

# Infrared Spectra of U.S. Automobile Original Topcoats (1974-1989): VI. Identification and Analysis of Yellow Organic Automotive Paint Pigments—Isoindolinone Yellow 3R, Isoindoline Yellow, Anthrapyrimidine Yellow, and Miscellaneous Yellows\*

**REFERENCE:** Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): VI. Identification and analysis of yellow organic automotive paint pigments—Isoindolinone yellow 3R, isoindoline yellow, anthrapyrimidine yellow, and miscellaneous yellows. *J Forensic Sci* 1999;44(6):1151–1175.

**ABSTRACT:** Two yellow organic pigments, Benzimidazolone Yellow 3G and Benzimidazolone Yellow 4G, were identified in some U.S. automobile original (OEM) topcoats (1974–1989) in previous work in this study. The topcoats consisted of single layer finishes (monocoats) from the Reference Collection of Automotive Paints, and the pigments were identified in situ using infrared spectroscopy. The identification, analysis, and occurrence of other yellow organic pigments used in these finishes, including Isoindolinone Yellow 3R, Isoindoline Yellow, and Anthrapyrimidine Yellow, are described here. Based on a spectral survey of Reference Collection yellow, orange, brown and green nonmetallic monocoats, absorptions of Isoindolinone Yellow 3R were observed in the spectra of approximately three dozen yellow monocoats and one dozen orange ones. Isoindoline Yellow was identified in a single orange nonmetallic enamel. This pigment is now more common since it was one of several replacements for Chrome Yellow—a popular lead-containing pigment which is no longer used in U.S. automobile OEM finishes—and it was identified in several recent yellow nonmetallic basecoat/clearcoat finishes. Weak absorptions of Anthrapyrimidine Yellow were identified in the spectrum of a single yellow nonmetallic enamel. Spectra of several other yellow organic automotive paint pigments are also presented and discussed.

**KEYWORDS:** forensic science, criminalistics, paint analysis, automotive paint, infrared spectroscopy, pigment identification, Isoindolinone Yellow 3R, Isoindoline Yellow, Anthrapyrimidine Yellow, yellow organic pigments

In previous papers in this series, the identification of several organic pigments used in U.S. automobile original (OEM) topcoats (1974–1989) was described (1–3). The topcoats examined were single layer finishes (monocoats) from the Reference Collection of Automotive Paints. The pigments were identified in situ by infrared spectroscopy using spectral subtractions to help isolate and clarify pigment absorptions. The two yellow organic pigments which were identified were from the benzimidazolone family, Benzimidazolone Yellow 3G and Benzimidazolone Yellow 4G (1). The identification, analysis, and occurrence of three more yellow organic pigments which were used in these monocoats, Isoindolinone Yellow 3R, Isoindoline Yellow, and Anthrapyrimidine Yellow, are described in this paper.

Spectral data for several other yellow organic pigments which are currently marketed for applications which include automotive finishes are presented and discussed. These spectra are intended to serve as a reference, but they are also useful for evaluating the extent to which the absorptions of Isoindolinone Yellow 3R, Isoindoline Yellow, and Anthrapyrimidine Yellow—as observed in topcoat spectra—can be distinguished from those of other pigments which might be found in finishes having similar colors.

Yellow pigments are used in the paint industry to assist in the production of colors besides yellow itself, including orange, brown, and green (4). Hydrrous ferric oxide, for example, is a common yellow inorganic pigment which was identified in a large number of Reference Collection of Automotive Paints monocoats having a very wide range of colors, including yellow, orange, red, brown and green nonmetallic, and yellow, orange, brown, olive, and green metallic (5). This pigment is particularly common in finishes having yellowish-gold metallic, and off-white, beige or pale yellow nonmetallic hues.

Yellow, orange and red pigments absorb the shorter wavelengths of visible light, and due to anomalous dispersion, these pigments have relatively high indices of refraction for the longer wavelengths which are not absorbed and for some which are. For blue and green pigments, this phenomenon occurs in the near-infrared region.<sup>2</sup> Compared to blue and green pigments, yellow, orange and red pigments are therefore more effective in scattering visible light. The pigments, and the paints which contain them, are viewed primarily by diffuse reflectance: incident light penetrates the sample

<sup>1</sup> Forensic scientist, Washington State Crime Laboratory, Washington State Patrol, Seattle, WA.

<sup>2</sup> Titanium dioxide has a strong absorption in the near-ultraviolet region and due to anomalous dispersion, this pigment has relatively high indices of refraction in the visible region (6). This is the main reason for its high opacity and ability to provide effective hiding power in paints.

\* Presented in part at Microscopy and Microanalysis 1999, a joint meeting of the Microscopy Society of America and the Microbeam Analysis Society, Portland, OR, August 1999.

Received 5 Feb. 1999; accepted 8 March 1999.

surface<sup>3</sup> and those wavelengths which are not absorbed are scattered back to the surface. Strong scattering decreases the penetration depth of this light, and the average pathlengths which the various light rays travel while in the sample become shorter (7). When pigments having comparable absorption strengths, particle sizes, and concentrations are used to produce paints of various hues, the average pathlengths experienced by light diffusely reflected from the yellow, orange and red paints are less than those from the blues and greens. The yellow, orange and red paints will therefore have fainter colors,<sup>4</sup> and to compensate, heavier pigment loads must be used. Infrared absorptions of pigments of these colors are thus more likely to be evident in paint spectra, and this is particularly true if only organic pigments are involved.<sup>5</sup>

Empirically, organic pigment absorptions tend to be most prominent in spectra of red automotive paints, especially for nonmetallic finishes, but they are also observed for some yellow, orange, and brown nonmetallic and brown metallic finishes. As demonstrated previously, these absorptions can serve as a means to characterize better the pigment compositions of the finishes, and revealing information about an OEM automobile paint can sometimes be obtained from a knowledge of the particular pigments which were used in them (1–3,5,11). Information about the frequencies of occurrence of specific pigments or pigment combinations in topcoats of various colors can also be helpful for vehicle identification determinations, and for assessing the significance of a match in a comparative analysis.

## Experimental

### *Instrumentation and Sample Analysis Procedures*

Infrared spectra were acquired at a resolution of  $4\text{ cm}^{-1}$  using an extended range (4000–220  $\text{cm}^{-1}$ ) Digilab FTS-7 Fourier transform infrared spectrometer. This instrument was equipped with cesium iodide (CsI) optics and a deuterated triglycine sulfate (DTGS) detector. All of the paint samples were analyzed as thin slices placed over a 1 mm circular aperture in a metal disk, which was mounted in a Digilab 5X beam condenser. The slices were pressed with a

<sup>3</sup> For a colored sample, the fraction of incident light which is reflected without penetrating the sample surface may also have a different wavelength distribution than the incident light itself. This can occur for some materials which are very strong absorbers, as the strongly absorbed wavelengths are reflected more than those which are not due to the dependence of specular reflection on the absorption coefficient (7). This produces the bronzing effect (8), which is common for certain inks. Some automobiles from the 1950s with weathered dark blue nonmetallic finishes also had noticeable bronzing effects, which produced an unattractive blotchy red coloration (6).

<sup>4</sup> A good example of the dependence of color intensity on pathlength occurs for neat colored samples having relatively large particles sizes. When such colored particles are ground to a fine powder, color intensity decreases considerably (9,10), and some weakly absorbing compounds may become colorless (white). The smaller particles sizes of the fine powder cause more scattering to occur, and this decreases the average pathlengths of the diffusely reflected light while in the sample.

<sup>5</sup> Significant infrared absorptions of blue and green organic pigments are not observed in topcoat spectra, but very prominent cyano stretching absorptions of iron ferrocyanide (Prussian Blue), a blue inorganic pigment, sometimes occur (11). Inorganic pigments are generally weak absorbers in the visible region and strong absorbers in the infrared, so they require relatively high pigment loads to impart color, and their infrared absorptions are more likely to be observed than those of organic pigments having similar hues. For spectra of some green nonmetallic and metallic Reference Collection monocoats, infrared absorptions of hydrous ferric oxide are observed (5), but the absorptions of the blue organic pigment (most likely Copper Phthalocyanine Blue) which was used with it to produce the green colors are not evident.

roller device to produce a more uniform thickness and 1000 scans were collected. To obtain a slice of the basecoat of a basecoat/clearcoat finish, the clearcoat was first removed from a portion of each sample panel by scraping off this layer using a scalpel. Care was taken to remove all of the clearcoat prior to obtaining the basecoat slice, and to exclude any undercoat material from this slice. More details about the spectrometer, acquisition parameters used for data collection, and paint sample preparation methods are given elsewhere (5).

Spectra of all of the pigments were acquired using both a low pressure diamond anvil cell (DAC) mounted in the 5X beam condenser, and a Digilab diffuse reflectance (DRIFTS) accessory. The two methods were used since previous results with organic pigments (1,2) indicated that pressure-induced spectral changes were common, especially for the benzimidazolones (1). The DAC is a specially-designed version of the miniature diamond cell (High Pressure Diamond Optics, Tucson AZ) constructed so that the beveled diamond edges are not included in the area encompassed by the apertures of the cell.

For DRIFTS analyses, pigments were dispersed in excess powdered CsI without grinding to minimize pressure. Pressure effects were noted for some of the pigments as clear differences between the DRIFTS and DAC spectra sometimes occurred, and in general, spectral absorptions were better resolved for the DRIFTS data. All of the pigment spectra which are presented were obtained using DRIFTS, and 200 scans were collected.

### *U.S. Automobile OEM Finishes*

Most of the finishes discussed in this work are monocoats from the Reference Collection of Automotive Paints (Collaborative Testing Services, Inc., Herndon, Virginia) and they will be referred to by their nine character identification codes, which have been described previously (11). Prior to vehicle model year 1983, the Reference Collection finishes (12) were divided into general color categories according to the Inter-Society Color Council—National Bureau of Standards method of designating colors (10). The description of topcoat color used in the present work is based on this classification, and finishes added to the Reference Collection for model years 1983 and later were assigned colors by comparing them to those previously classified.

Panels of several recent U.S. automobile OEM finishes were obtained from the BASF Laboratory at the General Motors Shreveport, Louisiana plant, which produces Chevrolet S10, GMC Sonoma, and Isuzu Hombre compact pickup trucks. Spectra of the basecoat and clearcoat of one of these, a bright orange-yellow nonmetallic finish, are presented in this work. The BASF identification code of this finish system is R97YE402 and its General Motors color code is WACC253A (Wheatland Yellow). This finish is closest in hue to that of Reference Collection color H0500, and it may be used for a number of different special order/fleet vehicles including the 1998 Chevrolet S10.

### *Pigments*

The following pigments were used (pigment *Colour Index* (13) designations are given in parentheses since the cited generic names are not universally used, and trade names are given in italics): Isoindolinone Yellow 3R (Pigment Yellow 110), Ciba Specialty Chemicals Corp. *Irgazin*® Yellow 3RLTN; Isoindolinone Yellow 2G (Pigment Yellow 109), Ciba Specialty Chemicals Corp. *Irgazin* Yellow 2GLTN; Isoindolinone Orange (Pigment Orange 61), Ciba Specialty Chemicals Corp. *Cromophthal*® Orange 2G; Quinoph-

thalone Yellow (Pigment Yellow 138), BASF Corp. *Paliotol® Yellow L 0962 HD*; Isoindoline Yellow (Pigment Yellow 139), Bayer Corp. *Fanchon® Fast Yellow Y-5700* and BASF Corp. *Paliotol Yellow L 2140 HD*; Anthrapyrimidine Yellow (Pigment Yellow 108), BASF Corp. *Paliogen® Yellow L 1560*; Pyrimidine Yellow (Pigment Yellow 150), Bayer Corp. *Fanchon Fast Yellow Y-5688*; and Copper Azo Methine Yellow (Pigment Yellow 129), Ciba Specialty Chemicals Corp. *Irgazin Yellow 5GLT*. Spectra of Quinacridone Red Y, rutile (titanium oxide), ferric oxide, and hydrous ferric oxide are also discussed in this work, and these pigments have been described previously (2,5).

#### *In Situ Organic Pigment Identification Procedure*

The spectral subtraction procedure which is used for the initial identification of an organic pigment in situ has been described in detail previously (1) and only a very brief summary is presented here. For a topcoat containing an unidentified pigment of interest, another topcoat having a very similar binder formulation—but lacking this pigment—is used to produce a subtrahend spectrum. Subtractions involving a number of different topcoat and subtrahend spectra are usually performed, and the difference spectrum which is presented represents the best result for illustrative purposes. These difference spectra are therefore not typical and this method of analysis is not usually applicable to most case samples, for which specific binder formulations are normally not known. Once pigments have been identified by this means, however, their absorptions can usually be recognized in other topcoat spectra, and in many cases, this is true even when significant amounts of other pigments are also present.

#### *Spectral Calculations*

Spectral analysis and mathematical processing were performed using Spectra Calc™ software. Spectral data are presented in transmittance but all of the calculations were performed with data in the absorbance format. In most cases, topcoat and pigment spectral absorption intensities were scaled so that the most intense peak had a transmittance value between 3 and 10%, and baselines were adjusted to have their highest values near 100% (but baselines were not flattened). For spectral subtraction, a subtrahend factor was chosen which produced minimal residual binder features and the baseline of the difference spectrum was usually adjusted. Except where noted, however, difference spectra baselines were not flattened. In those cases where they were, a ten point correction was used. Spectral additions were performed with the subtraction routine using negative subtrahend factors. Reflectance spectra of pigments obtained using the DRIFTS accessory were converted to a transmittance format (7).

#### *Elemental Analyses*

Elemental analyses were performed using X-ray fluorescence (XRF) spectrometry with a KeveX 0700 XRF spectrometer which has been described previously (5). Numerous slices of each topcoat were mounted under a strip of adhesive tape and analyzed, and data collected for a blank strip of tape were subtracted from each spectrum. The slices covered a surface area of approximately 2 cm<sup>2</sup>. X-rays from titanium and tin secondary targets were used for excitation, produced with X-ray tube voltages of 25 and 45 kV, respectively, and currents of 2.0 mA. The instrument chamber was evacuated and data were collected for 50,000 seconds (total live time).

## **Results and Discussion**

In general, organic pigment absorptions are more prominent in spectra of nonmetallic finishes since the metal flakes of metallic finishes usually provide much of their hiding power, and there is less need for the pigments to provide opacity. There are relatively few yellow and orange metallic monocoats in the Reference Collection of Automotive Paints, and organic pigment absorptions are not evident in the vast majority of their spectra. The scope of this paper is thus limited to pigment use in nonmetallic finishes.

Although yellow organic pigments have higher indices of refraction than blue or green ones, they are not usually as opaque as titanium dioxide and some other inorganic pigments. To achieve greater hiding power for nonmetallic automotive finishes, yellow organic pigments are used together with more opaque inorganic pigments—usually rutile. This is also done for economic reasons since organic pigments are considerably more expensive than inorganic ones (8 and personal communications, Edward E. Jaffe Associates Inc., December 1998, and DuPont Automotive Products, December 1998). Some of the orange and red organic pigments previously identified in Reference Collection monocoats were occasionally used alone or with only small amounts of other pigments (1–3). A survey of the spectra of the yellow nonmetallic monocoats in this collection indicates, however, that all of those which contain organic pigment absorptions also have strong absorptions of rutile.

#### *Isoindolinone Yellow 3R*

The molecular structure of Isoindolinone Yellow 3R (I), a yellow-orange heterocyclic pigment of the isoindolinone family, is depicted in Fig. 1 and its infrared spectrum is shown in Fig. 2d. The spectrum of a yellow nonmetallic acrylic melamine enamel monocoat, NW78H0461, which contains this pigment is depicted in Fig. 2b. Above that is the spectrum (Fig. 2a) of a white nonmetallic enamel monocoat, NW76A0044, having a similar binder formulation which was used for spectral subtraction. A finish containing a large amount of rutile (Fig. 2e) was used to produce a subtrahend spectrum because NW78H0461 also appears to contain a large amount of this titanium dioxide pigment. The difference spectrum (the spectrum of NW76A0044 subtracted from that of NW78H0461) is shown in two segments: Fig. 2c depicts the results between 4000 and 780 cm<sup>-1</sup>, while Fig. 2g depicts the region from 850 to 220 cm<sup>-1</sup>. The ordinate of the latter is offset in this display since most of the difference spectrum below 800 cm<sup>-1</sup> corresponds to transmittance values above 100% in Fig. 2c. Relative to binder absorptions, the titanium dioxide absorption of NW76A0044 (Fig. 2a) is stronger than that of NW78H0461 (Fig. 2b), which causes these broad upward-tending features in the difference spectrum. To observe better the weak peaks in this low frequency region, the segment depicted in Fig. 2g was baseline flattened to remove the broad features, and the result is depicted in Fig. 2f.

