum—Fig. 18c
KN79E0561	Red	Acrylic melamine enamel	Quinacridone Magenta B, Molybdate Orange	9c	XRF spectrum—Fig. 18d
PA79E0471	Maroon	Acrylic lacquer	Quinacridone Violet, Ferric oxide	11b	This topcoat is not in the Reference Collection of Automotive Paints and was obtained from the FBI Laboratory
DC77E0054	Orange-red	Acrylic melamine enamel	Quinacridone Red Y, Benzimidazolone Orange, Ferric Oxide, Rutile	13b	XRF spectrum—Fig. 18e
NW77E0054	Orange-red	Acrylic melamine enamel	Quinacridone Red Y, Molybdate Orange	13c	XRF spectrum—Fig. 18f
LC77E0235	Red-maroon	Acrylic melamine enamel	Quinacridone Violet, Molybdate Orange, Ferric oxide	13d	EDX: Al, Si, Pb, Cr, Fe
DB76E0076	Red	Acrylic lacquer	Quinacridone Violet, Quinacridone Red Y, Silica-encapsulated Molybdate Orange	14b	An expanded portion of Fig. 14b depicting the pigment hydrogen stretching absorptions is shown in Fig. 17k EDX: Al, Si, Pb, Cr, Fe
NA76E0076	Red	Acrylic lacquer	Quinacridone Violet, Quinacridone Red Y, Molybdate Orange, Ferric oxide	14c	An expanded portion of Fig. 14c depicting the pigment hydrogen stretching absorptions is shown in Fig. 17j
PA76E0076	Red	Acrylic lacquer	Quinacridone Violet, Silica-encapsulated Molybdate Orange	14d	An expanded portion of Fig. 14d depicting the pigment hydrogen stretching absorptions is shown in Fig. 17l EDX: Al, Si, Pb, Cr, Fe
DB78E0436	Orange-red	Acrylic lacquer	Quinacridone Red Y, Benzimidazolone Orange	15c	
DB79E0599	Dark red	Acrylic lacquer	Quinacridone Red Y, Quinacridone Violet, Benzimidazolone Orange	16a	XRF spectrum—Fig. 18g
NB79E0599	Dark red	Acrylic lacquer	Quinacridone Red Y, Benzimidazolone Orange, Ferric oxide, May also contain Quinacridone Violet	16b	XRF spectrum—Fig. 18h
NA79E0599	Dark red	Acrylic lacquer	Quinacridone Red Y, Ferric oxide, May also contain Quinacridone Violet	16c	XRF spectrum—Fig. 18i

\*Elements detected by SEM/EDX analysis for some topcoats are listed. The instrument and analysis conditions used for this are described elsewhere (3).

red)—NN79E0561 (Fig. 9b) contains Quinacridone Magenta and Molybdate Orange, whereas KN79E0561 (Fig. 9c) contains Quinacridone Magenta B and Molybdate Orange. And (3) 0214 (metallic orange-red rust)—PA76E0214 (Fig. 12a) and DB76E0214 (Fig. 12b), both lacquers, have weak spectral absorptions of Quinacridone Magenta B, and DB76E0214 also has weak absorptions

of a second (unidentified) organic pigment; an enamel of this color, NW76E0214 (Fig. 12c), contains Quinacridone Red Y, an unidentified organic pigment, and probably a small amount of ferric oxide; a second enamel, DC76E0214 (Fig. 12d), has only very weak pigment absorptions.

Three additional colors provide examples of some of the other

types of pigment compositional differences that can occur: (1) 0659 (nonmetallic *orange-red*)—NN82E0659 (Fig. 6*b*) contains Quinacridone Red Y, Benzimidazolone Orange, and hydrous ferric oxide, whereas DN87 0659 (Fig. 6*c*) contains Quinacridone Red Y, Benzimidazolone Orange, ferric oxide and rutile. (2) 0054 (nonmetallic *orange-red*)—DC77E0054 (Fig. 13*b*) also contains Quinacridone Red Y, Benzimidazolone Orange, ferric oxide and rutile, and NW77E0054 (Fig. 13*c*) contains Quinacridone Red Y and Molybdate Orange (see Footnote 7). And (3) 0599 (nonmetallic *dark red*)—DB79E0599 (Fig. 16*a*) contains Quinacridone Red Y and Benzimidazolone Orange (a small amount of Quinacridone Violet also appears to be present); NB79E0599 (Fig. 16*b*) also contains these two pigments together with a small amount of ferric oxide; the amount of Benzimidazolone Orange relative to Quinacridone Red Y is much less for this topcoat compared with DB79E0599; and NA79E0599 (Fig. 16*c*) contains Quinacridone Red Y and ferric oxide.

