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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*

ABSTRACT: As part of a study of the chemical compositions of U.S. automobile original topcoats (1974 to 1989) using infrared spectroscopy, a number of organic pigments used in these finishes have been identified. The topcoats examined were single-layer finishes (monocoats) from the Reference Collection of Automotive Paints, and pigments from the benzimidazolone and quinacridone families were previously identified. The *in situ* identification of two other organic pigments used in these finishes, DPP Red BO and Thioindigo Bordeaux, is described here. DPP Red BO is a relatively new pigment which was first marketed in 1987, and it was only identified in two red nonmetallic enamels produced in 1989, the last year covered in this study. It is now quite common in automotive paints and its presence in an unknown *original finish* indicates that a fairly recent vehicle (most likely from the 1990s) was the source. In contrast, Thioindigo Bordeaux, which was identified in a few red and brown nonmetallic and brown metallic enamels, was more common in the 1950s and 1960s but was largely replaced by Quinacridone Violet in the 1970s. It is no longer used much in automotive paint. Spectra of several DPP automotive paint pigments introduced after 1989 are also presented and discussed.

KEYWORDS: forensic science, criminalistics, paint analysis, automotive paint, infrared spectroscopy, pigment identification, organic pigments, DPP Red BO, DPP pigments, Thioindigo Bordeaux

In a series of classic seminal papers (1–3), Rodgers et al. described some applications of infrared spectroscopy for the forensic analysis of automotive paint. These authors demonstrated the value of identifying individual paint components, and to facilitate this process, they presented spectral data for a number of common automotive paint binders and pigments. The data for the pigments were intended primarily to aid in the interpretation of automobile undercoat spectra, and all were collected for inorganic compounds. During a recent survey (4,5) of the infrared spectra of U.S. automobile topcoats (1974 to 1989), however, absorptions indicative of

organic pigments were frequently observed. These topcoats are original (OEM) single-layer finishes (monocoats) from the Reference Collection of Automotive Paints, and most of the organic pigment absorptions occur in spectra of red nonmetallic monocoats, and to a lesser extent in spectra of yellow, orange and brown nonmetallic, and red and brown metallic ones. To more fully characterize these finishes and provide additional groundwork for the creation of a database of automotive paint compositions, it was desirable to identify the organic pigments responsible, and such analyses were the subject of the two prior papers in this study.

Part III of this series (6) demonstrated the feasibility of identifying organic pigments *in situ* using infrared spectroscopy and described the analysis of four benzimidazolone pigments, Benzimidazolone Orange, Benzimidazolone Yellow 3G, Benzimidazolone Yellow 4G, and Benzimidazolone Brown, which were identified in some yellow, orange and red nonmetallic and brown metallic monocoats. Part IV (7) presented the analysis of four quinacridone pigments, Quinacridone Red Y, Quinacridone Violet, Quinacridone Magenta, and Quinacridone Magenta B, which were used in some red and brown nonmetallic and metallic monocoats.

This paper describes the analysis of two more organic pigments that were identified in red nonmetallic, and brown nonmetallic and metallic monocoats: DPP Red BO and Thioindigo Bordeaux. In contrast to some of the benzimidazolones and quinacridones, which were very common in U.S. automobile original finishes (1974 to 1989) of certain colors, DPP Red BO and Thioindigo Bordeaux were only used in a few monocoats of this period. Confirmation of the presence of one of the two pigments in an unknown *original* monocoat thus has considerable potential for aiding in the identification of vehicles from this time span. Several other automotive paint pigments from the DPP family were introduced after the period covered by the Reference Collection of Automotive Paints, and spectra of some of these are also presented and discussed.

Experimental

Instrumentation and Analysis Procedures

Infrared spectra were acquired at a resolution of 4 cm^{-1} using a Digilab FTS-7 Fourier transform infrared (FT-IR) spectrometer. This extended range (4000 to 220 cm^{-1}) instrument was equipped with cesium iodide (CsI) optics and a deuterated triglycine sulfate (DTGS) detector. Topcoats were analyzed as thin slices placed over a 1 mm circular aperture in a metal disk that was mounted in a Digilab ×5 beam condenser. The slices were pressed with a roller device to produce a more uniform thickness, and a total of

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1000 scans were collected and averaged. Pigments were diluted with excess CsI and analyzed using diffuse reflectance (DRIFTS). A Digilab DRIFTS accessory was used and a total of 200 scans were collected and averaged. More information about the spectrometer, sampling accessories, acquisition parameters used for data collection, and sample preparation methods is given elsewhere (5).

Topcoats and Pigments

All of the monocoats discussed in this work are from the Reference Collection of Automotive Paints (Collaborative Testing Services, Inc., Herndon, VA). These finishes will be referred to by their nine character Reference Collection identification codes, which have been described previously (4).

The following pigments were used (pigment *Colour Index* (8) designations are given in parentheses since the cited generic names are not universally employed, and trade names are given in italics): DPP Red BO (Pigment Red 254), Ciba-Geigy *Irgazin® DPP Red BO;* DPP Scarlet EK (Pigment Red 255), Ciba-Geigy *Irgazin DPP Scarlet* EK; DPP Rubine TR (Pigment Red 264), Ciba-Geigy *Irgazin DPP Rubine TR;* DPP Orange RA (Pigment Orange 73), Ciba-Geigy *Irgazin DPP Orange RA;* DPP/quinacridone solid solution, Ciba-Geigy *Monastral® Scarlet RT-390-D;* and Thioindigo Bordeaux (Pigment Red 88), BASF *Paliogen® Red Violet L 5080.* Spectra of Quinacridone Violet and other quinacridones and ferric oxide and other inorganic pigments are also discussed in this work, and these pigments have been described previously (5,7).

In Situ *Pigment Identification Procedure*

The procedure used to identify organic pigments *in situ* has been described in detail previously (6), so only a brief summary is provided here. Spectral subtractions were performed 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 binder composition, but lacking this pigment, was used to produce a subtrahend spectrum. For a given pigment, subtractions involving a number of different topcoats, each with its own set of subtrahend spectra, were usually tested. The difference spectra depicted thus represent the best possible results for illustrative purposes, and they are *not* typical. This analysis works best for topcoats having a ''known'' binder formulation where many other similar topcoats are also available for testing, and it is not usually applicable to most case samples, for which the binder composition itself is usually in question. Once pigments have been identified by this means, however, their absorptions can usually be recognized in other topcoat spectra and, frequently, this is true even if more than one pigment is present.

Spectral Calculations

Spectral calculations were performed using Spectra Calc™ software. For transmittance spectra, all calculations were performed with data in the absorbance format, then reconverted to transmittance. Topcoat spectral absorption intensities were adjusted so that the strongest peak had a transmittance value of between 2 and 5%, and baselines were set to have their highest values near 100%, but they were not flattened. For spectral subtraction, a subtrahend factor was chosen that produced minimal residual binder features and the baseline of the difference spectrum was adjusted but not flattened. 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 (9).