Essentially all of the significant absorptions of Isoindolinone Yellow 3R (Fig. 2d) above 600 cm<sup>-1</sup> are observed in the subtraction spectra (Figs. 2c, 2f, and 2g) with frequencies which are all within 2 cm<sup>-1</sup> of those of the pigment itself, except for the carbonyl stretching peak. This peak overlaps a very strong binder carbonyl fundamental and differs by 4 cm<sup>-1</sup>. The relative absorption intensities of the subtraction result are also consistent with those of the pigment spectrum (compare Figs. 2c and 2d). Note that a relatively strong unidentified peak at 700 cm<sup>-1</sup> (Figs. 2f and 2g) is not from Isoindolinone Yellow 3R; styrene (14) contributes to this feature in Fig. 2b, but this component is not the source of the residual 700 cm<sup>-1</sup> peak of Figs. 2f and 2g. Most of the Isoindolinone Yellow 3R

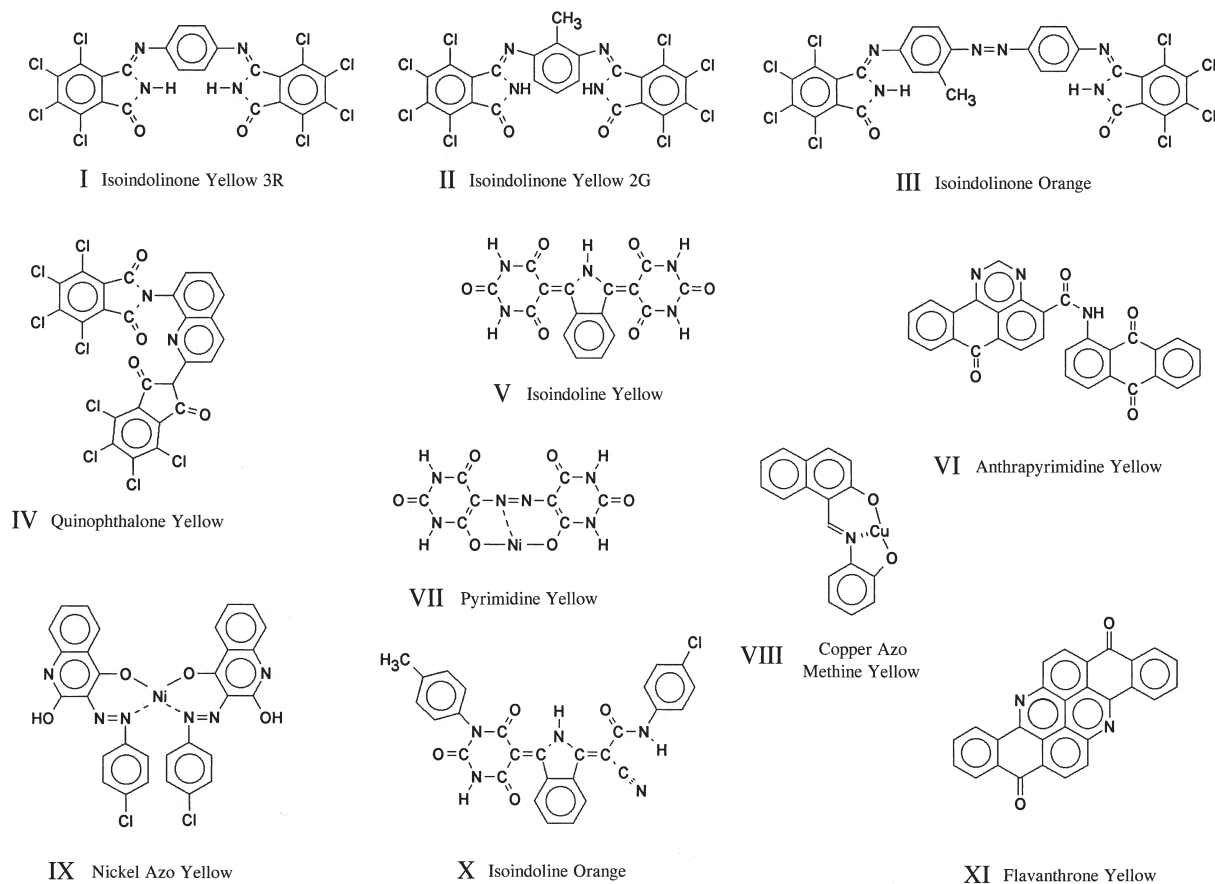


FIG. 1—Molecular structures of the pigments discussed in this work.

absorptions below  $600\text{ cm}^{-1}$  are observed in Fig. 2g, and more clearly in Fig. 2f.

The frequencies of the Isoindolinone Yellow 3R absorptions (Fig. 2d) are presented in Table 1. Of the 54 peaks listed, 42 are observed in the subtraction results. The 12 pigment absorptions which are not observed are either very weak, or they occur in a region where a residual binder feature is present.

**Pigment Absorptions Observed in Topcoat Spectra**—The strongest absorption of Isoindolinone Yellow 3R (Fig. 2d) is not observed in topcoat spectra because, as noted, it overlaps an intense binder carbonyl stretching fundamental. For topcoats with acrylic melamine enamel and acrylic lacquer binders, the  $1657\text{ cm}^{-1}$  absorption (which may have an accompanying very weak peak or unresolved shoulder near  $1672\text{ cm}^{-1}$ ) is usually the most conspicuous pigment feature. When relatively high pigment loads are used, several other Isoindolinone Yellow 3R absorptions are also observed, and for enamels these may include a fairly broad feature at  $3233\text{ cm}^{-1}$  and weak or very weak peaks at 1310, 1267, 1181, 1086, 963, 937, 853, 791, 743, 677, 650, 596, 492, and  $413\text{ cm}^{-1}$  (Fig. 2b). Some of these may not necessarily be observed in the spectra of all enamels due to individual differences in binder absorptions, especially in the C—O stretching region between  $1250$  and  $1050\text{ cm}^{-1}$  (14,15). Other Isoindolinone Yellow 3R peaks, including some which are not readily observed but which might be revealed by a detailed examination or expansion of select spectral regions, are included in the list of Table 1. For yellow finishes, the pigment absorptions below  $800\text{ cm}^{-1}$  will more than

likely be superimposed on a broad titanium dioxide feature, as seen in Fig. 2b. Because of the logarithmic nature of the transmittance scale, it should be remembered that any Isoindolinone Yellow 3R peaks near the bottom of such a strong absorption will have apparent intensities which are much weaker than might be expected.

The Isoindolinone Yellow 3R absorptions observed for NW78H0461 (Fig. 2b) are relatively strong, but they are weaker in spectra of all of the other Reference Collection finishes which contain this pigment. Spectra of two yellow nonmetallic mono-coats which have Isoindolinone Yellow 3R absorptions more typical of those usually observed are presented; the spectrum of an enamel, DC78H0506, is shown in Fig. 3b, while that of an acrylic lacquer, DB82H0870, is depicted in Fig. 4a. Both spectra also have strong absorptions of rutile (Fig. 2e), and that of DC78H0506 (Fig. 3b) additionally has absorptions of hydrous ferric oxide (Fig. 3d) at  $905$  and  $276\text{ cm}^{-1}$  (5). The Isoindolinone Yellow 3R absorptions at  $1657$  and  $1655\text{ cm}^{-1}$  (Figs. 3b and 4a, respectively) are quite weak and the  $1672\text{ cm}^{-1}$  peak is not observed for Fig. 4a, but the  $1657\text{ cm}^{-1}$  absorption of Figs. 3b does have an unresolved shoulder in this region. This shoulder peak is resolved in the DRIFTS spectrum of the pigment itself (Fig. 2d), but not in the spectrum of the pigment obtained using the DAC (not depicted). This difference may be caused by pressure-induced effects, which appear to be quite common for the organic pigments which have been examined in this series (1,2). During the paint manufacturing process the pigments may also be subjected to pressure when they are dispersed, and it is possible that

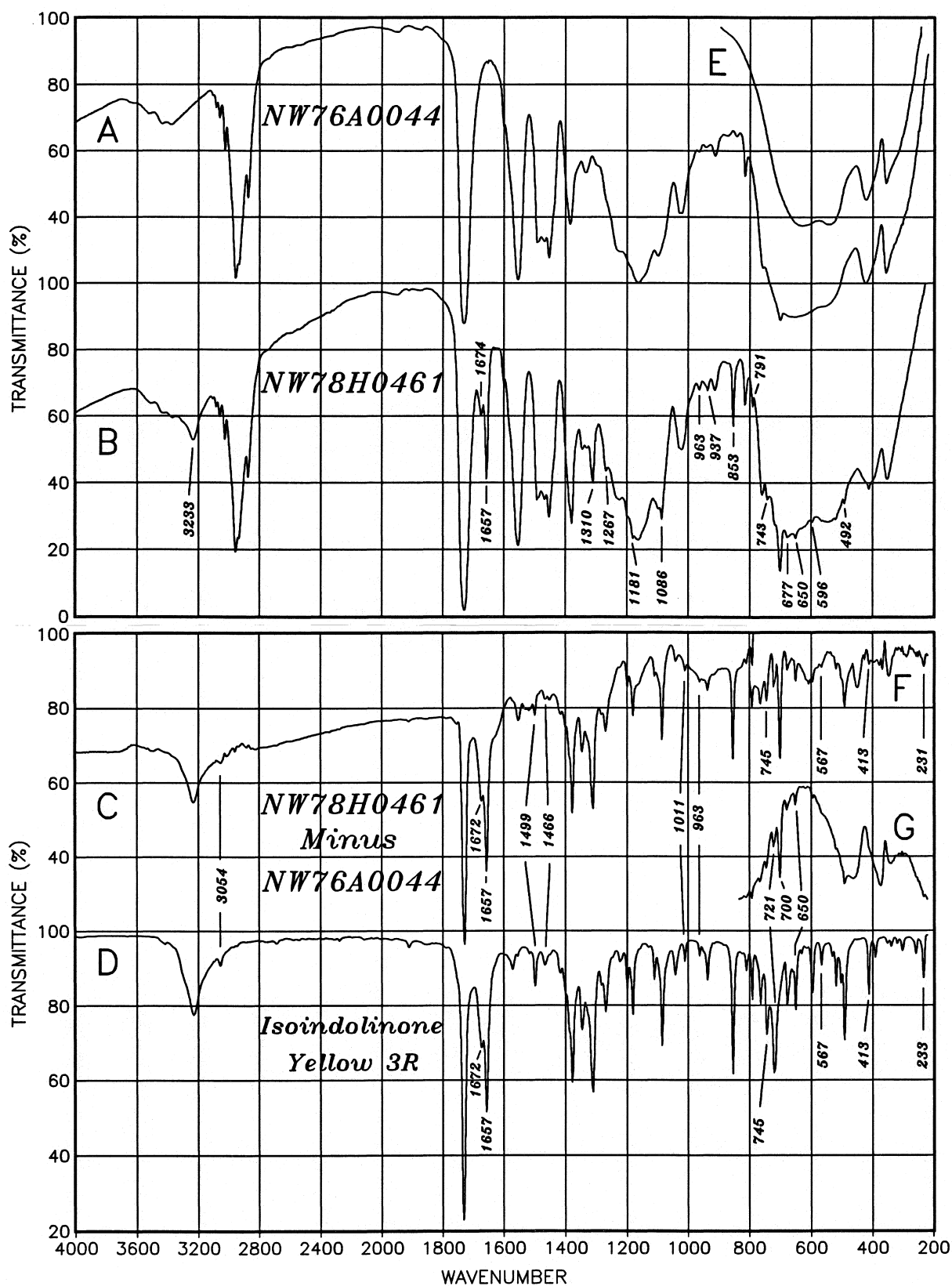


FIG. 2—Spectra of: (a) a white nonmetallic enamel monocoat, NW76A0044, which contains rutile; (b) a yellow nonmetallic enamel monocoat, NW78H0461, which contains Isoindolinone Yellow 3R and Nickel Titanate; (c) and (g) subtraction results—spectrum (b) minus spectrum (a); (d) Isoindolinone Yellow 3R; (e) rutile; and (f) the segment depicted in (g) after baseline flattening to remove the broad peaks.



TABLE 1 - *Infrared absorption frequencies of the pigments discussed in this work.*

Pigment <sup>a</sup>	Spectrum	Infrared Absorption Frequencies <sup>b</sup>
Isoindolinone Yellow 3R (PY110) Ciba	Fig. 2d, Fig. 9a	3418w, 3229m, 3054w, 2685vw, 2276vw, 1912w, 1852vw, 1732vs, 1672sh, 1657s, 1570w, 1555vw, 1516vw, 1499w, 1466w, 1416sh, 1377s, 1346m, 1310s, 1283sh, 1269m, 1223w, 1200w, 1181m, 1111w, 1086m, 1042w, 1011w, 963w, 936w, 853s, 810w, 791w, 764m, 745m, 721/718s, 677m, 650m, 631vw, 596m, 567w, 532vw, 519w, 503w, 492m, 413m, 392w, 351vw, 339vw, 318vw, 303w, 258w, 233w
Isoindolinone Yellow 2G (PY109) Ciba	Fig. 9b	3300m, 3044w, 2951w, 2938w, 1931vw, 1867vw, 1744vs, 1732vs, 1661s, 1564w, 1514vw, 1460w, 1377s, 1335m, 1308s, 1267m, 1240w, 1204w, 1181w, 1092w, 1055m, 1034sh, 966vw, 953vw, 937w, 891w, 829vw, 799m, 791sh, 764w, 748m, 721w, 700m, 660m, 615m, 592w, 572vw, 567vw, 552w, 532w, 519w, 502w, 461w, 451sh, 388vw, 351vw, 330vw, 276w, 260w
Isoindolinone Orange (PO 61) Ciba	Fig. 9c	3420w, 3223w, 3050w, 2961w, 2924w, 2677vw, 1929vw, 1896vw, 1844vw, 1734vs, 1663s, 1595w, 1589w, 1572sh, 1516vw, 1491w, 1481w, 1462w, 1454w, 1412sh, 1400sh, 1379s, 1344m, 1310s, 1289vw, 1271m, 1233w, 1204w, 1196w, 1184m, 1148w, 1101sh, 1084m, 1042w, 1007w, 966sh, 957w, 934w, 912w, 882w, 853m, 824w, 791w, 772m, 764sh, 748w, 735m, 721m, 679w, 660w, 627w, 608w, 581w, 557w, 538w, 521w, 503w, 492sh, 461w, 446vw, 428vw, 413vw, 382vw, 366vw, 349vw, 339vw, 309vw, 249w, 226vw
Quinophthalone Yellow (PY138) BASF	Fig. 9d	3497vw, 3121w, 3094w, 3044w, 3023w, 2884vw, 2764vw, 2745vw, 1956vw, 1896vw, 1786m, 1738vs, 1728s, 1670m, 1642s, 1620vs, 1607sh, 1593s, 1532s, 1483m, 1460w, 1414vs, 1379m, 1368s, 1354m, 1333m, 1306s, 1283sh, 1229m, 1200w, 1186w, 1173w, 1159w, 1140m, 1115m, 1047w, 1020w, 997w, 964w, 934w, 920w, 868sh, 853m, 812w, 789w, 772w, 754m, 743s, 729m, 691vw, 679w, 652w, 621w, 588w, 581vw, 552w, 540w, 523w, 500w, 473w, 413w, 394vw, 365vw, 351vw, 326w, 303w, 270vw, 239w, 233w
Isoindoline Yellow (PY139) Bayer, BASF	Fig. 11d	3190m, 3127m, 3081m, 3059m, 2839w, 2687w, 2511w, 2475vw, 2338w, 2315w, 2294w, 2112w, 2022vw, 1983vw, 1948vw, 1757sh, 1736vs, 1711s, 1680vs, 1661s, 1582m, 1535vs, 1454s, 1435s, 1418m, 1398s, 1354m, 1317sh, 1302s, 1265s, 1236m, 1200m, 1179w, 1136m, 1094sh, 1076m, 1061sh, 974vw, 959w, 907m, 893sh, 835s, 797m, 777s, 770m, 752m, 743s, 712w, 689w, 679w, 648vw, 635w, 600m, 557s, 517m, 430m, 334m, 289w, 245w
Anthra- pyrimidine Yellow (PY108) BASF	Fig. 12a	3312w, 3084w, 3055w, 2904w, 2662vw, 1984w, 1914vw, 1877vw, 1715sh, 1670vs, 1588s, 1580sh, 1547m, 1514vs, 1481sh, 1476s, 1460m, 1406m, 1333s, 1310s, 1273vs, 1236m, 1221m, 1184w, 1169sh, 1154vw, 1140w, 1109vw, 1086w, 1020w, 997m, 976w, 959w, 922w, 907w, 887w, 872w, 831m, 801m, 774s, 731m, 704vs, 656w, 646sh, 619w, 610w, 583w, 548sh, 542w, 517vw, 469vw, 455vw, 430w, 421vw, 409w, 388vw, 357w, 334vw, 301vw, 264w
Pyrimidine Yellow (PY150) Bayer	Fig. 12b	3470m, 3422m, 3345s, 3235m, 3115m br, 2900m br, 2755 m vbr, 1719s, 1638vs, 1593vs, 1551s, 1518sh, 1462s, 1422vs, 1306w, 1271m, 1244sh, 1173w, 1055m, 900w br, 812m, 791m, 777m, 750w, 681w, 619sh, 594m, 577sh, 534sh, 505s, 488s, 442s, 395sh, 307vw, 284w, 260vw, 237w, 228w
Copper Azo Methine Yellow (PY129) Ciba	Fig. 12c	3586vw, 3563vw, 3387w br, 3055w, 3036sh, 2913vw, 2891vw, 2770vw, 2587w, 2552w, 1944sh, 1925w, 1883w, 1869vw, 1840vw, 1819vw, 1794w, 1767w, 1659vw, 1613s, 1603vs, 1580vs, 1535vs, 1505s, 1479vs, 1456s, 1425s, 1400s, 1387s, 1354s, 1339vs, 1304vs, 1289s, 1267s, 1248sh, 1211m, 1198m, 1177s, 1163s, 1154m, 1142m, 1109m, 1092m, 1040w, 1028m, 978m, 961vw, 943w, 920w, 874m, 856s, 843s, 828vs, 777w, 760s, 741vs, 735vs, 685vw, 650m, 629w, 604vw, 579s, 561m, 550w, 523w, 503s, 467m, 457s, 417m, 403vw, 370m, 357m, 336w, 299w, 276m, 262m

<sup>a</sup> The *Colour Index* designation is given in parentheses using the abbreviations PY = Pigment Yellow and PO = Pigment Orange. The manufacturer of the pigment is also listed.