These examples are not meant to imply that for most colors there are significant differences in pigment composition (which is not the case, since use of the same pigment for a given color is common), but rather to illustrate the differences that *can* occur and the diversity of pigment compositions that may be used to produce similar shades.

#### Elemental Analyses

Elemental analysis data for twelve topcoats containing various pigments or pigment combinations are presented in Fig. 18; the infrared spectra of these topcoats were previously discussed. XRF spectra acquired using two different excitation conditions are depicted: the left spectra (1 to 3.3 keV) were obtained using a titanium secondary target and those on the right (1 to 21 keV) were collected with a tin target. The weak broad features observed in some tin target spectra near 19 keV are not peaks of the sample, but arise from differences in the amounts of rhodium primary target K $\alpha$  lines that have been Compton-scattered from the sample and the reference.

Quinacridone Magenta B (III) is the only quinacridone pigment identified in Reference Collection topcoats that contains an element, chlorine, that can be detected by most XRF or SEM/EDX systems. Figure 18*a* and 18*b* depict, respectively, the XRF spectra of two metallic lacquers, 74K0087 (green) and 74E0085 (red). The infrared spectrum of the former was subtracted from that of the latter to produce the difference spectrum matching that of Quinacridone Magenta B (Fig. 10). Aluminum, bromine, chlorine, copper, titanium, and iron were detected for 74K0087, and aluminum, chlorine, and iron were detected for 74E0085. The aluminum is from the metal flakes, and although the bromine L lines partially overlap the aluminum K lines, most of the peak observed for 74K0087 (far left peak in the 1 to 3.3 keV region) is from aluminum. The ratios of the chlorine peaks to those of aluminum and the relative chlorine peak counts<sup>11</sup> both suggest that there is much more chlorine in 74E0085 than in 74K0087, which is consistent with the presence of Quinacridone Magenta B in 74E0085. The chlorine,

bromine and copper of 74K0087 are most likely due to Polychloro-bromo Phthalocyanine Green (Pigment Green 36), a green organic pigment that may be used in automotive paint (4).

XRF spectra of NN79E0561 and KN79E0561, the two red nonmetallic enamels that contain Molybdate Orange and Quinacridone Magenta or Quinacridone Magenta B (Fig. 9), are shown in Fig. 18*c* and 18*d*, respectively. Both topcoats contain primarily<sup>12</sup> lead, chromium, and molybdenum, with small amounts of titanium, nickel, and antimony (the nickel peak of NN79E0561 is too weak to be seen with the ordinate scale used in Fig. 18*c*). The latter three elements may be from Titanium Nickel Yellow, a yellow inorganic pigment (3,11). KN79E0561 contains Quinacridone Magenta B (Fig. 9*c*), but the chlorine K lines of this pigment cannot be seen in the spectrum obtained using the tin target (Fig. 18*d*, right spectrum), since it is buried in the shoulder of the strong lead M lines. Subtraction of the tin target spectrum of Fig. 18*c* from that of Fig. 18*d*, however, does indicate the presence of a weak chlorine peak. Use of a titanium target, which produces different excitation efficiencies, permits the chlorine peak to be observed directly (compare left spectra, Fig. 18*c* and 18*d*).

XRF spectra of two red nonmetallic enamels of color 0054, DC77E0054 and NW77E0054, are shown in Fig. 18*e* and 18*f*, respectively. Four pigments were identified from the infrared spectrum of DC77E0054 (Fig. 13*b*), and elements of three of these were detected: chlorine from the Benzimidazolone Orange (3), iron from the ferric oxide, and titanium from the rutile; Quinacridone Red Y, the fourth pigment identified in this topcoat, does not have any elements that can be detected using XRF analysis. Although not apparent from the infrared spectrum (Fig. 13*b*), DC77E0054 also contains Molybdate Orange, as small amounts of lead, chromium, and molybdenum were detected in ratios consistent with this pigment (the peaks of chromium and molybdenum are too weak to be observed in the presentation shown in Fig. 18*e*). NW77E0054 contains mainly lead, chromium, and molybdenum (Fig. 18*f*), consistent with the previous identification of Molybdate Orange and Quinacridone Red Y in this topcoat (Fig. 13*c*); a small amount of antimony was also found.