Elemental Analyses

Elemental analyses were conducted using X-ray fluorescence (XRF) spectrometry with a Kevex 0700 XRF spectrometer which has been described previously (5). 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. Thioindigo Bordeaux powder was smeared onto a similar strip of tape for analysis. X-rays from titanium, tin and gadolinium secondary targets were used for excitation, produced with X-ray tube voltages of 25, 45 and 60 kV, respectively, and currents of 2.0 mA. The instrument chamber was evacuated and data were collected for 50 000 s (total live time) for all of the topcoats, and 10 000 s for Thioindigo Bordeaux.

Results and Discussion

The description of topcoat color cited in this work is based on the classification system used in the Reference Collection of Automotive Paints (4,10). More specific designations of shades within these general color categories are given in italics to indicate that they are not Reference Collection colors.

Although both acrylic melamine enamel and acrylic lacquer binders were commonly used for U.S. automobile original monocoats (1974 to 1989), DPP Red BO and Thioindigo Bordeaux were only identified in finishes having acrylic melamine enamel binders. The number of paints involved is quite small, however, and there are no inherent reasons why the two pigments cannot be used in lacquers.[2] Because it is possible that they were, in fact, used in such finishes which are missing from the Reference Collection, in lacquers produced before 1974 (except for DPP Red BO) or after 1989, or in refinishes having acrylic lacquer binders, the pigment absorptions which are likely to be observed in the spectra of both enamels and lacquers are discussed.

Organic pigment absorptions are generally quite sharp and they are narrower than most binder and inorganic pigment absorptions. The frequency values of organic pigment peaks observed in the spectra of a large number of different topcoats are also quite reproducible, and they are essentially identical to those of the pigment itself (6,7). In most cases, pigment peak frequency values obtained from topcoat spectra should thus be within 2 or 3 cm^{-1} of those cited here.

DPP Red BO

The structure of DPP Red BO (I), a bright yellowish red pigment of the 1,4-diketopyrrolo (3,4-c) pyrrole (DPP) family, is shown in Fig. 1. The spectrum of a red nonmetallic acrylic melamine enamel, DC89 1629, which contains this pigment is depicted in Fig. 2*b.* As a comparison, the spectrum of a blue metallic enamel (DC89 1359) which has a similar binder composition, but which lacks observable pigment absorptions, is shown in Fig. 2*a.* Subtraction results for DC89 1629 minus DC89 1359 (the spectrum of Fig. 2*a* subtracted from that of Fig. 2*b*) are depicted in Fig. 2*c,* and the spectrum of DPP Red BO is shown below (Fig. 2*d*).

Although some weak residual binder features are also observed, all of the significant absorptions of DPP Red BO may be seen

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[2] Personal communications, Hoechst Celanese Corp., June 1997, and DuPont Automotive Products, Oct. 1997.

I

DPP Red BO

II

DPP Scarlet EK

III

DPP Orange RA

IV

DPP Rubine TR

V

Thioindigo Bordeaux

VI

Quinacridone Red Y and
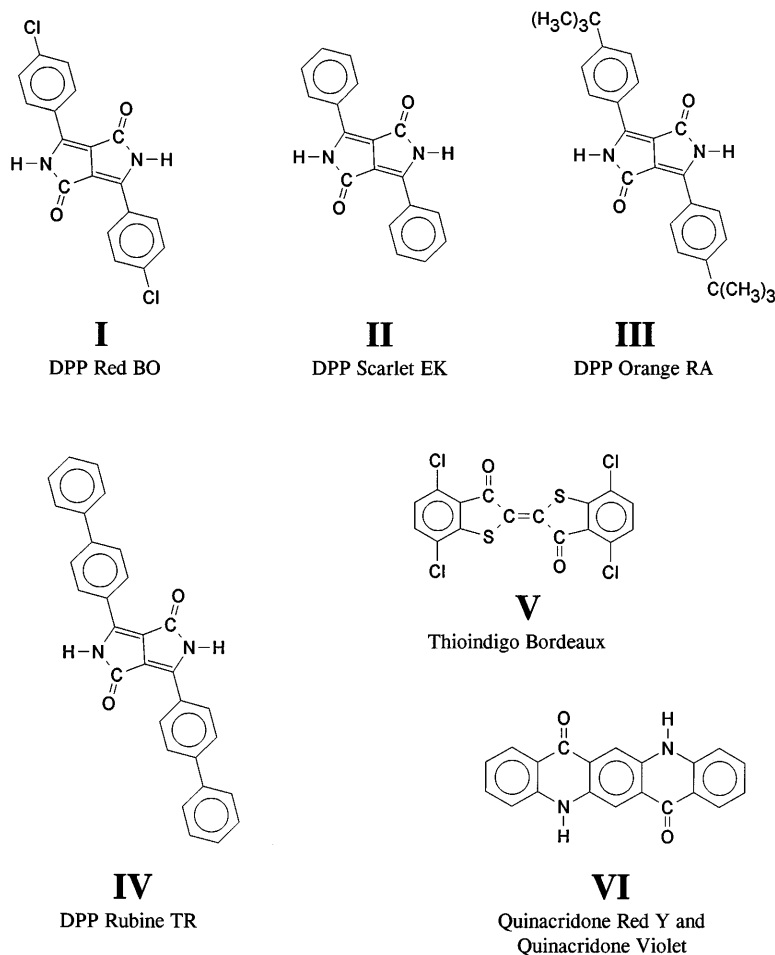Quinacridone Violet

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

in this difference spectrum and the relative peak intensities are consistent. The frequencies of the DPP Red BO absorptions (Fig. 2*d*) are presented in Table 1, and of the 57 peaks listed, 45 are observed in the difference spectrum, including nine of the eleven very weak overtone/combination features occurring between 2600 and 1650 cm^{-1}. With the exception of three absorptions (which differ by 3 or 4 cm^{-1}), the 45 all have frequency values within 2 cm^{-1} of those of the pigment itself. The 12 pigment peaks that are not clearly observed in the difference spectrum are mostly quite weak, and they are either obscured by residual binder features or there are hints of their presence, such as a very weak unresolved shoulder.

The spectrum of DC89 1629 (Fig. 2*b*) contains a weak peak at 3270 cm^{-1} (and a barely visible second peak at 3238 cm^{-1}) but this is not the very weak peak of DPP Red BO (Fig. 2*d*), which occurs at 3298 cm^{-1}. The possible presence of a second organic pigment is thus indicated, although most of the other non-binder peaks which are readily observed in Fig. 2*b* can be attributed to DPP Red BO. The frequency and shape of the 3270 cm^{-1} absorption and the second very weak peak at 3238 cm^{-1} suggest a possible quinacridone pigment (7), excluding Quinacridone Red Y. A very weak peak at 1339 cm^{-1} further points to a quinacridone, and very weak peaks at 791 cm^{-1} and 540/530 cm^{-1} indicate that Quinacridone Magenta B is a likely possibility (7). An examination of the difference spectrum (Fig. 2*c*) reveals additional weak or very weak peaks at 1470, 1254, 905, 897, 806, and 685 cm^{-1},

together with weak shoulder peaks at 1626 and 1586 cm^{-1}, and these do not appear to be residual binder features. These absorptions (including their relative intensities) indicate that the second pigment is, in fact, Quinacridone Magenta B (7).