<sup>b</sup> 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, sh = a shoulder peak, br = broad, and vbr = very broad.

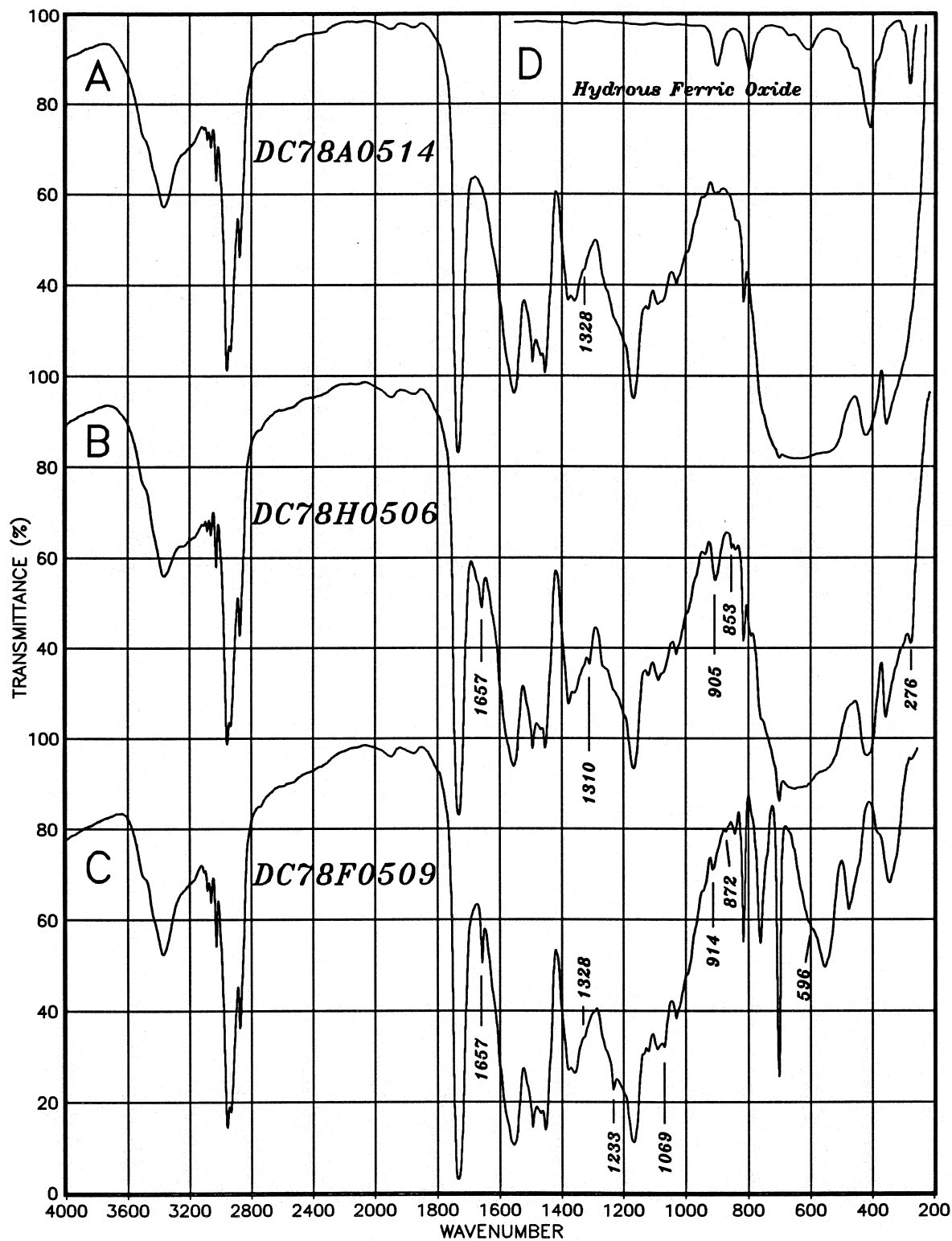


FIG. 3—Spectra of: (a) a white nonmetallic enamel monocoat, DC78A0514, which contains rutile; (b) a yellow nonmetallic enamel monocoat, DC78H0506, which contains rutile, hydrous ferric oxide, and a small amount of Isoindolinone Yellow 3R; (c) a brown nonmetallic enamel monocoat, DC78F0509, which contains Thioindigo Bordeaux and ferric oxide; and (d) hydrous ferric oxide.

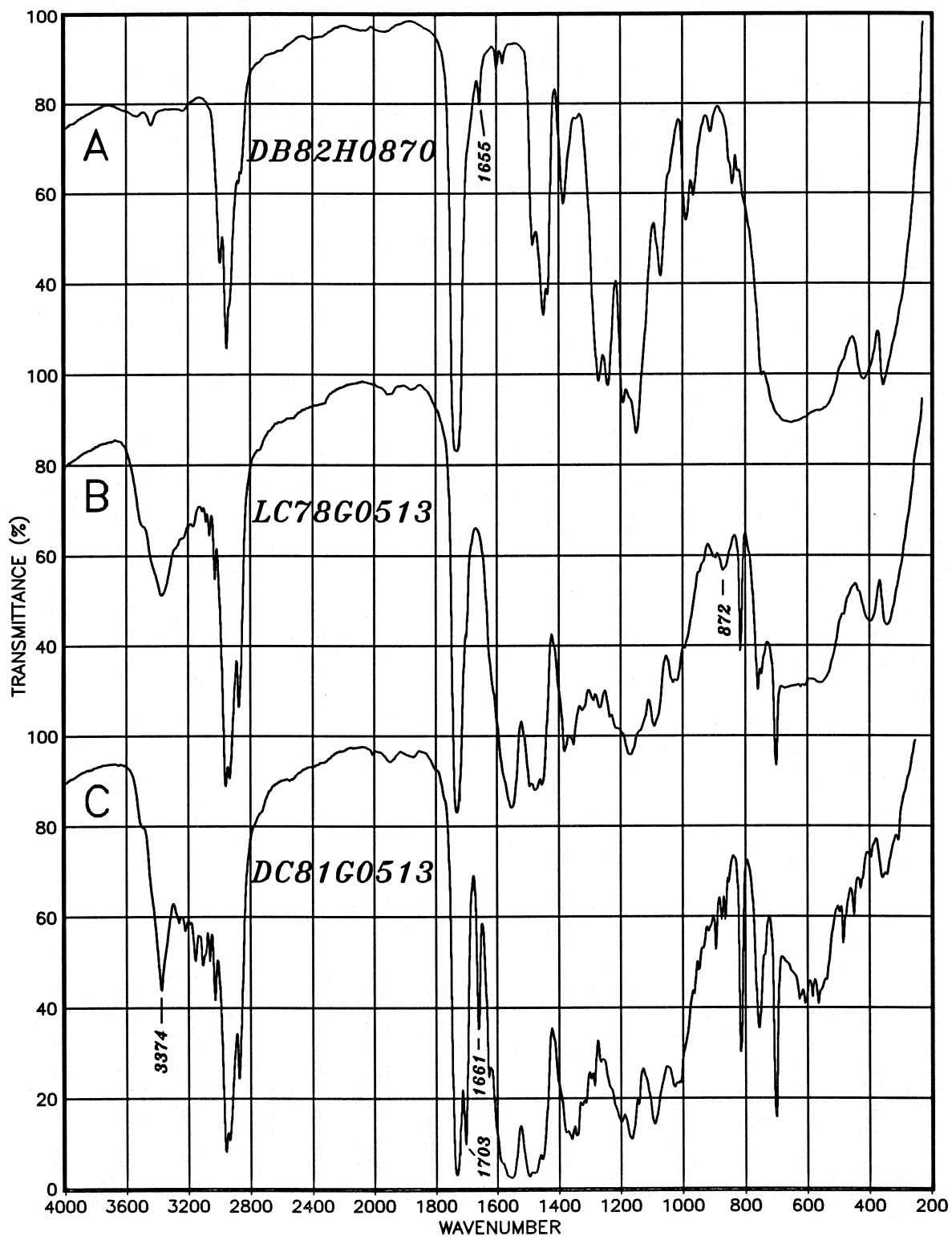


FIG. 4—Spectra of: (a) a yellow nonmetallic acrylic lacquer monocoat, DB82H0870, which contains rutile and a small amount of Isoindolinone Yellow 3R; (b) an orange nonmetallic enamel monocoat, LC78G0513, which contains rutile and a small amount of a chromate pigment; and (c) an orange nonmetallic enamel monocoat, DC81G0513, which contains Benzimidazolone Orange, Quinacridone Red Y, rutile and ferric oxide.



this unresolved peak in some spectra reflects the manufacturing history of the paint. Caution is dictated when interpreting such minor spectral differences, however, as they may be caused by other factors. For DC78H0506, two other very weak Isoindolinone Yellow 3R peaks at 1310 and 853  $\text{cm}^{-1}$  are also observed (Fig. 3b). The two peaks are quite inconspicuous and it may help to compare this spectrum to that of DC78A0514 (Fig. 3a), a similar white nonmetallic enamel.

The spectrum of DC78A0514 was subtracted from that of DC78H0506 and portions of the resulting difference spectrum are shown in Fig. 5a. Data for Isoindolinone Yellow 3R are depicted in Fig. 5b and the main absorptions of this pigment can be seen in this difference spectrum, even in the presence of relatively strong residual binder features and two absorptions (at 905 and 799  $\text{cm}^{-1}$ ) of hydrous ferric oxide. The difference spectrum below 800  $\text{cm}^{-1}$  is not depicted, but it consists of a pronounced inverse broad feature arising from the stronger rutile absorption of DC78A0514 compared to that of DC78H0506. This broad feature was baseline flattened resulting primarily in absorptions of hydrous ferric oxide, but other very weak peaks, including two at 721 and 596  $\text{cm}^{-1}$  consistent with Isoindolinone Yellow 3R, were also observed.

Spectral subtractions were performed for the lacquer, DB82H0870 (Fig. 4a), using various "DB" metallic monocoats to produce subtrahend spectra. In addition to the 1655  $\text{cm}^{-1}$  peak, seven other absorptions consistent with Isoindolinone Yellow 3R at 3229, 1377, 1348, 1310, 1269, 1086, and 853  $\text{cm}^{-1}$  were detected in the various difference spectra (not shown). These eight absorptions are among the strongest in the spectrum of Isoindolinone Yellow 3R (Fig. 5b), and their relative intensities in the difference spectra are also consistent with those expected for this pigment.

While the subtraction data for DC78H0506 and DB82H0870 indicate the presence of Isoindolinone Yellow 3R, less can usually be inferred about pigment identities based on the much more limited number of pigment peaks which are normally observed in topcoat spectra themselves. A weak or very weak absorption between 1655 and 1659  $\text{cm}^{-1}$  occurs in the spectra of approximately three dozen Reference Collection yellow nonmetallic monocoats and one dozen orange ones. In two-thirds of these cases, a second very weak peak at 853 or 855  $\text{cm}^{-1}$  is observed, especially for the enamels. For half of these, one or two additional very weak peaks consistent with Isoindolinone Yellow 3R are observed, usually from the group of five absorptions at 3229, 1672, 1310, 1269, and 1181  $\text{cm}^{-1}$ . The presence of a weak sharp peak between 1655 and 1659  $\text{cm}^{-1}$ , which may have a very weak unresolved or resolved shoulder near 1672  $\text{cm}^{-1}$ , should thus be considered a prompt to seek these additional peaks. As discussed later, many of the major absorptions of Isoindolinone Yellow 3R are similar to those of two other isoindolinone pigments which may also be used in automotive finishes. Depending on which and how many pigment peaks are observed in topcoat spectra, the data may be consistent with an isoindolinone-type pigment but it may not be possible to determine which specific member is present.

Ten organic pigments have been identified previously in Reference Collection finishes (1–3), and these ten can be readily distinguished from Isoindolinone Yellow 3R based on relatively few absorptions. The four quinacridones (2), for example, do not have any absorptions between 2000 and 1630  $\text{cm}^{-1}$ , whereas DPP Red BO (3) has a strong doublet at 1645/1607  $\text{cm}^{-1}$ . Benzimidazolone Orange (1) has a peak at 1659  $\text{cm}^{-1}$ , but it also has a stronger absorption at 1705  $\text{cm}^{-1}$  which is observed on the side

of the binder carbonyl stretching absorption, and an additional conspicuous sharp feature at 3372  $\text{cm}^{-1}$ . The spectrum of an enamel which contains Benzimidazolone Orange is shown in Fig. 4c (note that the pigment frequencies are shifted very slightly, probably because they are superimposed on the side of binder absorptions). Benzimidazolone Yellow 3G (1) has somewhat similar strong absorptions at 3407, 1701, and 1670  $\text{cm}^{-1}$  (see Fig. 6a), and Benzimidazolone Yellow 4G (1) has absorptions at 3187, 1701, 1657, 1620, and 1599  $\text{cm}^{-1}$ . Benzimidazolone Brown (1) has absorptions at 1659 and 1626  $\text{cm}^{-1}$ ; it is used in metallic finishes (which are most likely brown in color) whereas Isoindolinone Yellow 3R is used primarily in nonmetallic ones.

Only Thioindigo Bordeaux (3) has an absorption at 1655  $\text{cm}^{-1}$  and no others in the enamel binder window region between 1700 and 1600  $\text{cm}^{-1}$ . Thioindigo Bordeaux lacks the 1672  $\text{cm}^{-1}$  shoulder peak, however, and the other weak absorptions of this pigment which might be observed in the spectra of acrylic melamine enamels occur at 1294, 1233, 1132, 1067, 914, 872, 596, and 478  $\text{cm}^{-1}$ . Except for the 596  $\text{cm}^{-1}$  peak, these are distinguished from those of Isoindolinone Yellow 3R, which occur at 1310, 1267, 1181, 1086, 963, 937, 853, 791, 743, 677, 650, 596, 492, and 413  $\text{cm}^{-1}$ . The spectrum of a brown (maroon) nonmetallic enamel (DC78F0509) which contains Thioindigo Bordeaux and ferric oxide is shown in Fig. 3c. This spectrum can be compared to that of DC78H0506 (Fig. 3b), a similar enamel which contains Isoindolinone Yellow 3R, rutile, and hydrous ferric oxide. Although the very weak pigment peaks are easy to overlook, they can provide important corroborative evidence and are more likely to be detected if they are being actively sought.

Spectral considerations aside, Thioindigo Bordeaux has a deep purple-violet shade so it is not likely to be found in significant quantities in yellow or orange finishes; it was, in fact, only identified in maroon Reference Collection finishes (3). In addition, all of the monocoats which contain Thioindigo Bordeaux also contain ferric oxide, whereas an Isoindolinone Yellow 3R/ferric oxide binary pigment combination—with no other pigments detected—has not been observed at all. Finally, Thioindigo Bordeaux is not common in Reference Collection monocoats and it is no longer used much in automotive paints (3), whereas Isoindolinone Yellow 3R continues to be used.

As discussed previously (1–3) and demonstrated above, the 1700 to 1600  $\text{cm}^{-1}$  spectral region is an important one for detecting and distinguishing organic pigment absorptions. The 1657  $\text{cm}^{-1}$  Isoindolinone Yellow 3R peak is often quite weak (Figs. 3b and 4a), however. Topcoat spectra should thus be free of water vapor absorptions when attempting to interpret features in the 1700 to 1600  $\text{cm}^{-1}$  region, as these vapor absorptions may completely obscure weak pigment peaks.