Data for three red nonmetallic lacquers of color 0599, DB79E0599, NB79E0599, and NA79E0599, are shown in Fig. 18*g*, 18*h*, and 18*i*, respectively. Benzimidazolone Orange and Quinacridone Red Y were identified in DB79E0599 (Fig. 16*a*), and the chlorine of the former pigment was the main element<sup>13</sup> detected, along with small amounts of iron and nickel. NB79E0599 (Fig. 16*b*) also contains these two pigments along with ferric oxide, but there is only a small amount of the Benzimidazolone Orange present; iron was the main element detected (Fig. 18*h*), together with chlorine and small amounts of copper and nickel. Quinacridone Red Y and ferric oxide were identified in NA79E0599 (Fig. 16*c*), and it contains mainly iron with little chlorine. Although not apparent from the infrared spectrum, Molybdate Orange is also present since small amounts of lead, chromium, and molybdenum, in ratios consistent with this pigment, were detected (the peaks of the latter two elements cannot be observed in the presentation

<sup>12</sup>Molybdate Orange also contains lead sulfate, but as discussed previously (2,3), the K lines of sulfur cannot be observed when excess lead (or molybdenum) is present because they overlap the lead M lines, which also occur in the region as the molybdenum L lines.

<sup>13</sup>Although it may not be obvious from the relative intensities of the three K lines of Fig. 18*g* (right spectrum), considerations involving the excitation and detection efficiencies of the analysis conditions make it clear that there is considerably more chlorine present than iron and nickel.

<sup>11</sup>While not a quantitative technique for the types of samples which were analyzed, the counts can provide a measure of the relative amounts of chlorine present since the total surface areas of the two samples were similar, and for chlorine X-rays the sample thicknesses were probably close to being "infinitely thick." Also, the samples consisted of numerous topcoat slices, so that any differences due to sampling geometry and sample morphology were averaged.