Although most of the absorptions of this second pigment are only apparent in the subtraction result, one can still obtain some information about pigment identities based on a very limited number of peaks observed in topcoat spectra, as illustrated by this example. Absorptions indicative of a particular pigment or type of pigment can prompt one, for instance, to seek additional characteristic peaks which are not readily observed by expanding certain spectral regions. Such scrutiny, however, is likely to yield the most useful information if one has some idea of what peaks are being sought, and some familiarity with the absorption patterns of common automotive organic pigments is desirable to provide a basis for such a search (there are actually relatively few *common* organic pigments which are used in OEM automotive finishes, so this facility is not really as difficult to achieve as it might seem).

Pigment Absorptions Observed in Topcoat Spectra—The absorptions of DPP Red BO which may be observed in spectra of topcoats having acrylic melamine enamel binders include the strong 1643/1605 cm^{-1} doublet, a high frequency feature at 3140 cm^{-1}, and additional weak absorptions at 845, 714, 623, 517, 480, 432, and 322 cm^{-1} (Fig. 2*b*). Weak peaks at 1327, 1192, and 1142 cm^{-1} might also be seen (Fig. 2*b*), depending on the particular
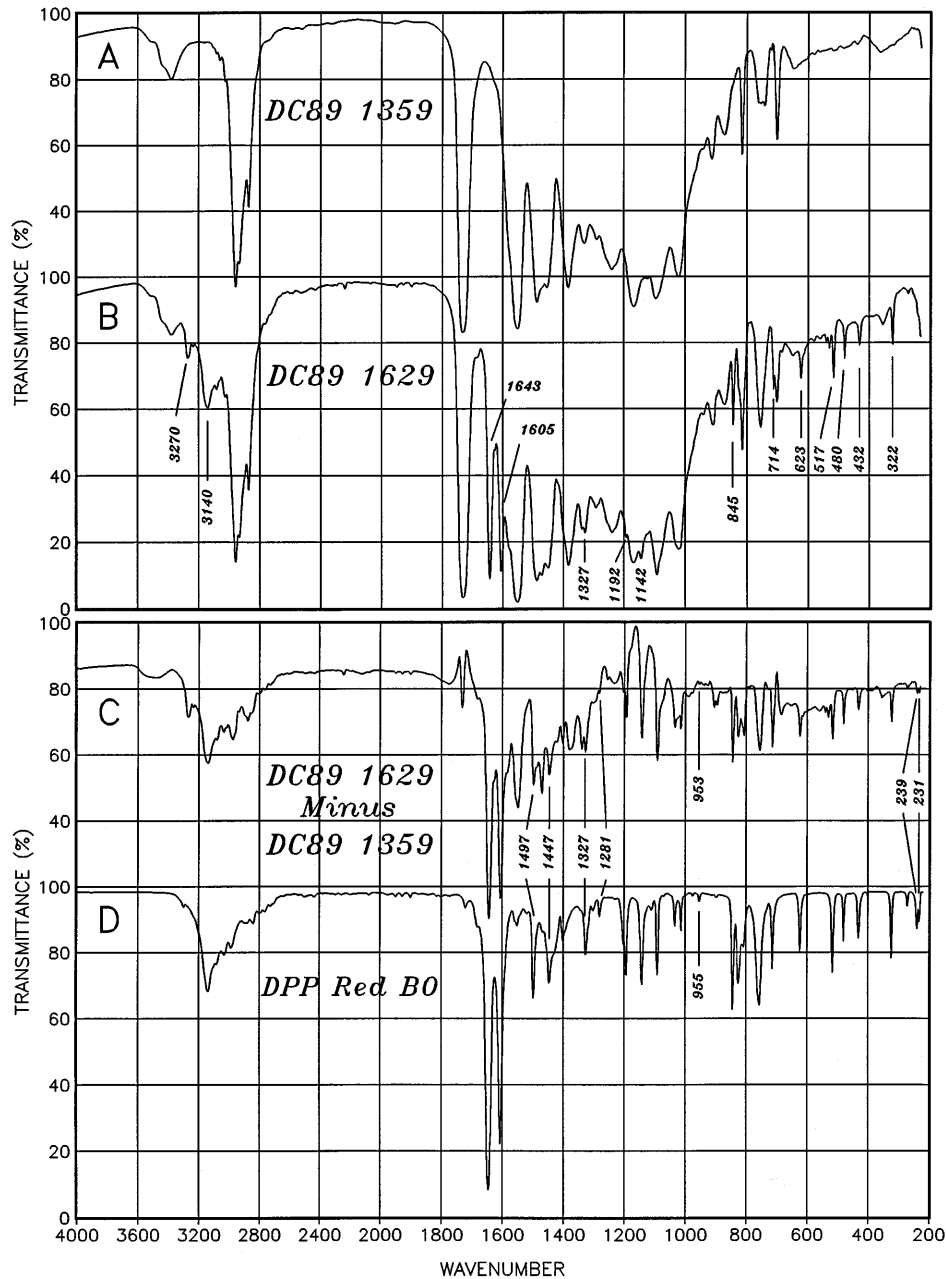
FIG. 2—*Spectra of: (a) a blue metallic enamel, DC89 1359; (b) a red nonmetallic enamel, DC89 1629, which contains DPP Red BO and a small amount of Quinacridone Magenta B; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) DPP Red BO.*

binder absorptions which occur in this region (differences in the C—O stretching vibrations of various acrylic monomer components occur between 1250 and 1050 cm^{-1} (1,11)). Other DPP Red BO peaks which might be observed, including very weak ones revealed by expanding select portions of spectra, are listed in Table 1. For topcoats that contain heavy pigment loads of DPP Red BO, these may include overtone/combination features such as the three observed at 1948, 1927 and 1900 cm^{-1} in Fig. 2b (compare to Fig. 2d; the very weak peak at 2239 cm^{-1} in Fig. 2b is from a small amount of acrylonitrile that was used in certain types of DuPont nonmetallic enamels (4)).