*Pigment Combinations*—As noted, all of the Reference Collection yellow nonmetallic monocoats which contain Isoindolinone Yellow 3R also contain rutile. Combinations of Isoindolinone Yellow 3R with other organic pigments were not observed for any of these, but they were identified for a few orange nonmetallic monocoats. Spectra of two of these, NC78G0513 and DC78G0513, are shown in Figs. 7b and 7c, respectively.

The spectrum of NC78G0513 should be compared to that of NC78L0498 (Fig. 7a), a blue metallic enamel with a similar binder composition which lacks noticeable pigment spectral features. A large number of pigment absorptions are observed in the spectrum of NC78G0513 (Fig. 7b), and most of these can be attributed to

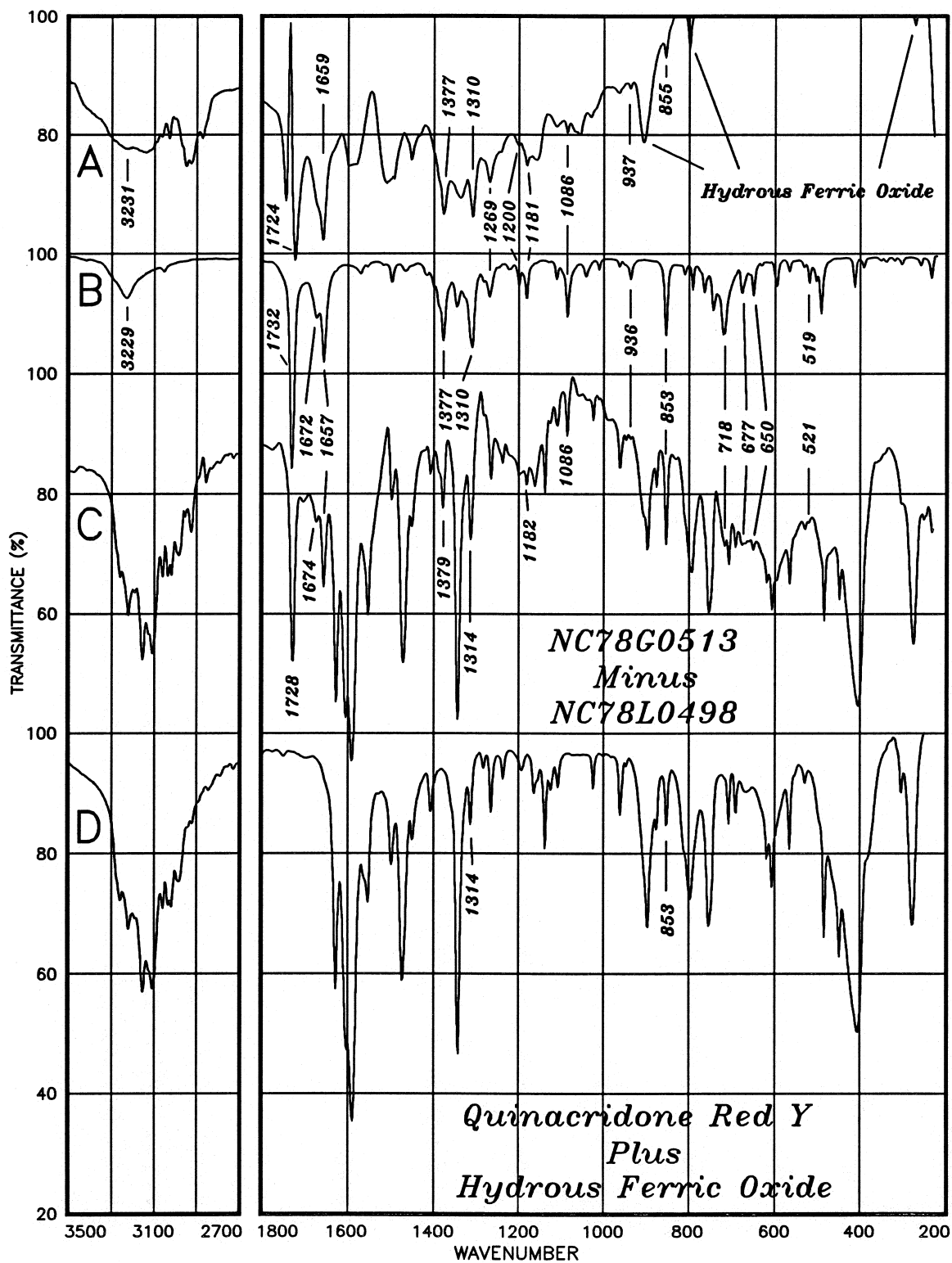


FIG. 5—(a) Results of a spectral subtraction—the spectrum of DC78A0514 (Fig. 3a) was subtracted from that of DC78H0506 (Fig. 3b); (b) a spectrum of Isoindolinone Yellow 3R; (c) results of a spectral subtraction—the spectrum of NC78L0498 (Fig. 7a) was subtracted from that of NC78G0513 (Fig. 7b); and (d) results of an addition of the spectra of Quinacridone Red Y and hydrous ferric oxide.

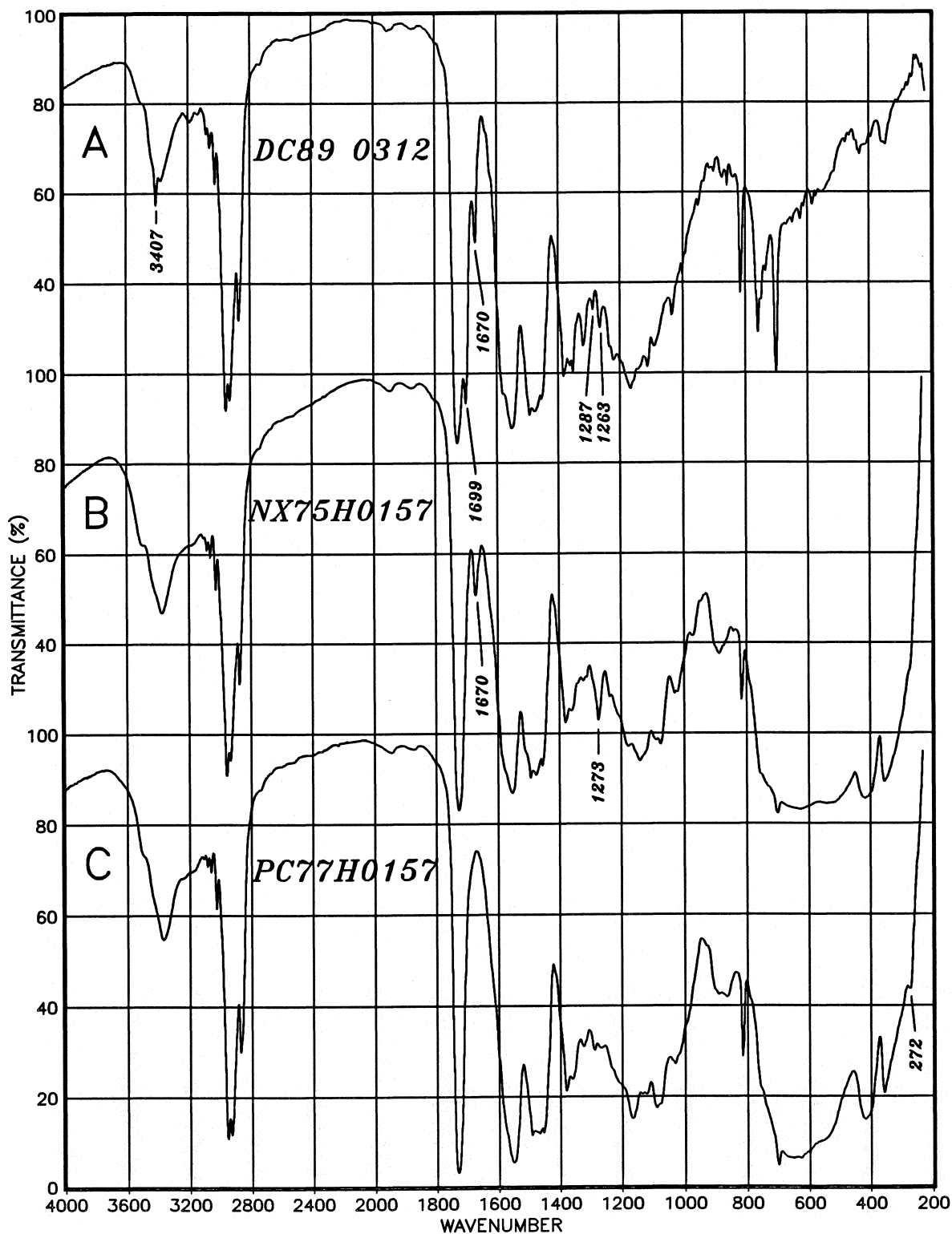


FIG. 6—Spectra of: (a) an orange nonmetallic enamel monocoat, DC89 0312, which contains Benzimidazolone Yellow 3G and rutile; (b) a yellow nonmetallic enamel monocoat, NX75H0157, which contains rutile, a chromate pigment, Anthrapyrimidine Yellow, and a small amount of hydrous ferric oxide; and (c) a yellow nonmetallic enamel monocoat, PC77H0157, which contains rutile, a chromate pigment, and hydrous ferric oxide.

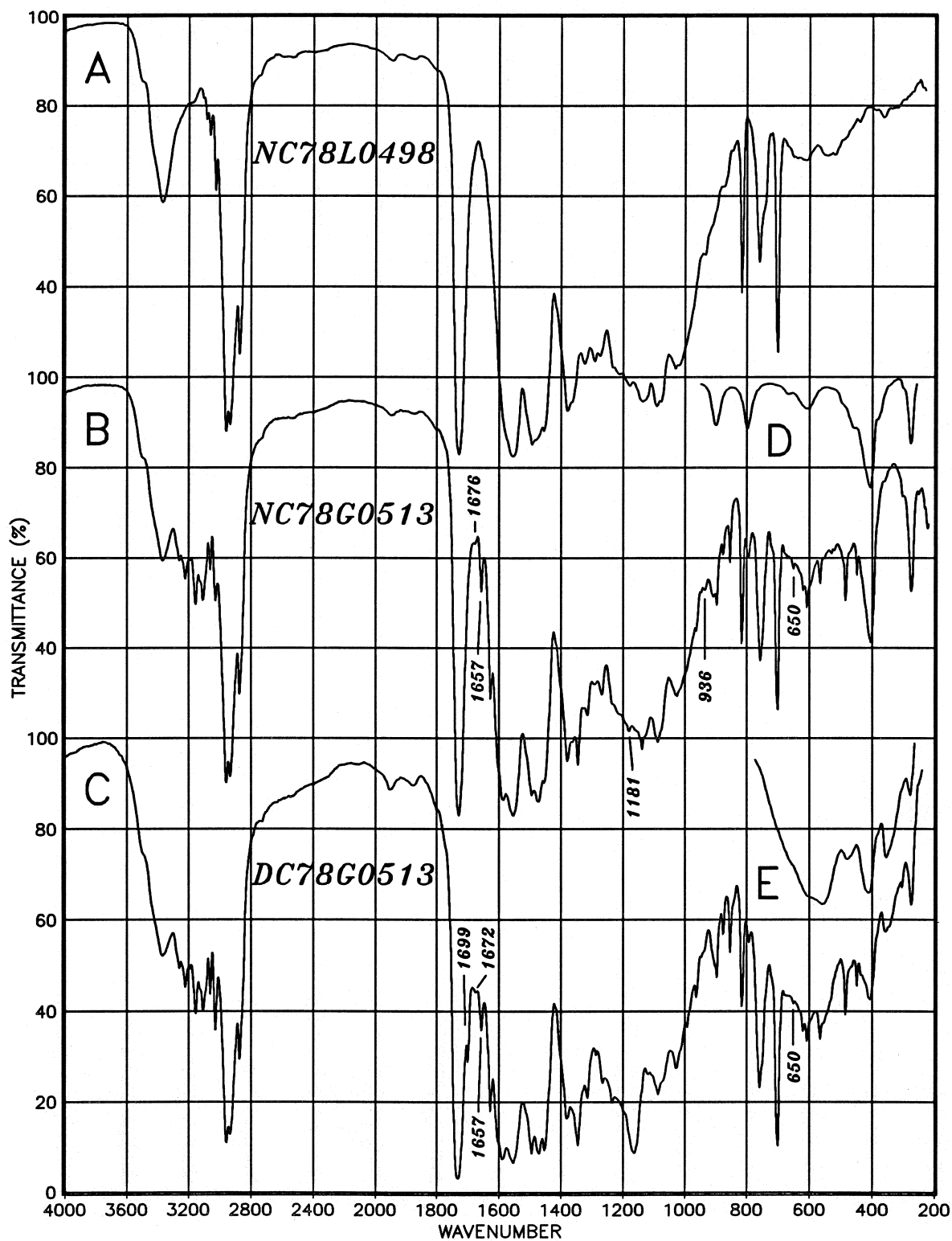


FIG. 7—Spectra of: (a) a blue metallic enamel monocoat, NC78L0498; (b) an orange nonmetallic enamel monocoat, NC78G0513, which contains Quinacridone Red Y, hydrous ferric oxide, Isoindolinone Yellow 3R, and probably rutile; (c) an orange nonmetallic enamel monocoat, DC78G0513, which contains Quinacridone Red Y, rutile, ferric oxide, hydrous ferric oxide, Isoindolinone Yellow 3R, and probably Perinone Orange; (d) hydrous ferric oxide; and (e) an addition of the absorptions of rutile, ferric oxide, and hydrous ferric oxide.

Quinacridone Red Y<sup>6</sup> (2) and hydrous ferric oxide (5). For Quinacridone Red Y<sup>6</sup> these include the sharp peaks at 3258, 3221, 3154, 3108, 3059, 1628, 1586, 1344, 1314, 1138, 897, 876, 853, 619, 608, 565, 529, 484, 448 and 303 cm<sup>-1</sup>, while the broader far infrared absorptions at 405 and 278 cm<sup>-1</sup>, and those near 900 and 600 cm<sup>-1</sup>, are from hydrous ferric oxide (Fig. 7d). The observed frequencies are all within 2 cm<sup>-1</sup> of those of the pigments themselves (2,5) except for the 1586 cm<sup>-1</sup> absorption, which differs by 3 cm<sup>-1</sup>, and the two features near 900 and 600 cm<sup>-1</sup>. The very broad dip in the baseline of Fig. 7b from 800 to 400 cm<sup>-1</sup> suggests that titanium dioxide (Fig. 2e) is probably also present.

The weak or very weak peaks at 1676, 1657, 1181, 936, and 650 cm<sup>-1</sup> (labeled in Fig. 7b) are those of Isoindolinone Yellow 3R. Additional absorptions of this pigment are observed in the result obtained (Fig. 5c) by subtracting the spectrum of NC78L0498 (Fig. 7a) from that of NC78G0513 (Fig. 7b). This difference spectrum should be compared to Fig. 5d, which was produced by adding the spectra of Quinacridone Red Y and hydrous ferric oxide, and to Fig. 5b, which depicts the absorptions of Isoindolinone Yellow 3R. Residual binder features are minimal for this difference spectrum and the agreement between most of the observed absorptions and those of the simulated Quinacridone Red Y/hydrous ferric oxide mixture is good. All of the stronger absorptions of Isoindolinone Yellow 3R can be seen in the difference spectrum for those spectral regions where Quinacridone Red Y and hydrous ferric oxide do not absorb; the frequencies and relative intensities of these peaks are also consistent with those of the pigment. Note that two of the stronger absorptions of Isoindolinone Yellow 3R at 1310 and 853 cm<sup>-1</sup> (Fig. 5b) overlap absorptions of Quinacridone Red Y at 1314 and 853 cm<sup>-1</sup> (Fig. 5d). Relative to the 1314 and 853 cm<sup>-1</sup> peaks of Quinacridone Red Y (Fig. 5d), the 1314 and 853 cm<sup>-1</sup> peaks in the difference spectrum (Fig. 5c) both appear to have enhanced intensities when compared to nearby absorptions, which is consistent with a contribution to these features by both pigments.

The spectrum of DC78G0513 (Fig. 7c) presents an interesting case where absorptions of six different pigments—three organic and three inorganic—are observed. Like NC78G0513 (Fig. 7b), DC78G0513 contains Quinacridone Red Y and Isoindolinone Yellow 3R. Only three Isoindolinone Yellow 3R absorptions at 1672, 1657, and 650 cm<sup>-1</sup> are evident in Fig. 7c, but several more at 1200, 1181, 1086, 936, 810, 716, and 677 cm<sup>-1</sup> were revealed by spectral subtractions. For these, spectra of DC78L0503 and DC78K0504, a blue and a green metallic monocoat respectively, were subtracted from the spectrum of DC78G0513. The results from 1690 to 800 cm<sup>-1</sup> (not depicted) strongly resemble Fig. 5c, except that a few extra absorptions are evident, and a few of the absorptions have apparent enhanced intensities. The extra absorptions (1699, 1287, 1010, and 991 cm<sup>-1</sup>) and those which appear enhanced (1495, 1451, 1383, 1235, and 876 cm<sup>-1</sup>) are all consistent with the presence of an orange organic pigment, Perinone Orange (the identification of this particular pigment, which is not a common one, will be discussed further in a future report).