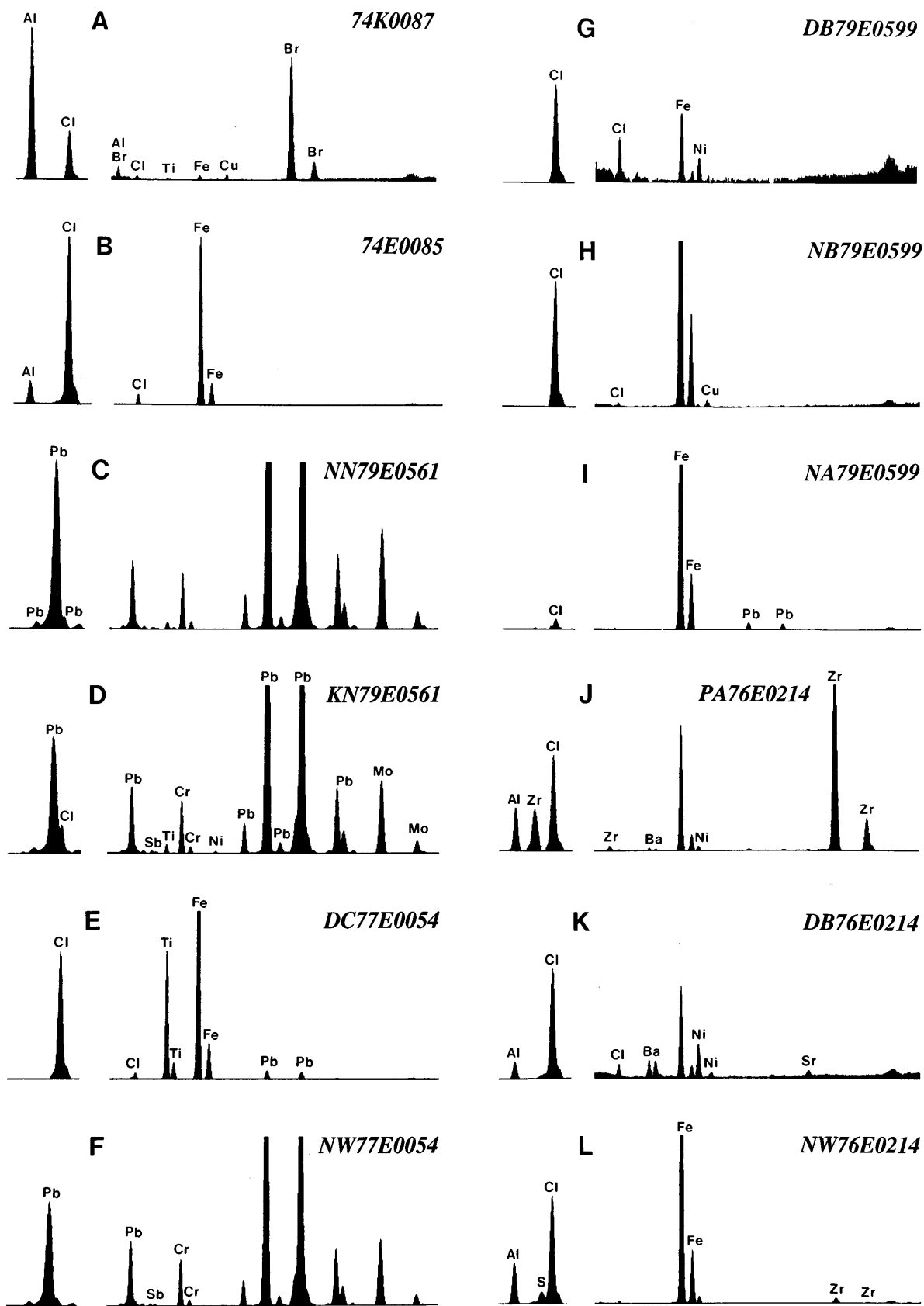


FIG. 18—XRF spectra of topcoats acquired using two different secondary targets for excitation (the spectra on the left from 1 to 3.3 keV were obtained using a titanium target, while those on the right from 1 to 21 keV were collected using a tin target): (a) 74K0087; (b) 74E0085; (c) NN79E0561; (d) KN79E0561; (e) DC77E0054; (f) NW77E0054; (g) DB79E0599; (h) NB79E0599; (i) NA79E0599; (j) PA76E0214; (k) DB76E0214; and (l) NW76E0214. A background spectrum was subtracted from each of the above spectra.

shown in Fig. 18i). The titanium target spectra of Fig. 18g, 18h, and 18i are shown with full ordinate scales of 200,000, 50,000, and 50,000 counts, respectively, so decreasing amounts of chlorine are indicated for these three topcoats (see Footnote 11), consistent with the infrared results.

XRF spectra of three red metallic topcoats of color 0214, PA76E0214, DB76E0214, and NW76E0214, are shown in Fig. 18j, 18k, and 18l, respectively. Weak absorptions of Quinacridone Magenta B were detected in the infrared spectra of PA76E0214 and DB76E0214 (Fig. 12a and 12b), whereas Quinacridone Red Y was identified in NW76E0214, along with an unidentified organic pigment and what appears to be ferric oxide (Fig. 12c). All three topcoats contain aluminum, chlorine, iron, and small amounts of nickel, but NW76E0214 contains the most iron, supporting the infrared indications of ferric oxide. The detection of chlorine in PA76E0214 and DB76E0214 is consistent with Quinacridone Magenta B, but NW76E0214 also contains this element, which is probably from the unidentified organic pigment (chlorine occurs in many automotive organic pigments (3)). Smaller quantities of the following elements were also detected: PA76E0214, barium, and possibly a small amount of lead; DB76E0214, barium, strontium, and possibly a small amount of lead; and NW76E0214, sulfur.

Zirconium was also detected (Fig. 18j) for PA76E0214, a lacquer, and a small amount was observed (Fig. 18l) for NW76E0214, an enamel. Zirconium compounds may be used in some automotive paints as driers for alkyds (4,11), where they are often combined with cobalt compounds. Cobalt was not detected for these two topcoats, however, neither of which has an alkyd binder. Zirconium is not found in most common automotive paint pigments, inorganic or organic. According<sup>14</sup> to PPG Industries, which produced PA76E0214, the likely source of this element is the zirconium oxide balls used to disperse the pigments in the paint. Previously, it was noted that a similar transfer may occur when steel balls are used (2), resulting in increased levels of iron. PPG indicated that zirconium oxide balls were used for metallic finishes, since steel balls may darken the finish due to such transfers.

As a contaminant that may be introduced during the paint manufacturing process, the amount of zirconium that results in such a case is likely to be batch-dependent; the differences in the levels of this element observed for PA76E0214 and NW76E0214, for example, are consistent with such an occurrence. A sample of PA76E0214 from the Georgia State Crime Laboratory Reference Collection of Automotive Paints was also tested,<sup>15</sup> and it too was found to contain zirconium at a level similar to the level observed here; the samples in the Reference Collection, however, may all have been produced from the same batch. Detection of zirconium in a topcoat that has a non-alkyd binder may thus reflect the presence of a manufacturing contaminant, and for identification purposes the possibility that the level of this element may not be the same in all paints of that type should be considered.