To determine which pigment absorptions are likely to be observed for lacquers, spectra of an acrylic lacquer binder and DPP Red BO were added. As evidenced by the notable lack of both

pigment absorption peak shifts and peak shape distortions observed in numerous topcoat spectra (6,7), the interaction between pigments and binders is clearly minimal and such spectral additions are expected to provide accurate depictions of the data expected for such finishes. The spectrum of DB76L0195 (Fig. 3a), a blue metallic monocoat lacking observable pigment peaks, was used to represent the absorptions of a typical acrylic lacquer binder. Acrylic lacquers may have a few very weak sharp absorptions below 1000 cm^{-1} which could be confused with organic pigment peaks, and these are labeled with their frequencies in Fig. 3a. These very weak absorptions may differ somewhat between lacquers, and Fig. 3d depicts a portion of the spectrum of another lacquer, DA78K0444, which has more of these features (which are clearly not due to color-imparting pigments since they are

TABLE 1 - *Infrared absorption frequencies of DPP automotive paint pigments and Thioindigo Bordeaux.*

Pigment	Manufacturer/ Trade Name	Color	Spectrum	Infrared Absorption Frequencies[a]	Comments
DPP Red BO (Pigment Red 254)	Ciba-Geigy Iragazin DPP Red BO	Bright Yellow Red	Figs. 2d, 5a	3298vw, 3138m, 3084m, 3032m, 2988m, 2897w, 2882m, 2839w, 2801w, 2762w, 2726w, 2496vw, 2434vw, 2294vw, 2255vw, 2195vw, 2072vw, 1948vw, 1927vw, 1900vw, 1721vw, 1680vw, 1645vs, 1607vs, 1559w, 1551w, 1497m, 1468vw, 1447m, 1402w, 1327w, 1302vw, 1281w, 1202sh, 1192m, 1142m, 1111vw, 1092m, 1034w, 1013w, 976vw, 955w, 897vw, 845m, 826m, 808sh, 756m, 714m, 623w, 517m, 480w, 432w, 401vw, 324w, 270w, 239w, 231w	First DPP pigment to be marketed; introduced in 1987. Identified in two red nonmetallic enamels, DC89 1629 and NC89 1629. Used mostly in nonmetallic finishes at present.
DPP/Quin- acridone Solid Solution (No *Colour Index* Number)	Ciba-Geigy Monastral Scarlet RT-390-D	Dark Red Maroon	Fig. 5b	3694w, 3651w, 3621w, 3270m, 3138m, 3075sh, 3054sh, 2984m, 2872w, 2839w, 2072vw, 1888vw, 1649vs, 1611s, 1555m, 1497m, 1470m, 1454m, 1429sh, 1402w, 1341m, 1290w, 1256w, 1206w, 1177vw, 1148m, 1117vw, 1094m, 1071vw, 1036w, 1013w, 920w, 905w, 895w, 874vw, 831m, 814m, 791vw, 770w, 743m, 716m, 679m, 662w, 631w, 625sh, 613vw, 540w, 532w, 517m, 475w, 451w, 434w, 353vw, 334vw, 324w, 270w	Not identified in any Reference Collection of Automotive Paints monocoats. Introduced in 1995. Used mostly in metallic finishes.
DPP Scarlet EK (Pigment Red 255)	Ciba-Geigy Iragazin DPP Scarlet EK	Red Orange	Fig. 5c	3293sh, 3138m, 3050m, 2986m, 2870w, 2843w, 2807sh, 2782w, 2737w, 2504vw, 2481vw, 2457vw, 2294vw, 2253vw, 2072vw, 1958vw, 1946vw, 1894vw, 1838vw, 1802vw, 1728sh, 1709sh, 1659vs, 1616s, 1568m, 1501m, 1456s, 1425m, 1352vw, 1344vw, 1329w, 1298vw, 1263vw, 1204m, 1146m, 1098w, 1067vw, 1044w, 1024vw, 999w, 916w, 833vw, 814s, 766m, 748m, 675m, 664m, 633m, 615vw, 455m, 436m, 334w, 270w	Not identified in any Reference Collection of Automotive Paints monocoats. Introduced in 1993. Used mostly in nonmetallic finishes.
DPP Rubine TR (Pigment Red 264)	Ciba-Geigy Iragazin DPP Rubine TR	Dark Red	Fig. 5d	3297vw, 3125m, 3096sh, 3065m, 3054m, 3032m, 2983m, 2880m, 2857m, 2839m, 2807sh, 2766w, 2739sh, 2484vw, 2450vw, 2299vw, 2261vw, 2066vw, 1954vw, 1929vw, 1912vw, 1888vw, 1811vw, 1761vw, 1734vw, 1696sh, 1647vs, 1611vs, 1578sh, 1549w, 1520w, 1485m, 1452s, 1441s, 1404w, 1333m, 1321m, 1314sh, 1287w, 1204m, 1182vw, 1144m, 1123sh, 1074w, 1045w, 1034w, 1005w, 918w, 847m, 839m, 824m, 779sh, 768m, 737s, 696m, 642m, 633m, 544w, 509w, 502sh, 482sh, 473w, 457w, 448w. 407vw. 399vw, 372vw, 311w, 262w	Not identified in any Reference Collection of Automotive Paints monocoats. Introduced in 1995. Used mostly in metallic finishes.
DPP Orange RA (Pigment Orange 73)	Ciba-Geigy Iragazin DPP Orange RA	Bright Orange	Fig. 5e	3300vw, 3133m, 3079m, 3036m, 2959s, 2901m, 2864m, 2809sh, 2772sh, 2739sh, 2496vw, 2446vw, 2299vw, 2263vw, 2199vw, 2160vw, 2076vw, 1985vw, 1948vw, 1931vw, 1906vw, 1724vw, 1686sh, 1642vs, 1611vs, 1553w, 1520w, 1510w, 1452m, 1443m, 1408w, 1364w, 1335w, 1325w, 1292w, 1269w, 1200m, 1146s, 1130sh, 1111w, 1040w, 1017vw, 974vw, 959vw, 924vw, 845m, 833w, 816m, 779w, 760w, 745vw, 716m, 689vw, 646vw, 635w. 573w. 542w, 476w, 446m, 403vw, 339w, 289w	Not identified in any Reference Collection of Automotive Paints monocoats. Introduced in 1995. Used mostly in nonmetallic finishes.
Thioindigo Bordeaux (Pigment Red 88)	BASF[b] Paliogen Red Violet L 5080	Dark Purple Violet	Figs. 6d, 7d	3304vw, 3106sh, 3075w, 2851vw, 2585vw, 1910w, 1655vs, 1620vw, 1605vw, 1562s, 1516w, 1449s, 1354w, 1341sh, 1294m, 1248sh, 1233vs, 1182m, 1132m, 1111vw, 1067m, 914m, 872w, 824s, 783sh, 779m, 706vw, 685w, 656w, 619vw, 596w, 556w, 530vw, 478m, 442w, 351w, 326vw, 278vw	An older pigment which is no longer used much in automotive paints. Identified in three red and two brown nonmetallic, and one brown metallic enamel. Used mostly in nonmetallic finishes.

[a] 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.