The absorptions of some inorganic pigment combinations have been discussed previously to facilitate the identification of such mixtures based on their absorption profiles in topcoat spectra. The

combinations included ferric oxide/hydrous ferric oxide (5), ferric oxide/rutile (2), and hydrous ferric oxide/rutile (1). These particular binary mixtures were identified in some brown, orange, and red nonmetallic monocoats, respectively. The infrared absorptions of DC78G0513 below 1000 cm<sup>-1</sup>, on the other hand, are consistent with a mixture of all three of these inorganic pigments. The results of an addition of the spectra of rutile (Fig. 2e), hydrous ferric oxide (Fig. 7d) and ferric oxide are depicted in Fig. 7e. The features of this profile can be seen in the spectrum of DC78G0513 below 800 cm<sup>-1</sup>; the weak sharp peaks superimposed on this pattern are primarily those of Quinacridone Red Y (along with two strong absorptions of styrene from the binder). The weak broad absorption of DC78G0513 near 900 cm<sup>-1</sup> (which has a weaker sharp peak superimposed on it) is from hydrous ferric oxide (see Fig. 7d).

Combinations of Isoindolinone Yellow 3R with other organic pigments which result in noticeable spectral absorptions are not common in Reference Collection finishes, and spectra such as that of DC78G0513 which exhibit absorptions of six or more pigments are quite unusual. There is thus merit in learning to recognize and identify such compositions, as they can be potentially quite helpful when identifying an unknown automotive paint, or when evaluating the significance of a match in a comparative analysis. Even when a limited number of observed peaks permits only a qualified conclusion regarding pigment identities, or when complete pigment compositions cannot be determined, this information can still be useful.

Such detailed examinations do require pattern recognition skills on the part of the analyst, and this is particularly true when interpreting mixtures involving two or more organic pigments. The organic/inorganic combinations are usually easier to recognize because organic pigment absorptions are generally quite narrow, whereas those of inorganic pigments are broader, fewer in number, and tend to occur in the lower frequency regions. When only numerous sharp absorptions are present, however, there are no simple criteria to indicate whether a mixture is involved or not. Analysts should therefore be familiar with the absorption patterns of the more common organic pigments so that they can recognize when "extra" absorptions indicative of a mixture are present. Such familiarity need not be extensive, and remembering the frequencies or patterns of a few key absorptions, such as those in the 1700 to 1600 cm<sup>-1</sup> region, may be all that is often required since the other absorptions can be compared to those in reference tables. As emphasized previously (1,2), analysts should first be familiar with the spectra of common binders so that the pigment absorptions themselves can be recognized as such.

*Differences in Pigment Compositions for Finishes Having Similar Colors*—Spectra of four enamels of Reference Collection color G0513 provide an example of the diversity of pigment compositions which can be used to produce finishes having similar hues (in this case, a very red shade of orange). The compositions of two of these enamels, NC78G0513 (Fig. 7b) and DC78G0513 (Fig. 7c), have been discussed in detail. The third, DC81G0513 (Fig. 4c), contains a relatively common pigment combination consisting of Benzimidazolone Orange, Quinacridone Red Y, ferric oxide, and rutile, which has been used in enamels to produce a bright orange-red shade (2,16). In contrast to the spectra of these three, the spectrum of the fourth enamel, LC78G0513 (Fig. 4b), has a prominent titanium dioxide feature but lacks significant absorptions of color-imparting pigments. A weak absorption at 872 cm<sup>-1</sup> is indicative of a chromate pigment (5), while a very weak peak at 748 cm<sup>-1</sup> and what appears to be a very weak unresolved low frequency shoulder to the binder

<sup>6</sup> In Paper IV in this series, it was stated that quinacridones were identified in Reference Collection red and brown nonmetallic and metallic monocoats (2). Mention of the use of Quinacridone Red Y in a few orange nonmetallic monocoats was inadvertently omitted, however. As might be expected, the orange monocoats which have spectra with noticeable absorptions of this pigment all have red shades.

carbonyl stretching fundamental suggest the presence of a small amount of an organic pigment (or pigments). Lead, chromium, and molybdenum were detected for this monocoat, indicating that the lead chromate pigment is Molybdate Orange (although the additional presence of a lesser amount Chrome Yellow, another lead chromate pigment, cannot be ruled out from these data).

A variety of colored inorganic and organic pigments in various combinations were thus used to produce this one color, including Quinacridone Red Y (pink-red), ferric oxide (rust), Molybdate Orange (orange-red), Benzimidazolone Orange (orange), hydrous ferric oxide (yellow), Isoindolinone Yellow 3R (yellow-orange), and probably Perinone Orange (orange). The finishes of color G0513 exhibit exceptional diversity regarding pigment compositions, and spectra of three other enamels from this group were previously presented in Paper III of this series (1) to illustrate this point for benzimidazolones. The compositions of these three are distinct from the four discussed here, and it may be useful to compare the seven spectra (the three prior spectra are depicted in Fig. 11 of Paper III). The pigment compositions of the enamels discussed previously are: CC78G0513—Benzimidazolone Orange, hydrous ferric oxide, and rutile; LC84 0513—Quinacridone Red Y, hydrous ferric oxide, rutile, Molybdate Orange, and probably Isoindolinone Yellow 3R; and KC78G0513—Isoindolinone Yellow 3R, Quinacridone Red Y, and rutile.

*Use in U.S. Automobile OEM Nonmetallic Monocoats (1974-1989)*—A survey of the spectra of all of the available yellow, orange, brown, and green nonmetallic monocoats (approximately 600 total) in the Reference Collection of Automotive Paints was conducted to determine the frequency of use of Isoindolinone Yellow 3R in these finishes. For the yellow monocoats, in addition to NW78H0461 (Fig. 2b), DC78H0506 (Fig. 3b), and DB82H0870 (Fig. 4a), an absorption between 1655 and 1659  $\text{cm}^{-1}$  was observed in 36 spectra, with many of these having additional very weak peaks consistent with Isoindolinone Yellow 3R as noted previously. For orange monocoats, in addition to NC78F0513 (Fig. 7b) and DC78G0513 (Fig. 7c), this was the case for eight spectra.

Isoindolinones were first synthesized in 1964 (17) and the finishes cited above were produced in most of the years covered by the Reference Collection. The presence of Isoindolinone Yellow 3R in an unknown OEM automotive paint thus provides only minimal information as far as limiting the possible model years of vehicles which could have been the source of such a finish.

Absorptions of Isoindolinone Yellow 3R or other yellow organic pigments of this study were not observed in spectra of any green nonmetallic monocoats. Isoindolinone Yellow 3R was used together with Phthalocyanine Green in some green nonmetallic monocoats produced before the time period covered by the Reference Collection of Automotive Paints (Personal communication, DuPont Automotive Products, December 1998). Isoindolinone Yellow 3R may also have been used in some Reference Collection green nonmetallic monocoats in concentrations too low to result in noticeable spectral absorptions. By far, the most common yellow pigment which was identified in green nonmetallic monocoats is hydrous ferric oxide. For brown nonmetallic monocoats, a few spectra do have absorptions between 1661 and 1655  $\text{cm}^{-1}$ , but the other absorptions which are present indicate that these are from either Benzimidazolone Orange (1), Thioindigo Bordeaux (3), or an unidentified organic pigment (3) which is observed in some maroon finishes. Absorptions of the other yellow organic pigments discussed in this paper were also not identified in the spectra of any brown nonmetallic monocoats, although a small amount of Benz-

imidazolone Yellow 3G (1) appears to have been used in at least one of these.

*Elemental Analyses*—X-ray fluorescence (XRF) spectra of some monocoats which were discussed regarding infrared data are shown in Fig. 8. The spectra on the left (depicted between 1 and 3 keV) were obtained using X-rays from a titanium secondary target for excitation, while those on the right resulted from excitation of this same sample with a tin target (1 to 20 keV). Each of the topcoat samples was comprised of numerous individual slices having more or less flat orientations on adhesive tape, and all had roughly the same total surface areas subjected to analysis. Comparisons between spectra displayed with the same ordinate scales (total counts full display) thus provide some measure of the relative amounts of elements in the respective topcoats, since differences arising from sample morphology and penetration effects are averaged.

XRF data for NW76A0044 and NW78H0461, the two enamels with infrared spectra depicted in Fig. 2, are shown in Figs. 8a and 8b, respectively. The presence of a large amount of rutile was indicated from the infrared spectrum of NW76A0044 (Fig. 2a), and titanium is the main element observed for this monocoat. Lesser amounts of iron, aluminum, and silicon are also present. NW78H0461 (Fig. 8b) contains primarily titanium and chlorine, with lesser amounts of antimony, iron, nickel, zinc, bromine, and niobium. The relatively large amount of chlorine observed for NW78H0461 supports the conclusion that this monocoat contains Isoindolinone Yellow 3R (I), since this pigment contains chlorine (Fig. 1). The presence of nickel, antimony, and titanium, the relative peak intensity ratios of these three elements, and some features in the infrared spectrum of NW78H0461 all indicate that this monocoat also contains Nickel Titanate. The analysis of this yellow inorganic pigment will be described in a subsequent paper. It is worth mentioning here, however, that the residual structures of the difference spectrum of Fig. 2g, apart from the overall inverse nature, are caused in large part by the presence of this pigment.

XRF spectra of DC78A0514 and DC78H0506, the white and yellow nonmetallic enamels with infrared spectra depicted in Fig. 3, are shown in Figs. 8c and 8d, respectively. A large amount of rutile was identified from the infrared spectrum of DA78A0514, and this monocoat contains primarily titanium, with lesser amounts of aluminum, silicon, and iron (Fig. 8c). The infrared spectrum of DC78H0506 also indicated the presence of a large amount of rutile, together with hydrous ferric oxide and Isoindolinone Yellow 3R. Aluminum, silicon, chlorine, titanium, and iron are observed for DC78H0506 (Fig. 8d), although the peaks of aluminum and silicon are not easily seen with the particular ordinate scale used for the left display. The relatively large amounts of titanium and iron which are observed are consistent with the presence of rutile and hydrous ferric oxide, while the chlorine is consistent with the presence of Isoindolinone Yellow 3R.

XRF data for DB82H0870, the yellow nonmetallic lacquer which contains rutile and a small amount of Isoindolinone Yellow 3R (Fig. 4a), are shown in Fig. 8e. This monocoat contains primarily aluminum, silicon, chlorine and titanium, with lesser amounts of antimony, iron, nickel, zinc and niobium. The titanium and chlorine are consistent with the presence of rutile and Isoindolinone Yellow 3R. A small amount of Nickel Titanate is probably also present, as indicated by the presence of antimony, nickel, and titanium, and the antimony/nickel peak ratio.

XRF spectra of NC78L0498, NC78G0513, and DC78G0513, the three enamels with infrared spectra depicted in Fig. 7, are shown in Figs. 8f, 8g, and 8h, respectively. NC78L0498, a blue



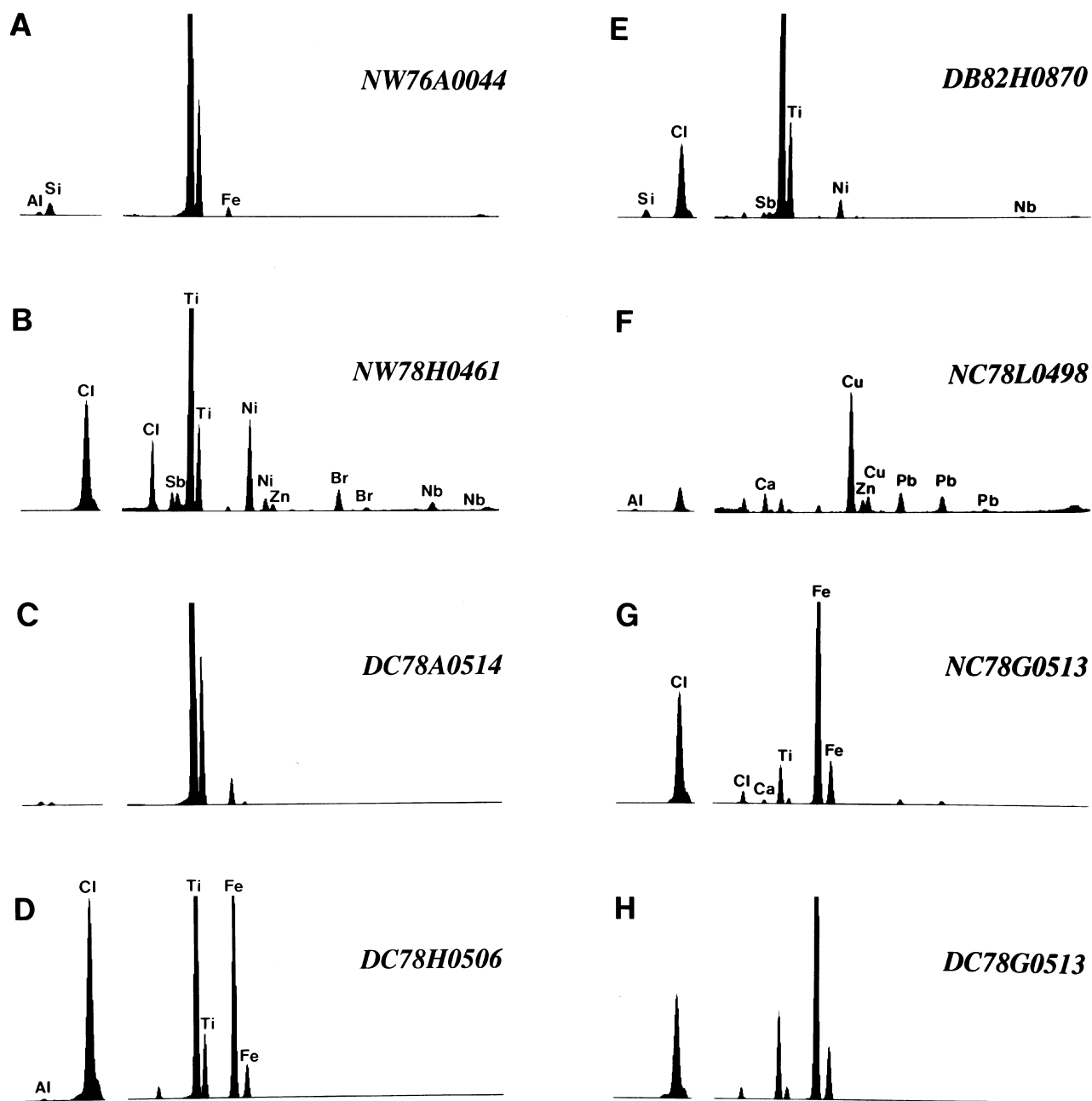


FIG. 8—XRF spectra of some monocoats acquired using two different secondary targets for excitation. The spectra on the left (depicted from 1 to 3 keV) were obtained using a titanium target, and those on the right (1 to 20 keV) were collected using a tin target. The total counts for the right spectrum of NC78L0498 is 20,000, and 100,000 for all of the others. The total counts for the left spectra are listed. (a) NW76A0044, 500,000; (b) NW78H0461, 5,000,000; (c) DC78A0514, 500,000; (d) DC78H0506, 500,000; (e) DB82H0870, 500,000; (f) NC78L0498, 1,000,000; (g) NC78G0513, 1,000,000; and (h) DC78G0513, 1,000,000. The weak broad features near 19 keV in some of the spectra are not peaks of the samples, but are caused by differences in the amounts of rhodium primary target K $\alpha$  lines which have been Compton-scattered from the sample and the reference.

metallic monocoat, contains aluminum, chlorine, calcium, titanium, and copper, together with lesser amounts of iron, zinc, and lead (Fig. 8f). The aluminum is from the metal flakes, while the copper is undoubtedly from Copper Phthalocyanine Blue. The chlorine is likely from chlorinated copper phthalocyanine, which is often used to stabilize Copper Phthalocyanine Blue (3,4,8,17).

The infrared spectrum of NC78G0513 indicated the presence of Quinacridone Red Y, hydrous ferric oxide, Isoindolinone Yellow 3R, and probably a small amount of titanium dioxide (Figs. 7b and 5c). Consistent with this, iron is the main element observed for this

monocoat, together with chlorine, titanium, and small amounts of calcium and lead (Fig. 8g). Note that Quinacridone Red Y does not contain any elements other than carbon, hydrogen, oxygen, and nitrogen (2).