## Summary

Five quinacridone pigments are currently marketed for use in automotive paints, and four of these, Quinacridone Red Y, Quinacridone Violet, Quinacridone Magenta, and Quinacridone Magenta B, were identified in some U.S. automobile original finishes (1974–1989) from the Reference Collection of Automotive Paints.

<sup>14</sup>PPG Industries Inc., personal communication, Feb. 1997.

<sup>15</sup>Tammy Jergovich, Georgia Bureau of Investigation Crime Laboratory, personal communication, March 1997.

Quinacridone Red Y and Quinacridone Violet are two polymorphic forms of the same unsubstituted quinacridone ring structure, but they have noticeably different colors and distinguishable infrared spectra—especially in the hydrogen stretching region. A mix of these two is sold commercially, and they may also be combined by paint formulators. Quinacridone Red Y and Quinacridone Violet were identified in approximately 40% and 20% of Reference Collection red nonmetallic monocoats, respectively, and at least one dozen more have spectra indicative of a mixture of the two. Quinacridone Magenta B was identified in approximately one dozen of these, whereas Quinacridone Magenta was found in only a couple. Overall, the four quinacridones were used in two-thirds of red nonmetallic monocoats. Quinacridone Violet was identified in approximately one dozen brown nonmetallic monocoats, and the two polymorphs and Quinacridone Magenta B were found in some red and brown metallic monocoats as well.

The presence of one of these four pigments in topcoats having acrylic lacquer or acrylic melamine enamel binders can usually be recognized from spectral absorptions occurring in three regions: 3300–3000  $\text{cm}^{-1}$  (Quinacridone Red Y has absorptions distinct from the other three); 1640–1570  $\text{cm}^{-1}$ , where a very characteristic quinacridone multiplet feature occurs; and 1343–1339  $\text{cm}^{-1}$ , where a single peak occurs. Other weaker absorptions, most of which are observed below 1000  $\text{cm}^{-1}$ , may then be used to characterize further the pigment responsible. The four quinacridones are more readily recognized in lacquer spectra since the entire multiplet feature can be observed, and for both lacquers and enamels the two polymorphs are often easier to identify because their absorption intensities are usually greater than those of the two magenta pigments.

Except for a few red nonmetallic monocoats that contain Quinacridone Red Y and a few red metallic ones that contain Quinacridone Magenta B, spectra of all of the other Reference Collection finishes in which quinacridones were identified contain significant absorptions of other pigments. A number of different quinacridone pigment combinations were identified, but ones with ferric oxide, Molybdate Orange, or Benzimidazolone Orange were especially common. Quinacridone combinations with hydrous ferric oxide, rutile, silica-encapsulated Molybdate Orange, and other (unidentified) organic pigments were also observed.

Quinacridone Magenta B is the only pigment of the four that contains an element, chlorine, that can be identified by most X-ray elemental analysis techniques, and this element was detected in several monocoats containing this pigment. Even when one of the other quinacridones is used, however, elemental analyses still provide very useful information since inorganic pigments are frequently also present. In addition, elements are often detected for pigments and other components that cannot be discerned by infrared spectroscopy.

## Conclusions and Caveats

As illustrated by several of the examples presented, topcoats that are difficult to distinguish based on color can also have very similar infrared spectra that may differ in only minor or subtle features. Information about the origin and nature of these features can provide the analyst with a better means to gauge their significance, and help rule out external sources such as contaminants (including those introduced from adjacent paint layers during sampling) and other analysis artifacts.

Recognition of pigment peaks requires that analysts have a very

good familiarity with common binder absorptions. For the applications described, it is preferable that analysts be able to recognize binder absorptions from their patterns rather than having to rely entirely upon the use of binder identification flow charts. These charts are intended for use primarily with topcoats lacking significant pigment features. The spectra of topcoats having heavy pigment loads of one or more organic pigments may have numerous pigment peaks, and analysts unfamiliar with binder patterns may not be able to distinguish between binder and pigment absorptions easily.

The amount of pigment used in a topcoat can vary continuously and a wide range of pigment spectral absorption intensities can occur. This, together with differences in binder absorptions and the possibility of the presence of other pigments, leads to a similar variation as far as the number of absorptions that can be observed for—and assigned to—a pigment in a particular topcoat spectrum. A “continuum” in the degree of confidence with which one can attribute the absorptions of a particular topcoat to a specific pigment or pigment type is thus involved, and analysts must evaluate and determine what weight should be given to the information obtained by this means.

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