[b] Other manufacturers also produced this pigment in the past, but BASF is now the only company which markets it.
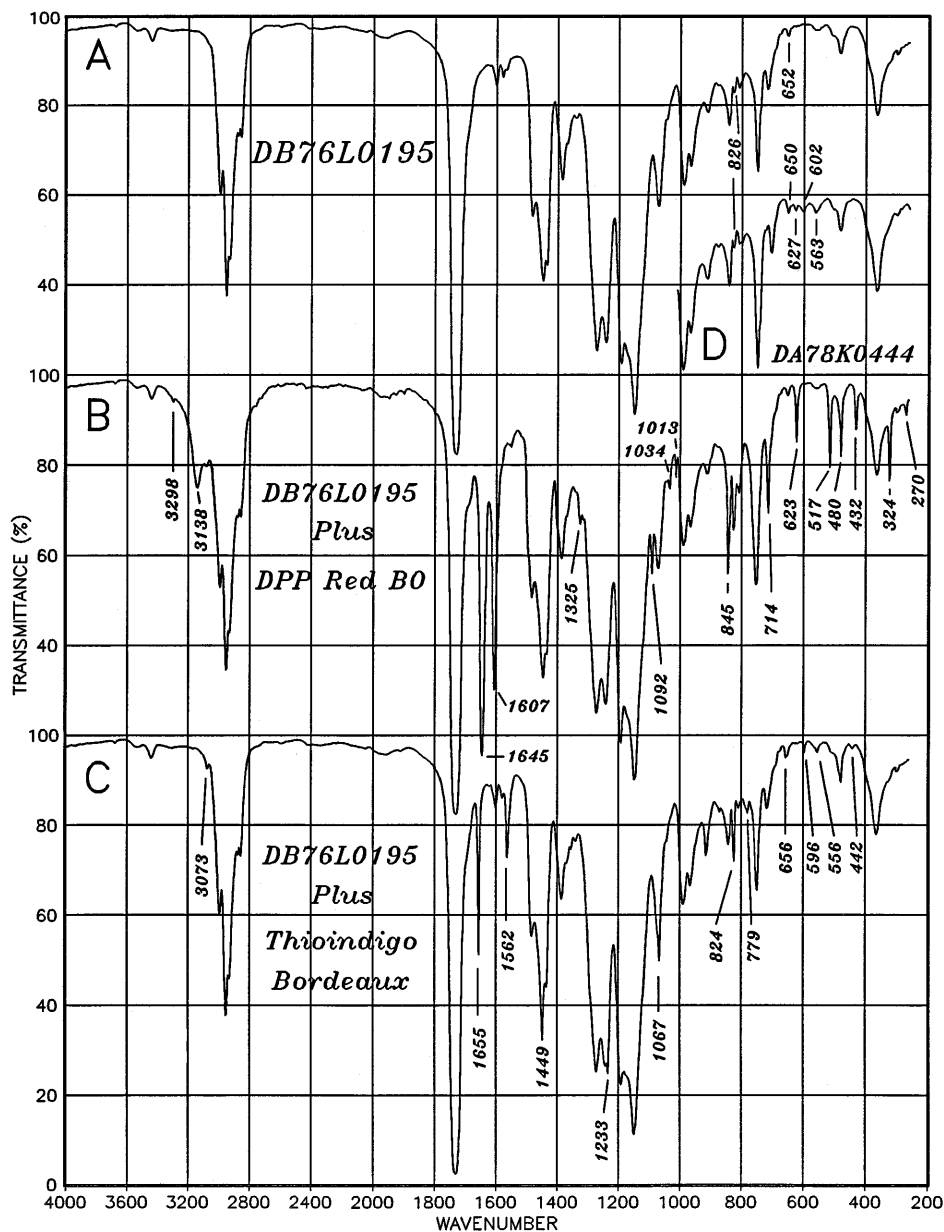
FIG. 3—(a) Spectrum of a blue metallic acrylic lacquer, DB76L0195, that lacks observable pigment absorptions; (b) results of an addition of the spectra of DB76L0195 (above) and DPP Red BO; (c) results of an addition of the spectra of DB76L0195 (above) and Thioindigo Bordeaux; and (d) a portion of the spectrum of a green metallic acrylic lacquer, DA78K0444, that also lacks observable pigment absorptions.

observed for nonmetallic and metallic finishes of essentially all colors).

The spectra of DB76L0195 and DPP Red BO were added in a ratio chosen to simulate a high pigment load, and the results (Fig. 3b) indicate that, except for the 1192 and 1142 cm^{-1} absorptions, the same DPP Red BO absorptions noted for an enamel are likely to be observed for lacquers. Additional weak or very weak peaks at 1092, 1034 and 1013 cm^{-1} may also be seen. All of the readily observed DPP Red BO absorptions in Fig. 3b are labeled with their frequencies; a comparison to their frequencies (Table 1) before the addition indicates that a few are shifted by 2 cm^{-1}, caused by their presence on the side of a binder absorption.

Occurrence in U.S. Automobile Original Monocoats (1974 to 1989): Beginning Usage Date—Spectra (4000 to 220 cm^{-1}) of

all of the available nonmetallic monocoats in the Reference Collection of Automotive Paints were acquired and examined (6,7); for metallic finishes, all of the orange and red monocoats and most of the dark brown ones, including all of those having *red-brown* or *maroon* shades, were analyzed as well. Absorptions of DPP Red BO were only identified in the spectra of two finishes, DC89 1629 (Fig. 2b) and NC89 1629. The two, which have the same Reference Collection color, are red nonmetallic enamels produced for 1989 vehicles, and there are no other panels of this color. Like DC89 1629, the spectrum of NC89 1629 has weak or very weak absorptions at 3268, 3235, 791, 540 and 530 cm^{-1}, consistent with the presence of a small amount of Quinacridone Magenta B.

The first patents for the synthesis of DPP pigments were granted in 1983 (12–14) and DPP Red BO, the first member of this family to be commercially produced (15), began to be marketed by Ciba-

Geigy in 1987.[3] As noted, the first use of this pigment in a U.S. automobile OEM monocoat apparently occurred for model year 1989. The identification of this pigment in an unknown *original finish* thus provides strong evidence that a relatively recent vehicle, most likely from the 1990s, was the source of the paint. For refinishes, a similar inference can be drawn that the vehicle was likely repainted sometime after 1986.

The introduction dates cited in this paper for DPP Red BO and other pigments represent the commercial launch dates, but the products were provided to select customers prior to the introduction dates for evaluation.[4] It is thus possible that they were in fact used on certain automobiles before these dates.