Absorptions of six pigments, Quinacridone Red Y, Isoindolinone Yellow 3R, Perinone Orange, rutile, ferric oxide, and hydrous ferric oxide, were observed in the infrared spectrum of DC78G0513 (Fig. 7c). Perinone Orange, like Quinacridone Red Y, does not contain any elements which can be detected by the XRF instrument used in this work. DC78G0513 contains chlorine, tita-

nium, and iron (Fig. 8h), supporting these assignments. The same ordinate scale is used for the tin target spectra of NC78G0513 and DC78G0513 (Figs. 8g and 8h, right), and the intensity of the titanium peak may be seen to be greater for DC78G0513. This is consistent with the relative intensities of the titanium dioxide absorptions observed in the corresponding infrared spectra (Fig. 7).

The intensities of the chlorine peaks of NW78H0461 (Fig. 8b), DC78H0506 (Fig. 8d), DB82H0870 (Fig. 8e), NC78G0513 (Fig. 8g), and DC78G0513 (Fig. 8h), when observed with similar ordinate scales, suggest that NW78H0461 contains more of this element than the other four. This is consistent with the relative intensities of the Isoindolinone Yellow 3R absorptions observed in the corresponding infrared spectra (Figs. 2b, 3b, 4a, 7b, and 7c), which indicate that NW78H0461 contains the largest amount of this pigment.

#### *Isoindolinone Yellow 2G, Isoindolinone Orange, and Quinophthalone Yellow*

In addition to Isoindolinone Yellow 3R (I), two other isoindolinones, Isoindolinone Yellow 2G (II) and Isoindolinone Orange (III), and a related heterocyclic pigment, Quinophthalone Yellow (IV), may also be used in automotive paints. The molecular structures<sup>7</sup> of these compounds are shown in Fig. 1 and their infrared spectra are depicted in Fig. 9.

On the basis of their structures, the two isoindolinones (II and III) are likely to have infrared spectra which are the most similar to that of Isoindolinone Yellow 3R as far as pigments which may be used in automotive paints are concerned. The spectra of the three isoindolinones (Figs. 9a, 9b and 9c) do have gross similarities, but they can be distinguished fairly easily. This is not the case, however, when only the absorptions which are likely to be observed in topcoat spectra are considered. Like Isoindolinone Yellow 3R, the other two isoindolinones have an absorption in the 1700–1600  $\text{cm}^{-1}$  window at 1661 or 1663  $\text{cm}^{-1}$  which includes an unresolved high frequency shoulder. For Isoindolinone Yellow 3R, Isoindolinone Yellow 2G, and Isoindolinone Orange, fairly strong absorptions occur, respectively, at 1377, 1377, 1379  $\text{cm}^{-1}$ ; 1310, 1308, 1310  $\text{cm}^{-1}$ ; 1269, 1267, 1271  $\text{cm}^{-1}$ ; 1181, 1181, 1184  $\text{cm}^{-1}$ ; and 1086, 1055, 1084  $\text{cm}^{-1}$ . Isoindolinone Yellow 3R and Isoindolinone Orange both have strong absorptions at 853  $\text{cm}^{-1}$ , but Isoindolinone Yellow 2G does not have any features in this region. Complete lists of absorptions for the three are presented in Table 1.

The absorptions observed in the difference spectra for NW78H0461 (Fig. 2c), DC78H0506 (Fig. 5a) and DB82H0870 indicate that Isoindolinone Yellow 2G and Isoindolinone Orange can be ruled out as possibilities, but for the much more limited number of peaks usually seen in topcoat spectra, this is not always true. For some of these topcoat spectra, a very weak resolved shoulder peak near 1672  $\text{cm}^{-1}$  occurs in addition to the 1657  $\text{cm}^{-1}$  peak (Figs. 2b, 7b and 7c), and this is significant since the spectra of Isoindolinone Yellow 2G and Isoindolinone Orange (Figs. 9b and 9c) lack this

feature (as noted, an unresolved shoulder in this region does not rule out Isoindolinone Yellow 3R). In addition, a peak at 855–853  $\text{cm}^{-1}$  is also observed for many of these spectra, and this serves to eliminate Isoindolinone Yellow 2G as a possibility. In other cases, the spectral data by themselves may not permit a clear choice between the three pigments and other factors must be considered.

Isoindolinone Yellow 2G, Isoindolinone Orange, and Quinophthalone Yellow do not appear to have been used in any Reference Collection nonmetallic monocoats, at least in detectable quantities. Although the two isoindolinones cannot be entirely ruled out as possibilities for many spectra where only a few peaks are observed, spectral subtractions involving some yellow nonmetallic monocoats other than those already cited reveal that in every case, Isoindolinone Yellow 3R is present. The observed topcoat spectral frequencies for the “window” peak of 1655 to 1659  $\text{cm}^{-1}$  also seem to indicate the presence of this pigment, which has a frequency of 1657  $\text{cm}^{-1}$ , rather than the other two, which have frequencies of 1661 and 1663  $\text{cm}^{-1}$ . Although the 853  $\text{cm}^{-1}$  absorption (which serves to rule out Isoindolinone Yellow 2G) is not always clearly observed, many spectra do have a shoulder in this region, the observation of which suggests that a weak peak may be present.

The above observations are consistent with information provided by Ciba Specialty Chemicals Corp., the manufacturer of Isoindolinone Yellow 3R, Isoindolinone Yellow 2G, and Isoindolinone Orange, that for OEM automotive paints, Isoindolinone Yellow 3R is by far the most common of the three (personal communications, Ciba Specialty Chemicals Corp., June 1997 and November 1998). Isoindolinone Yellow 2G and Quinophthalone Yellow are more common in refinishes (personal communications, BASF Corp., June 1997, and DuPont Automotive Products, December 1998). The three isoindolinones and Quinophthalone Yellow are used primarily in nonmetallic finishes, although use of Isoindolinone Orange in metallics has also been reported (17).

#### *Isoindoline Yellow*

Like the isoindolinones (I, II, III) and Quinophthalone Yellow (IV), Isoindoline Yellow (V), an orange-yellow heterocyclic pigment, also contains a phthalimide-type moiety (Fig. 1). Isoindoline Yellow otherwise bears few structural similarities to these chlorinated pigments, and its infrared spectrum (Fig. 10d) is not likely to be confused with those of the four (Fig. 9).

The spectrum of an orange nonmetallic enamel monocoat, NW81G0786, which contains Isoindoline Yellow and rutile, is shown in Fig. 10b. The spectrum of a similar gray nonmetallic enamel, NW79B0600 (Fig. 10a), which also contains rutile, was used for spectral subtraction. The difference spectrum (the spectrum of Fig. 10a subtracted from that of Fig. 10b) is depicted in Fig. 10c, and this result can be seen to compare well with the spectrum of Isoindoline Yellow (Fig. 10d).

The frequencies of the Isoindoline Yellow absorptions are listed in Table 1, and of the 59 peaks listed, 57 are observed in the difference spectrum; 50 of these have frequencies within 2  $\text{cm}^{-1}$  of those of the pigment spectrum, and five others differ by 4  $\text{cm}^{-1}$  or less. The listed frequencies include ten very weak overtone/composition bands between 2800  $\text{cm}^{-1}$  and 1800  $\text{cm}^{-1}$ , all of which are observed in the difference spectrum when this spectral region is expanded and examined in detail.

The spectrum of the basecoat of a recent BASF yellow nonmetallic basecoat/clearcoat finish, R97YE402, which also contains Isoindoline Yellow and rutile, is depicted in Fig. 11b. Data for a number of similar finishes were not available in this case, so the

<sup>7</sup> The molecular structure of Quinophthalone Yellow (IV) shown in Fig. 1, drawn with a diketo ring and a phthalimide moiety, is the one normally depicted for this compound (17). Rather than this diketo form, however, Quinophthalone Yellow actually consists primarily of the enol tautomer with the enol proton hydrogen-bonded with the quinoline nitrogen (personal communication, Edward E. Jaffe Associates Inc., December 1998). Note that this enol tautomer extends the conjugation considerably, and this is undoubtedly a major factor in the production of color by this pigment.

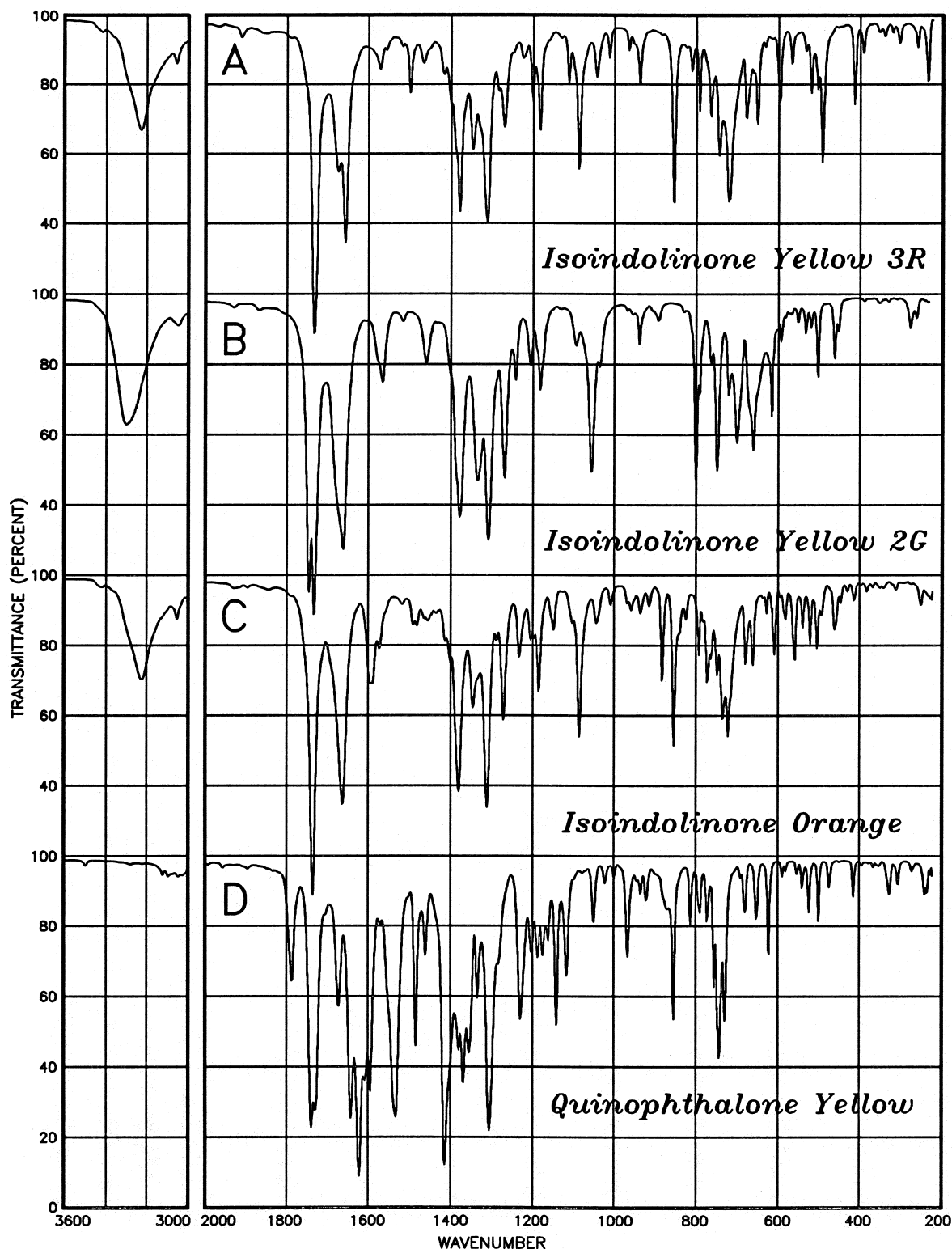


FIG. 9—Spectra of: (a) *Isoindolinone Yellow 3R*; (b) *Isoindolinone Yellow 2G*; (c) *Isoindolinone Orange*; and (d) *Quinophthalone Yellow*.

spectrum of the clearcoat of this same finish (Fig. 11a) was used for spectral subtraction. Both the basecoat and clearcoat of R97YE402 have acrylic melamine enamel binders and the difference spectrum is shown in Fig. 11c. Pronounced residual binder features are not evident in this subtraction result, indicating that the two layers do

in fact have quite similar binder compositions. Since the subtrahend spectrum does not contain absorptions of rutile, there is a strong broad feature of this pigment in the difference spectrum. All of the significant absorptions of Isoindoline Yellow (Fig. 11d) may be seen, however, including those occurring below  $900\text{ cm}^{-1}$  which

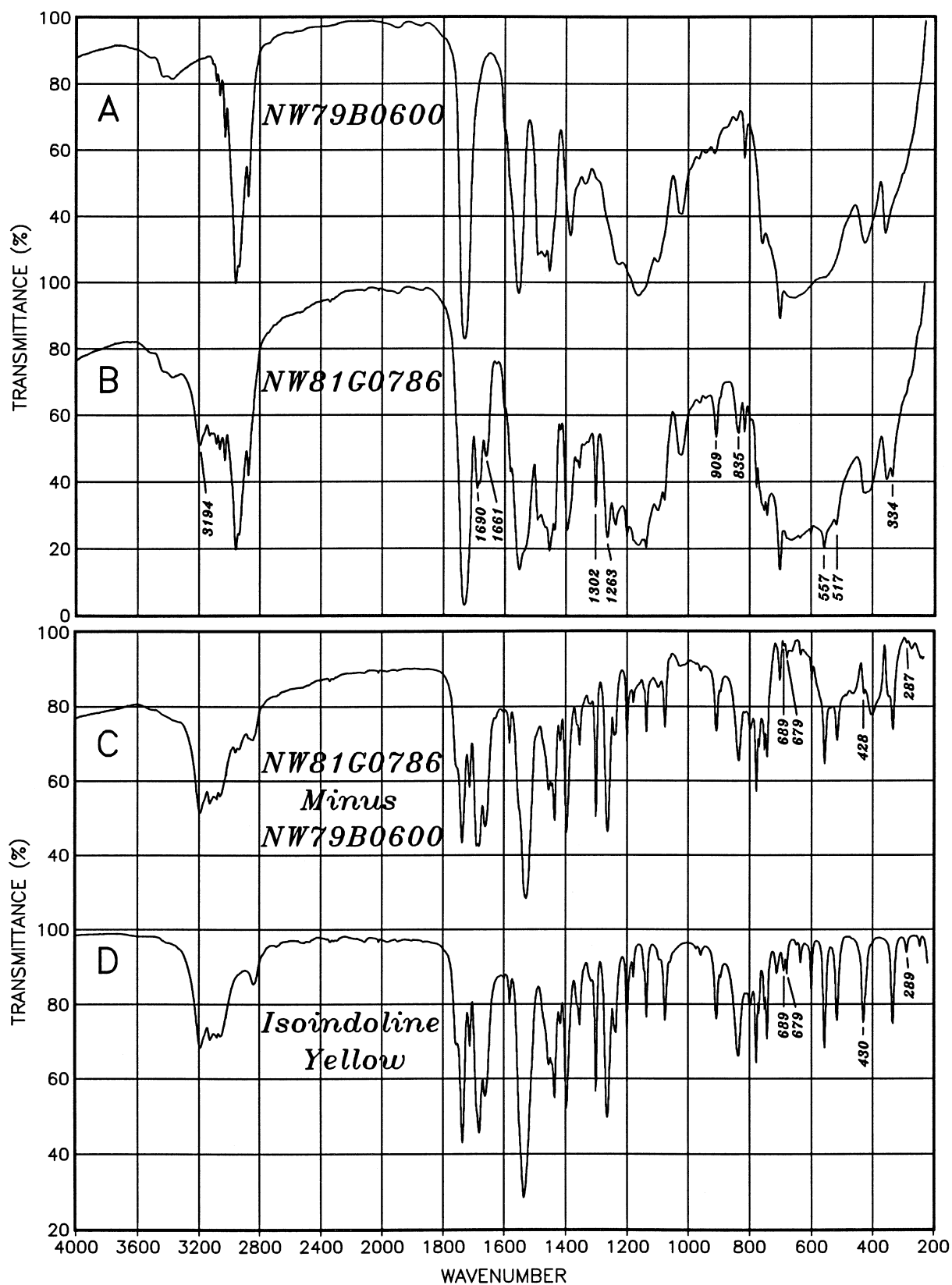


FIG. 10—Spectra of: (a) a gray nonmetallic enamel monocoat, NW79B0600, which contains rutile; (b) an orange nonmetallic enamel monocoat, NW81G0786, which contains Isoindoline Yellow and rutile; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Isoindoline Yellow.

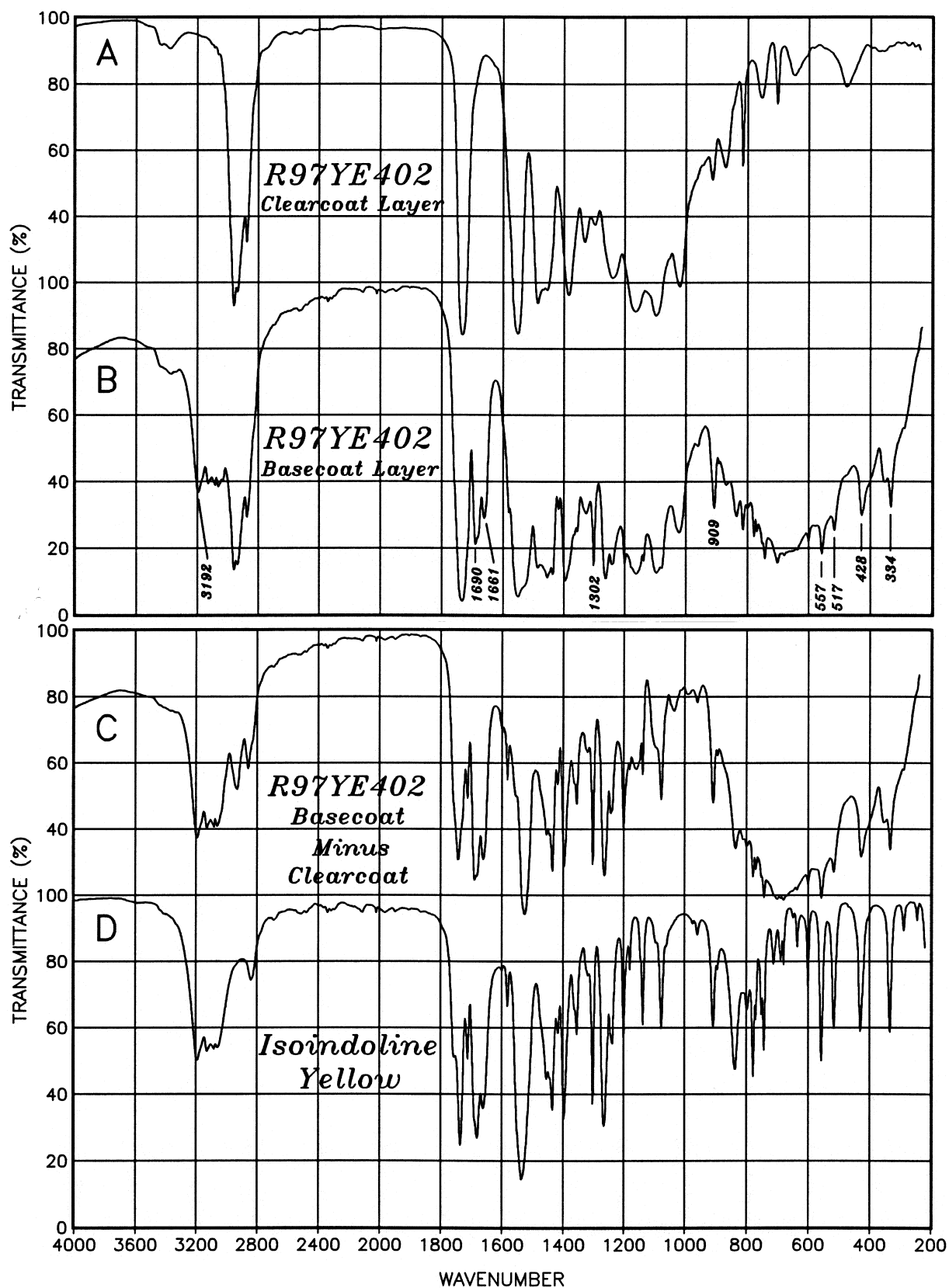


FIG. 11—Spectra of: (a) the clearcoat layer of BASF R97YE402, a yellow nonmetallic basecoat/clearcoat finish system; (b) the basecoat layer of R97YE402 which contains Isoindoline Yellow and rutile; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Isoindoline Yellow.

are superimposed on the broad rutile feature. Of the 59 listed peaks of Isoindoline Yellow (Table 1), 52 are observed in the difference spectrum, and 47 of these have frequencies within  $2\text{ cm}^{-1}$  of those of the pigment spectrum.

**Pigment Absorptions Observed in Topcoat Spectra**—For spectra of acrylic melamine enamels containing heavy pigment loads of Isoindoline Yellow, a large number of pigment absorptions are observed. Relatively strong and conspicuous Isoindoline Yellow peaks can be seen at 3192, 1690, 1661, 1302, and  $909\text{ cm}^{-1}$ , since these occur in binder window regions (see Figs. 10b and 11b). Weaker peaks may be observed at 3127, 1582, 1454, 1437, 1418, 1354, 1263, 1238, 1200, 1138, 1076, 835, 777, 752, 743, 679, 637, 600, 557, 517, 428, and  $334\text{ cm}^{-1}$  (some of these are labeled in Figs. 10b and 11b). The peaks in the low frequency region are likely to be superimposed on a broad rutile feature as observed for NW81G0786 and R97YE402. Some very weak overtone/composition bands between  $2800$  and  $1800\text{ cm}^{-1}$  might also be observed if this region is examined in detail, and the ones most likely to be detected occur at 2340, 2315, 2112, 2022, 1983, and  $1948\text{ cm}^{-1}$  (to be able to observe the first of these, spectra should be free of absorptions of atmospheric carbon dioxide). Other Isoindoline Yellow absorptions which might be observed are listed in Table 1.

**Use in U.S. Automobile OEM Nonmetallic Monocoats (1974–1989)**—Isoindoline Yellow was introduced in 1979 (17) but it was identified in only a single Reference Collection monocoat, NW81G0786, as described above. Almost all of the monocoats in this collection which have colors closest in hue to that of NW81G0786, and also to that of the BASF finish R97YE402, contain significant amounts of Chrome Yellow. This lead chromate pigment was last used in U.S. automobile OEM finishes in the early 1990s, although it was mostly phased-out in the 1980s (5). The reason for the infrequent use of Isoindoline Yellow in monocoats (1974–1989) of the present study undoubtedly reflects the superior performance characteristics of Chrome Yellow. This inorganic pigment could be used to produce hues similar to those obtained with Isoindoline Yellow, but Chrome Yellow is more durable, has a greater opacity, and is considerably less expensive (17). Isoindoline Yellow was thus one of several pigments (1) which replaced Chrome Yellow when use of lead-containing pigments was discontinued by American automobile manufacturers, and this pigment was identified in some other recent yellow nonmetallic basecoat/clearcoat finishes in addition to R97YE402.

#### *Anthrapyrimidine Yellow*

The molecular structure and infrared spectrum of Anthrapyrimidine Yellow (VI), a tan-yellow anthraquinone pigment, are depicted in Figs. 1 and 12a, respectively. Weak absorptions of this pigment are observed in the spectrum of a single Reference Collection monocoat, NX75H0157 (Fig. 6b), which has a yellow nonmetallic finish. Isolation of pigment absorptions using spectral subtractions was hampered in this case, not only because of the weak intensities involved, but also because closely-matched subtrahend spectra were not easily found. The “X” of NX75H0157 indicates that the binder composition for this finish was not specified by the manufacturer, Inmont. The binder was identified as an acrylic melamine enamel from its spectrum, however, and spectra of Inmont and other enamels were examined to see if their absorption patterns might be similar. The ones which visually appeared to have absorptions most like those of NX75H0157 were then tested as subtrahend spectra.

The absorptions of Anthrapyrimidine Yellow above  $2800\text{ cm}^{-1}$  (Fig. 12a) are not observed in the spectrum of NX75H0157 (Fig. 6b) or in the various subtraction results because they are too weak, and because they overlap absorptions of styrene. Subtraction results are therefore presented only below  $2000\text{ cm}^{-1}$  and the spectrum of NX75H0157 in this region is shown in Fig. 13b. There are no other “NX” samples in the Reference Collection and an enamel which closely matched NX75H0157 was not found. The spectrum of a beige nonmetallic enamel, NN78H0408 (Fig. 13a), was chosen for subtraction for illustrative purposes. The difference spectrum (the spectrum of Fig. 13a subtracted from that of Fig. 13b) is shown in Fig. 13c, and this result can be compared to the absorptions of Anthrapyrimidine Yellow (Fig. 13d).

As expected, residual binder features are quite prominent and many of the weaker absorptions of Anthrapyrimidine Yellow are obscured, but its seven strongest absorptions can be seen together with a few weaker ones; these are all labeled in Figs. 13c. The stronger of these peaks are observed in all of the various subtraction results with the same frequencies, so it is clear that they are not artifacts produced from uncompensated binder absorptions; in contrast, most other features vary considerably between results. When the contours of the background on which these peaks appear are considered, the relative peak intensities can also be seen to be consistent with those of Anthrapyrimidine Yellow.

The broad absorption near  $890\text{ cm}^{-1}$  in Figs. 13b and 13c is from a chromate pigment, and a small amount of hydrous ferric oxide is also indicated. The  $276\text{ cm}^{-1}$  absorption of hydrous ferric oxide (Fig. 7d) is manifested as a barely noticeable shoulder to the broad rutile feature of Fig. 13b, but it is resolved and seen clearly in most of the difference spectra. The last portion of the low frequency region is not shown in Fig. 13c, but this  $276\text{ cm}^{-1}$  peak does not, in fact, occur in this particular difference spectrum because the subtrahend spectrum (Fig. 13a) also contains this absorption (which, as noted, is very common in spectra of beige nonmetallic finishes).

For the spectrum of NX75H0157 itself (Fig. 6b), only two absorptions of Anthrapyrimidine Yellow at  $1670$  and  $1273\text{ cm}^{-1}$  are observed. As mentioned earlier, Benzimidazolone Yellow 3G also has an absorption at  $1670\text{ cm}^{-1}$ , but it has additional absorptions at  $3407$ ,  $1701\text{ cm}^{-1}$  and elsewhere which distinguish it from those of Anthrapyrimidine Yellow. The spectrum of an orange nonmetallic enamel, DC89 0312, which has weak absorptions of Benzimidazolone Yellow 3G, is presented in Fig. 6a to illustrate these differences. This orange monocoat has only weak spectral absorptions of rutile, but the spectra of all of the yellow monocoats which contain Benzimidazolone Yellow 3G (1) have strong absorptions of rutile; most of these also have much stronger absorptions of Benzimidazolone Yellow 3G.

In addition to NX75H0157, there are two other monocoats of color H0175 in the Reference Collection—both enamels—but their spectra lack noticeable absorptions of organic pigments. The spectrum of one of these, PC77H0157, is shown in Fig. 6c. Absorptions of rutile and a chromate pigment are present in this spectrum, along with a weak peak at  $272\text{ cm}^{-1}$  of hydrous ferric oxide (Fig. 3d). The spectrum of the third enamel, FC76H0157 (not depicted), also contains absorptions of these three pigments, but it additionally has an absorption of acrylonitrile at  $2240\text{ cm}^{-1}$  (11). The three enamels of this color are therefore readily distinguishable based on both binder and pigment compositions.

Consistent with the observed occurrence of Anthrapyrimidine Yellow in Reference Collection monocoats, this pigment is not a common one for OEM automotive paints and it is used mostly in



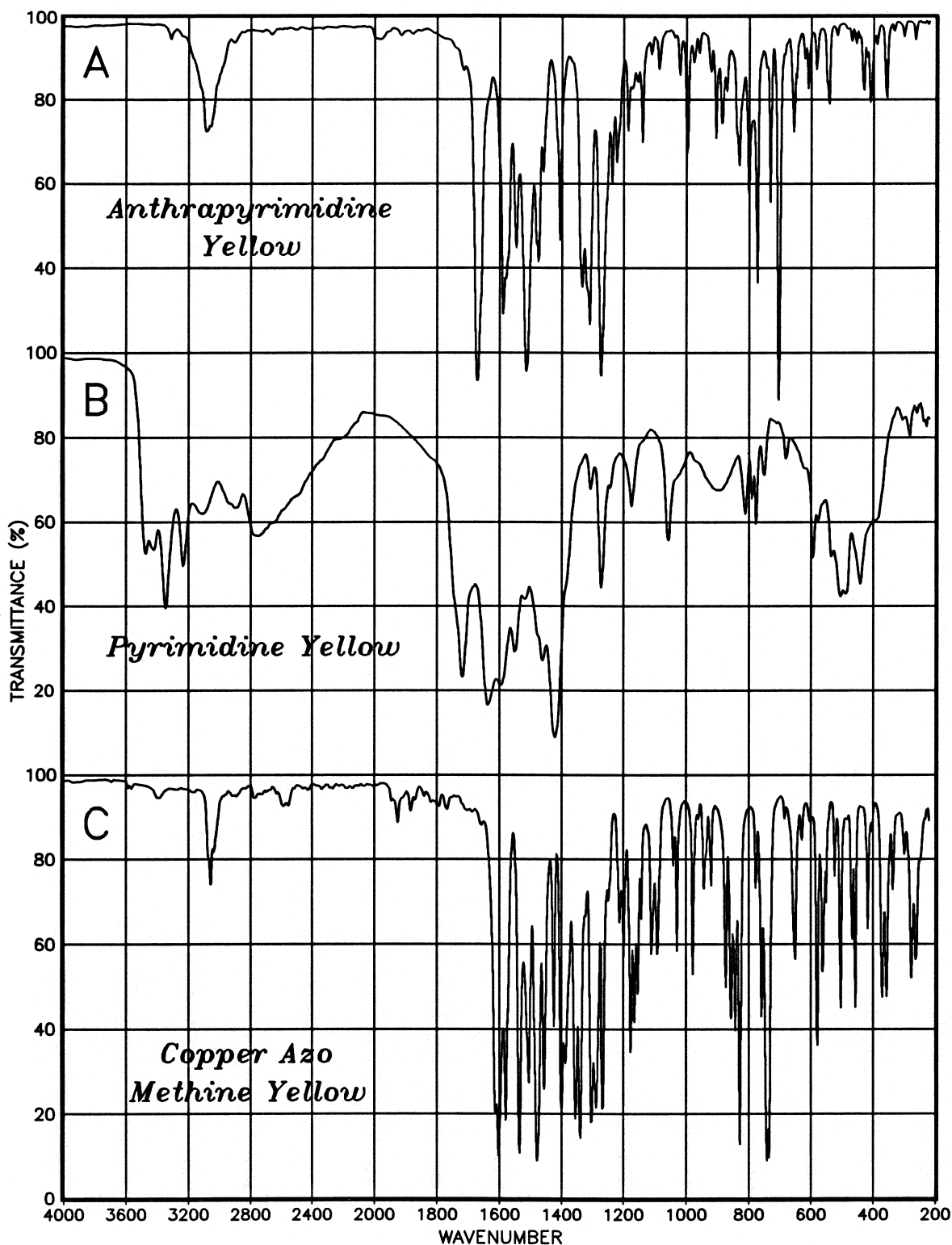


FIG. 12—Spectra of: (a) Anthrapyrimidine Yellow; (b) Pyrimidine Yellow; and (c) Copper Azo Methine Yellow.

refinishes (personal communications, BASF Corp., February 1998 and March 1998, and DuPont Automotive Products, April 1998). Anthrapyrimidine Yellow may be found in both nonmetallic and metallic finishes (personal communication, Edward E. Jaffe Associates Inc., December 1998).