DPP Red BO is now very common in automotive paints and it has replaced, to some extent, Quinacridone Red Y because of its greater color intensity and higher opacity (15,16). Because of this opacity, DPP Red BO is intended for use in nonmetallic finishes, but a transparent version for use in metallic finishes will be introduced[5] in the next year or two. Although replaced in some applications, Quinacridone Red Y—the most common organic pigment identified (7) in Reference Collection red nonmetallic monocoats—is likely to remain an important automotive pigment because it is used to produce finishes with bluer and darker shades of red than can be achieved with DPP Red BO.[6] In addition, Quinacridone Red Y is less expensive[7] than DPP Red BO and it serves to enhance the color retention and light-fast properties of blends containing these two pigments.[8]

Elemental Analysis—X-ray fluorescence (XRF) spectra of some topcoats are presented in Fig. 4. The left spectra (depicted between 1 and 3 keV) were obtained using X-rays from a titanium secondary target for excitation, while those on the right (1 to 20 keV) resulted from excitation of this same sample with a tin target. All of the samples, which were comprised of numerous topcoat slices having mostly flat orientations on adhesive tape, had roughly the same total surface areas subjected to analysis. Comparisons between spectra displayed with the same ordinate scales thus provide some measure of the relative amounts of elements in the respective topcoats.

The XRF spectrum of DC89 1359 is shown in Fig. 4a. Pigment absorptions were not observed in the infrared spectrum (Fig. 2a) of this dark blue metallic enamel, but the XRF results indicate the presence of aluminum, silicon, phosphorous, sulfur, chlorine, titanium, iron, copper, and probably also vanadium. The aluminum peak is not observed for the spectra depicted in Fig. 4a, but it can be seen when data are displayed with fewer counts full scale. This weak intensity is consistent with the relatively few metal flakes that are observed microscopically for this finish.

The copper of DC89 1359 is undoubtedly due to Copper Phthalocyanine Blue, a very common blue organic pigment used in automotive and other types of paint (15,17–20). The chlorine, and possibly the sulfur as well, may also be from this pigment. Copper Phthalocyanine Blue is polymorphic (15,17,18) and although it does not contain either chlorine or sulfur, a stabilized form of one of its polymorphs may. Addition of chlorinated copper phthlocyanine to this particular polymorph serves to prevent its conversion

to another polymorph having a greener shade, while sulfonated copper phthalocyanine may be used to coat the crystals to prevent them from flocculating (15,17,18). In addition to improving stability, the chlorinated copper phthlocyanine also serves to help produce certain shades and ''flop'' effects in automotive finishes.[9]

Sulfur, chlorine, titanium, and iron were detected (Fig. 4b) for DC89 1629, the red nonmetallic enamel which contains a heavy pigment load of DPP Red BO and a small amount of Quinacridone Magenta B (Fig. 2b). The spectra of DC89 1359 and DC89 1629 which were obtained using the titanium target (left spectra in Figs. 4a and 4b respectively) are shown with the same ordinate scales, and a comparison of the two indicates that there is more chlorine in DC89 1629. This is consistent with the presence[10] of DPP Red BO in DC89 1629, since this pigment contains chlorine (see I in Fig. 1). Note, however, that Quinacridone Magenta B (7) is also a source of this element, which is very common in organic pigments used in automotive paint (6).

Newer DPP Automotive Paint Pigments

DPP Scarlet EK, DPP Rubine TR and DPP Orange RA—After the Reference Collection of Automotive Paints was discontinued following vehicle model year 1989,[11] Ciba-Geigy introduced three more DPP pigments which may be used in automobile finishes. Structures of these pigments, DPP Scarlet EK (II), DPP Orange RA (III), and DDP Rubine TR (IV), are shown in Fig. 1. DPP Scarlet EK was introduced in 1993, while DDP Rubine TR and DPP Orange RA were introduced in 1995.[12] Identification of one of these pigments in an unknown original finish thus indicates that a very recent vehicle was the source of the paint. DPP Scarlet EK and DPP Orange RA are primarily intended for use in nonmetallic finishes, while the more transparent DPP Rubine TR is used mostly in metallic finishes.[13] Spectra of the three are depicted in Fig. 5 and their absorption frequencies are listed in Table 1.

As expected from their molecular structures, the spectra of DDP Red BO and the three newer DPP pigments exhibit gross similarities. All four have a prominent pair of strong absorptions between 1660 and 1600 cm^{-1} and two other fairly strong absorptions near 1200 and 1145 cm^{-1}. These features, together with a high frequency absorption between 3140 and 3125 cm^{-1}, can serve as indicators of the presence of a DPP pigment. For both acrylic melamine enamels and acrylic lacquers, the first pair occurs in an important window region[14] for detecting absorptions of many organic pigments (6), and the pair is easily observed. Note, however, that for U.S. automobile OEM finishes, acrylic lacquer bind-

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[9] Personal communication, Sun Chemical Corp., March 1998.

[10] As discussed previously (6), due to anomalous dispersion and scattering/opacity considerations, the pigment load required to produce a red finish is greater than that required for a blue finish when light-absorbing pigments are used to impart color. The phthalocyanines also have very high pigment strengths (15,17,18), and nonmetallic finishes use higher pigment loads than metallic finishes, which must be semi-transparent. On a molar basis, there is thus much more DPP Red BO present in DC89 1629 than there is Copper Phthalocyanine Blue in DC89 1359, which is the reason absorptions of this blue pigment are not observed in Fig. 2a.

[11] The Reference Collection of Automotive Paints included panels from model year 1991, but these were color representations only and not actual topcoats.

[12] See Footnote 4.

[13] Personal communication, Ciba-Geigy Corp., Jan. 1998.

[14] The absorptions of eight different organic pigments in this window region are depicted in Fig. 14 of paper III (6) in this series. Figure 14f is the spectrum of NC89 1629, which contains DPP Red BO, and the differences between the 1660 to 1600 cm^{-1} pair and the absorptions of other organic pigments as observed in topcoat spectra may be seen clearly.

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[3] Personal communication, Ciba-Geigy Corp., Oct. 1997.

[4] Personal communication, Ciba-Geigy Corp., Feb. 1998.

[5] See Footnote 3.

[6] Personal communication, DuPont Automotive Products, Oct. 1997.

[7] Personal communications, Ciba-Geigy Corp., Feb. 1996, and Clariant Corp. (formerly Hoechst Celanese Corp.), Nov. 1997.
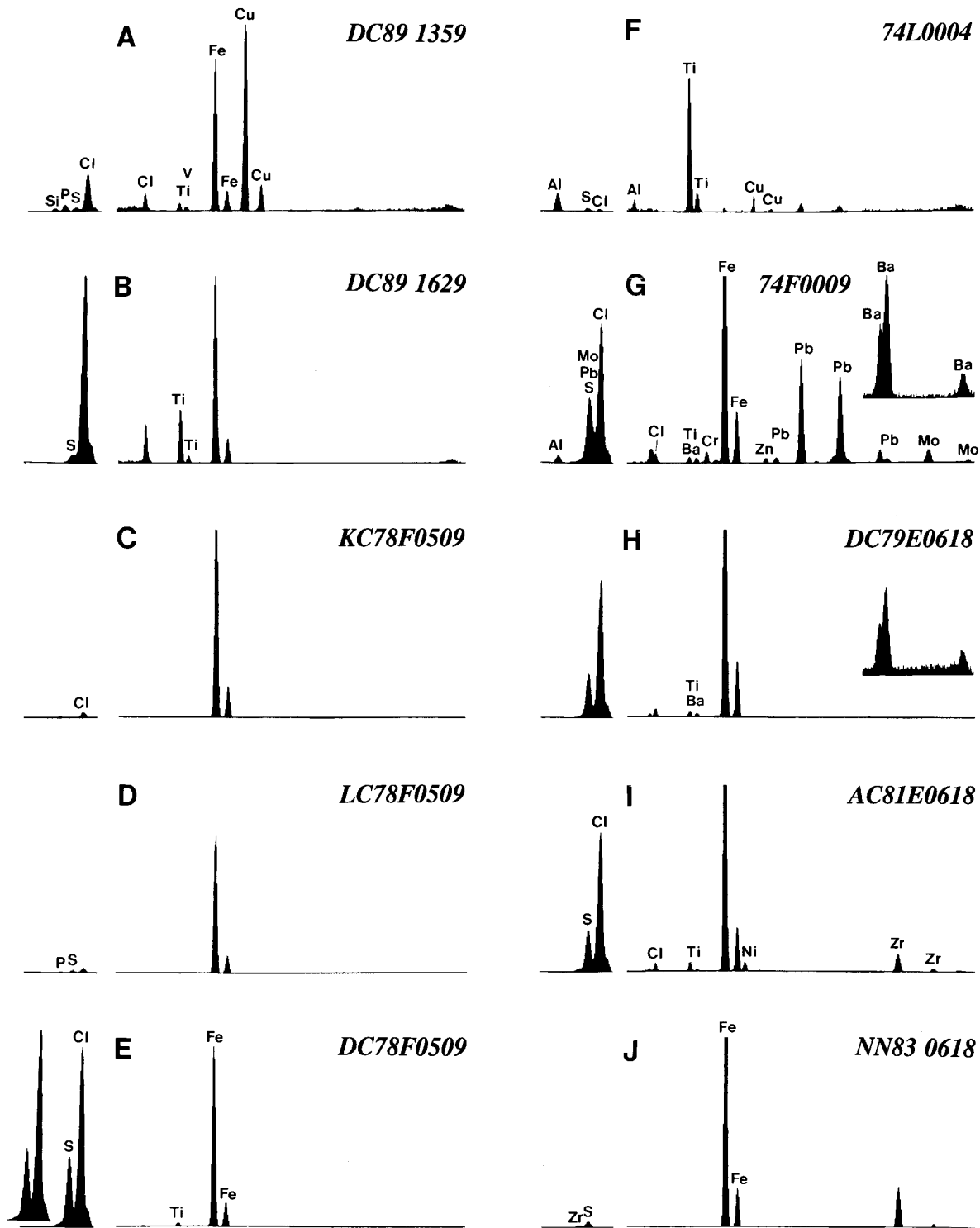
[8] See Footnote 6.

FIG. 4—*XRF spectra of some topcoats acquired using two different secondary targets for excitation. The spectra on the left from 1 to 3 keV were obtained using a titanium target, and those on the right from 1 to 20 keV were collected using a tin target. The total counts for each ordinate scale are listed. (a) DC89 1359, 1 000 000 left and 23 370 right; (b) DC89 1629, 1 000 000 left and 55 150 right; (c) KC78F0509, 200 000 left and right; (d) LC78F0509, 200 000 left and right; (e) DC78F0509, 200 000 left and right; the spectrum of Thioindigo Bordeaux which was obtained with a titanium target is shown as an insert to the left spectrum; (f) 74L0004, 1 000 000 left and 20 000 right; (g) 74F0009, 1 000 000 left and 200 000 right; the barium K lines from 31 to 37 keV which were obtained using a gadolinium target are shown as an insert to the right spectrum, 5000 counts; (h) DC79E0618, 1 000 000 left and 200 000 right; the barium K lines from 31 to 37 keV which were obtained using a gadolinium target are shown as an insert to the right spectrum, 10 000 counts; (i) AC81E0618, 1 000 000 left and 200 000 right; and (j) NN83 0618, 1 000 000 left and 200 000 right. The weak broad features near 19 keV in some of the right spectra are not peaks of the sample, but arise from differences in the amounts of rhodium primary target Kα lines which have been Compton-scattered from the sample and the reference.*
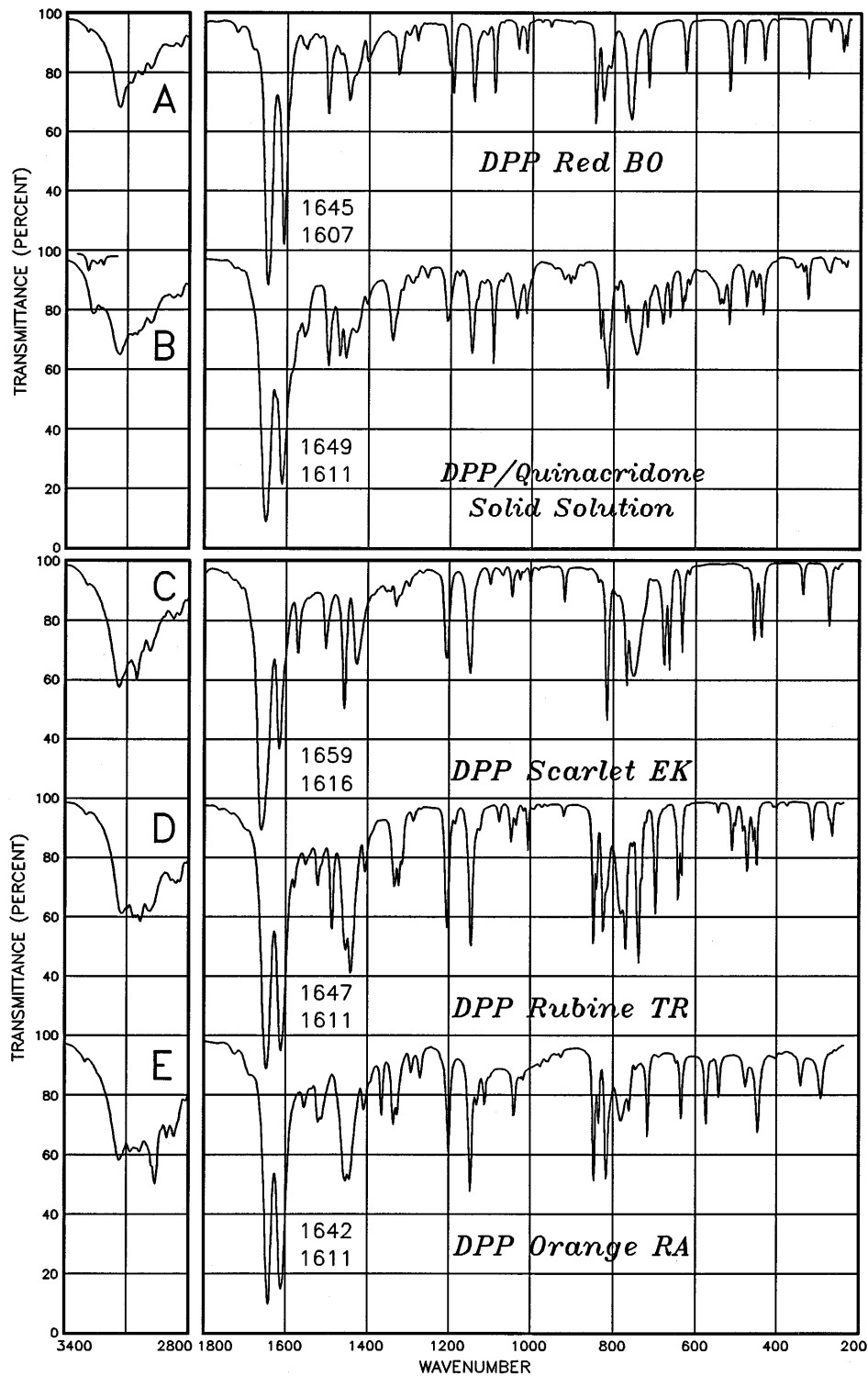
FIG. 5—*Spectra of five DPP pigments used in automotive paints: (a) DPP Red BO; (b) DPP/quinacridone solid solution; a portion of the spectrum between 3750 and 3550 cm^{-1} is shown as an insert in the upper left corner; (c) DPP Scarlet EK; (d) DPP Rubine TR; and (e) DPP Orange RA. The frequencies of the two strongest absorptions are listed for each spectrum.*