#### *Pyrimidine Yellow and Copper Azo Methine Yellow*

The molecular structures and infrared spectra of two other yellow organic pigments, Pyrimidine Yellow (VII) and Copper Azo Methine Yellow (VIII), are shown in Figs. 1 and 12. The two may

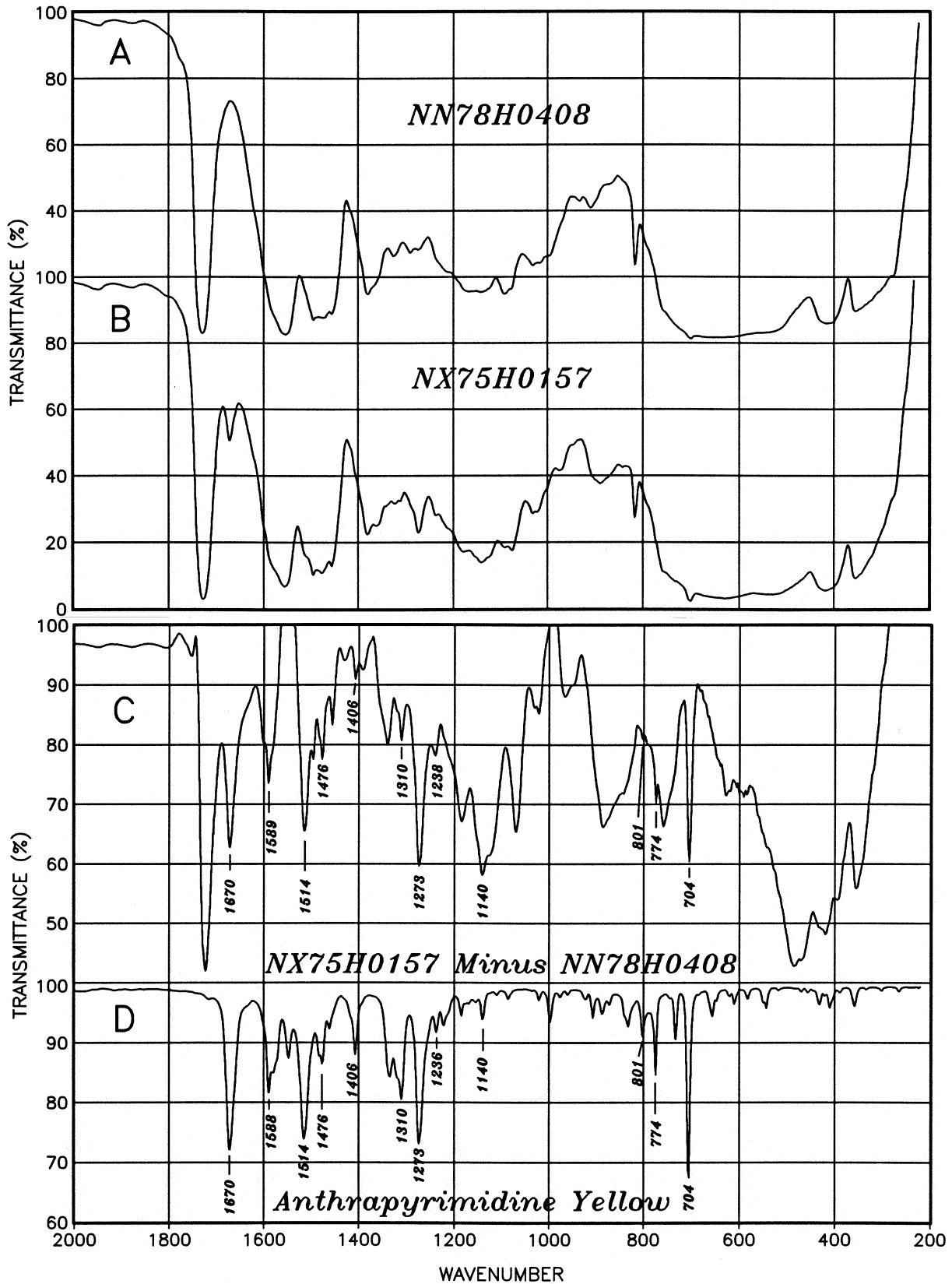


FIG. 13—Spectra of: (a) a yellow (beige) nonmetallic enamel monocoat, NN78H0408, which contains rutile and a small amount of hydrous ferric oxide; (b) a yellow nonmetallic enamel monocoat, NX75H0157, which contains rutile, a chromate pigment, Anthrapyrimidine Yellow, and a small amount of hydrous ferric oxide; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Anthrapyrimidine Yellow.

be used in automotive paints, but they also are not common (personal communications, BASF Corp., March 1998, and DuPont Automotive Products, April 1998) and their absorptions were not identified in spectra of any Reference Collection nonmetallic monocoats. Copper Azo Methine Yellow (which has a green-olive shade), however, is used primarily in metallic finishes (personal communication, Ciba Specialty Chemicals Corp., November 1998) and Pyrimidine Yellow (yellow-brown) is used mostly in industrial finishes (17).

Like Isoindoline Yellow (V), Pyrimidine Yellow (VII) contains a pair of barbituric acid-type rings (Fig. 1), but it has a very distinct spectrum which is easily differentiated from that of Isoindoline Yellow (compare Figs. 11d and 12b). Copper Azo Methine Yellow has a very rich infrared spectrum with many intense absorptions, although none are in the 1700 to 1600  $\text{cm}^{-1}$  window region (Fig. 12c). The frequencies of the Copper Azo Methine Yellow and Pyrimidine Yellow absorptions are listed in Table 1. Pyrimidine Yellow contains nickel and Copper Azo Methine Yellow contains copper (Fig. 1) so, elementally, the two are also distinct from the other yellow organic pigments which have been discussed (as noted earlier and discussed previously (2,3), copper is also present in some blue and green phthalocyanine pigments).

#### *Nickel Azo Yellow, Flavanthrone Yellow, and Isoindoline Orange*

Two other yellow organic pigments, Nickel Azo Yellow (IX) and Flavanthrone Yellow (XI), and an orange pigment related to Isoindoline Yellow, Isoindoline Orange (X), have also been used in automotive paints (8,16). The three are no longer produced, however, and attempts to obtain samples of them were not successful. They are mentioned here since it is possible that they were used in a few Reference Collection finishes, and also because it is useful to know if there might be other pigments which could be mistaken for those discussed. Considering their molecular structures (Fig. 1), it is unlikely that spectra of the three bear gross similarities (such as occurs for the isoindolinones) to those of the other yellow or orange organic pigments which have been discussed to date. Flavanthrone Yellow may have been used in only small amounts, if at all, in Reference Collection finishes. Concerning its use in automotive finishes, *Surface Coatings* (8) states that Flavanthrone Yellow has "best performance at low concentrations," and that it is "susceptible to chemical reduction." Nickel Azo Yellow (IX) has a very greenish yellow shade (8), and like Pyrimidine Yellow (VII), it contains nickel.<sup>8</sup>

#### *Yellow Organic Automotive Paint Pigments—A Summary*

Ten yellow organic pigments are currently marketed in the U.S. for applications which include automotive finishes. Three of the pigments, Benzimidazolone Yellow 3G, Benzimidazolone Yellow

4G, and Benzimidazolone Yellow 6G, were discussed in Paper III of this series (1), and seven (Isoindolinone Yellow 3R, Isoindolinone Yellow 2G, Quinophthalone Yellow, Isoindoline Yellow, Anthrapyrimidine Yellow, Pyrimidine Yellow, and Copper Azo Methine Yellow) in the present work. Absorptions of five of these pigments were identified in spectra of some U.S. automobile OEM yellow and orange nonmetallic monocoats (1974–1989). Isoindolinone Yellow 3R and Benzimidazolone Yellow 3G were the two most commonly used of the five, but the Benzimidazolone Yellow 3G absorptions are usually much stronger than those observed for Isoindolinone Yellow 3R and many peaks of the former are normally evident in topcoat spectra. Benzimidazolone Yellow 4G was identified in a single yellow nonmetallic lacquer, and absorptions of Anthrapyrimidine Yellow were identified in the spectrum of a single yellow nonmetallic enamel; these two pigments are used primarily in refinishes. Absorptions of Isoindolinone Yellow 3R were also identified in spectra of ten orange nonmetallic monocoats, and Benzimidazolone Yellow 3G and Isoindoline Yellow were each identified in a single orange nonmetallic enamel. Isoindoline Yellow is now a more common pigment since it was one of the replacements for Chrome Yellow, which is no longer used in U.S. automobile OEM finishes.

Spectra of the five pigments which were not identified in Reference Collection nonmetallic monocoats indicate that with the possible exception of Isoindolinone Yellow 2G, their absorptions as observed in topcoat spectra should not be difficult to distinguish from those of the others. Isoindolinone Orange may be used in automotive paints and it has some prominent absorptions similar to those of Isoindolinone Yellow 3R and Isoindolinone Yellow 2G. Isoindolinone Orange, however, was not identified in any Reference Collection nonmetallic monocoats and it is not a common automotive pigment.

To facilitate the in situ analysis of the ten yellow organic pigments, their absorptions in the 1700 to 1600  $\text{cm}^{-1}$  window region are listed in Table 2, together with some other absorptions which might be observed in spectra of finishes having acrylic melamine enamel binders. For Benzimidazolone Yellow 4G (which was only identified in an acrylic lacquer) and the five pigments which were not identified in any monocoats, the listed absorptions were determined by adding the spectrum of NW79B0600 (Fig. 10a), a gray nonmetallic enamel which contains rutile, to each pigment spectrum. All of the pigments except Copper Azo Methine Yellow have absorptions between 1700 and 1600  $\text{cm}^{-1}$ , but Copper Azo Methine Yellow has many intense absorptions in other spectral regions. A maximum of ten absorptions is listed in Table 2, but it is probable that for some of the pigments, the pigment loads which are required to produce this many observable absorptions are not normally used.

Five of the pigments contain elements which can be detected using X-ray methods of analysis and one pigment contains fluorine, which can be detected if an instrument equipped with a light element capability is used. These elements are also listed in Table 2.

#### *Acknowledgments*

The author would like to thank: BASF Corp., Bayer Corp., and Ciba Specialty Chemicals Corp. for providing samples and information; Clariant Corp., Consolidated Research Inc., Cookson Pigments Inc., DuPont Automotive Products, Edward E. Jaffe Associates Inc., Engelhard Corp., Ferro Corp., Ford Motor Co., General Motors Corp., Pigments Consultants, Inc., PPG Industries Inc., Sun Chemical Corp., and Wayne Pigment Corp. for providing information; and

<sup>8</sup> In Paper II of this series (5), it was mentioned that 74G0019, an orange nonmetallic monocoat, might contain Nickel Azo Yellow since nickel was detected for this enamel using XRF analysis. In view of the very green shade of this pigment (Nickel Azo Yellow is classified as green in the *Colour Index* [13]) and the yellow-brown shade of Pyrimidine Yellow, the latter nickel-containing pigment might seem to be a more likely candidate. Colors notwithstanding, if a yellow organic pigment which contains nickel was in fact used in 74G0019, it was probably Nickel Azo Yellow, which was much more common at that time (personal communications, Edward E. Jaffe Associates Inc., December 1998 and DuPont Automotive Products, December 1998). Nickel Titanate is also a possibility, but this pigment can be ruled out since 74G0019 does not contain antimony. There are red organic pigments which contain nickel, and some of these may also be used in automotive finishes.

TABLE 2 - Yellow organic pigments which may be used in automotive paints.

Pigment	Shade	Main Infrared Absorptions in Spectra of Enamels <sup>a</sup>	Elements <sup>b</sup>	Comments <sup>c</sup>
Benzimidazolone Yellow 3G (PY 154)	Deep Yellow	3407, 1699, 1670, 1622, 1287, 1263, 1001, 951, 858, 735	Fluorine	Absorptions of this pigment were identified in spectra of 14 yellow monocoats. This pigment was also identified in a single orange enamel, DC89 0312.
Benzimidazolone Yellow 4G (PY 151)	Slightly Greenish Yellow	3187, 1705 sh, 1657, 1618 sh, 1312, 1258, 833, 631, 588, 509	None	Identified in a single yellow acrylic lacquer, DA78H0464. Used mostly for automobile refinishes.
Benzimidazolone Yellow 6G (PY 175)	Bright Yellow	3329, 1697 sh, 1672, 1620 sh, 1362, 1316, 964, 947, 901, 866	None	Not identified in any monocoats. Used mostly for industrial paints.
Isoindolinone Yellow 3R (PY 110)	Orange	3233, 1674, 1657, 1310, 1181, 1086, 937, 853, 791, 650 (See Fig. 2b)	Chlorine	Absorptions of this pigment were identified in spectra of 39 yellow monocoats, and 10 orange monocoats.
Isoindolinone Yellow 2G (PY 109)	Deep Yellow	1661, 1335, 1308, 1267, 1240, 1055, 937, 799, 748, 461	Chlorine	Not identified in any monocoats. More common in automobile refinishes.
Quinophthalone Yellow (PY138)	Slightly Greenish Yellow	1784, 1672, 1642, 1620 sh, 1414, 1333, 1306, 1140, 964, 853	Chlorine	Not identified in any monocoats. More common in automobile refinishes.
Isoindoline Yellow (PY139)	Orange Yellow	3192, 1690, 1661, 1302, 1263, 909, 835, 557, 517, 334 (See Figs. 10b, 11b)	None	Identified in a single orange enamel, NW81G0786. More common now since it was one of the replacements for Chrome Yellow.
Anthrapyrimidine Yellow (PY 108)	Golden Tan Yellow	1672, 1512, 1335, 1310, 1271, 1236, 907, 801, 774, 731	None	Absorptions of this pigment were identified in the spectrum of a single yellow enamel, NX75H0157. Used mostly for automobile refinishes.
Pyrimidine Yellow (PY 150)	Yellow Brown	3345, 3235, 1638, 1304, 1269, 594, 536	Nickel	Not identified in any monocoats. Used mostly for industrial paints.
Copper Azo Methine Yellow (PY 129)	Dull Green Olive	1601 sh, 1354, 1339, 1265, 978, 874, 856, 843, 828, 741/735	Copper	Not identified in any monocoats. Used mostly in metallic finishes.

<sup>a</sup>These include all of the absorptions between 1700 and 1600  $\text{cm}^{-1}$  and some others which might be observed in spectra of finishes having acrylic melamine enamel binders, assuming that a relatively high pigment load is used. Given in wavenumbers. An "sh" indicates that the absorption occurs as a shoulder on the side of the strong binder carbonyl or melamine absorption; depending on the pigment load which was used, this peak may or may not be resolved.

<sup>b</sup>These are elements which can be detected by X-ray methods of analysis. Fluorine is included, but detection of this element requires a special window for the detector.

<sup>c</sup>The occurrence of the pigments in nonmetallic monocoats of the Reference Collection of Automotive Paints is indicated.

Ms. Stefani Banerian, Ms. Chesterene Cwiklik (Cwiklik and Associates), Dr. Bill Gresham (WSCL), Ms. Helen Griffin (WSCL), Dr. Ed Jaffe (Edward E. Jaffe Associates Inc.), Mr. Jim King (DuPont Automotive Products), and Dr. Jennifer Teske (WSCL) for taking the time to review this manuscript, or portions thereof.

## References

1. Suzuki EM, Marshall WP. Infrared spectra of U.S. automobile original topcoats (1974–1989): III. In situ identification of some organic pigments used in yellow, orange, red, and brown nonmetallic and brown metallic finishes-benzimidazolones. *J Forensic Sci* 1997;42:619–48.
2. Suzuki EM, Marshall WP. Infrared spectra of U.S. automobile original topcoats (1974–1989): IV. Identification of some organic pigments used in red and brown nonmetallic and metallic monocoats-quinacridones. *J Forensic Sci* 1998;43:514–42.
3. Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): V. Identification of organic pigments used in red nonmetallic and brown nonmetallic and metallic monocoats-DPP Red BO and Thioindigo Bordeaux. *J Forensic Sci* 1999;44:297–313.
4. Lambourne R. *Paint and surface coatings: theory and practice*. New York: Halsted Press 1987.
5. Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): II. Identification of some topcoat inorganic pigments using an extended range (4000–220  $\text{cm}^{-1}$ ) Fourier transform spectrometer. *J Forensic Sci* 1996;41:393–406.
6. Braun JH. *Federation series on coatings technology: introduction to pigments*. Philadelphia: Federation of Societies for Coatings Technology 1993.
7. Suzuki EM, Gresham WR. *Forensic science applications of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS): I. Principles, sampling methods, and advantages*. *J Forensic Sci* 1986;31:931–52.
8. The Oil and Colour Chemists' Association, Australia. *Surface coatings, Vol. 1—Raw materials and their usage*. 2nd ed. Randwick, Australia: Tafe Educational Books 1983.
9. Nassau K. *The physics and chemistry of color: The fifteen causes of color*. NY: John Wiley & Sons 1983.
10. Judd DB, Wyszecki G. *Color in business, science, and industry*. 3rd ed. NY: John Wiley & Sons 1975.
11. Suzuki EM. Infrared spectra of U.S. automobile original topcoats (1974–1989): I. Differentiation and identification based on acrylonitrile and ferrocyanide C≡N stretching absorptions. *J Forensic Sci* 1996;41:376–92.
12. Collaborative Testing Services, Inc. *Reference collection of automotive paints technical data*. Herndon, VA: Collaborative Testing Services, Sept. 1989.
13. The Society of Dyers and Colourists, The American Association of Textile Chemists and Colourists. *Colour index, 3rd ed., Vols. 1–7*. Bradford, Yorkshire 1982.
14. Rodgers PG, Cameron R, Cartwright NS, Clark WH, Deak JS, Norman EWW. The Classification of automotive paint by diamond window infrared spectrophotometry. Part I: Binders and pigments. *Can Soc Forensic Sci J* 1976;9:1–14.
15. Ryland SG. Infrared microspectroscopy of forensic paint evidence. In: Humecki H, editor. *Practical guide to infrared microspectroscopy*. NY: Marcel Dekker, Inc. 1995;163–243.
16. King JG. Impact of regulations on automotive colors: cost, performance, and styling. Program of the Color Pigments Manufacturing Association/Inter-Society Color Council Symposium on Color Pigments, Regulations, and the Environment; 1993 April 20–21; Newport, (RI). Alexandria (VA): Color Pigments Manufacturing Association 1993.
17. Lewis PA. *Federation series on coatings technology: organic pigments, 2nd ed.* Philadelphia: Federation of Societies for Coatings Technology 1995.

Additional information (reprints are not available from the author):

Ed Suzuki  
 Washington State Crime Laboratory  
 Public Safety Building, 2nd Floor  
 Seattle, WA 98104  
 E-Mail address: FTIRUser@aol.com