ers were not used[15] after model year 1990 so the three newer DPPs are not likely to be found in OEM lacquers. The high frequency absorption also occurs in a binder window, and for enamels having a high DPP pigment load, the two other absorptions near 1200 (1204 to 1192 cm^{-1}) and 1145 cm^{-1} (1146 to 1142 cm^{-1}) might also be observed, although they are likely to be very weak (see the 1192 and 1142 cm^{-1} peaks of Fig. 2b).

The 1660 to 1600 cm^{-1} pair not only serves as the main DPP indicator because of its intensity and location, but some differentiation might also be possible since the specific frequencies differ somewhat. These frequencies are listed on the spectra of the pigments in Fig. 5. Note that the higher frequency member of the pair has a greater intensity for all four pigments, but this may not be apparent in topcoat spectra since the lower frequency member is likely to occur on the shoulder of a strong melamine absorption (see Fig. 2b). This might also result in an apparent frequency shift to lower values; for DC89 1629 (Fig. 2b) the DPP Red BO 1607 cm^{-1} peak occurs at 1605 cm^{-1} (but note that the higher frequency member value is also 2 cm^{-1} lower in this case). Some differentiation between DPP pigments is additionally provided by the position of the high frequency absorption and the other weak or very weak peaks above 700 cm^{-1}. The most important spectral region for this, however, occurs below 700 cm^{-1}: this region is relatively free of binder absorptions for most acrylic melamine enamels (see Figs. 2a, 6a and 7a), and the differences between the absorptions of the four DPPs are quite evident there, particularly between 600 and 400 cm^{-1} (Fig. 5). Note, also, that DPP Red BO is the only pigment of the four which contains chlorine (Fig. 1).

DPP/Quinacridone Solid Solution—In addition to producing new DPP compounds, Ciba-Geigy has also formulated several solid solution combinations of DPPs with other pigments to extend the color range of these products. The most common of these is a DPP/quinacridone solid solution which was introduced in 1995.[16] The spectrum of this product is depicted in Fig. 5b and its absorption frequencies are listed in Table 1.

Solid solution combinations differ from simple physical mixtures of two or more pigments as they may involve considerable interaction between components. The infrared absorptions of two or more different pigments that are used together in a topcoat, for example, are essentially identical to those of the individual components (5–7) because there is little or no interaction between pigments. Spectra of solid solutions, on the other hand, may have absorptions with significant peak shifts and other differences compared to those of the individual components. In addition, solid solution combinations may contain components other than the pigments themselves.[17]

Although the exact formulation of the DPP/quinacridone solid solution is proprietary, a comparison of the spectrum of this product (Fig. 5b) to that of DPP Red BO (Fig. 5a) indicates that this pigment is very likely the main component. Several of the DPP Red BO absorption frequencies are shifted, however, some by as

much as 14 cm^{-1} (Table 1). The quinacridone cannot be easily identified since many of its absorptions are weak, frequency-shifted, or overlap those of DPP Red BO. The spectrum of the solid solution also has additional weak absorptions, including a triplet of peaks at 3694, 3651 and 3621 cm^{-1} (shown as an insert in the upper left corner of Fig. 5b), consistent with those of kaolin. Aluminum and silicon were identified (in addition to the chlorine of the DPP Red BO and sulfur and calcium) in an XRF analysis of this product, supporting the presence of this silicate clay. This particular product can thus be differentiated from DPP Red BO based on the peak shifts of the DPP Red BO absorptions and the extra features contributed by the quinacridone, kaolin, and possibly other constituents. Also, while DPP Red BO is currently used primarily in nonmetallic finishes because of its opacity, the DPP/quinacridone solid solution is used mostly in metallic finishes because it is quite transparent.[18]

Although the four newer DPP products were not commercially available at the time DC89 1629 was produced, it is still informative to compare their absorptions to the pigment features observed for this topcoat (Fig. 2b) and to the difference spectrum (Fig. 2c). Such a comparison provides some measure of the specificity and distinguishing ''resolution'' of the *in situ* identification method, since these four pigments are also used in topcoats and they have spectra which are likely to be the most similar to that of DPP Red BO (as far as automotive pigments are concerned). Note the similarities between the solid solution spectrum (Fig. 5b) and the difference spectrum (Fig. 2c), which occur because both contain extra absorptions of a quinacridone in addition to those of DPP Red BO.

Thioindigo Bordeaux

Several different compounds having the thioindigoid chromophore have been used as pigments, but of these, only the tetrachloro derivative, Thioindigo Bordeaux (structure V in Fig. 1), is durable enough for use in automotive finishes (15,17). This pigment has a deep purple-violet shade similar to that of Quinacridone Violet.

The spectrum of a red (*maroon*) nonmetallic enamel, DC82E0618, which contains Thioindigo Bordeaux is depicted in Fig. 6b. The spectrum of a blue metallic enamel, DC82L0866 (Fig. 6a), was subtracted from Fig. 6b to give the difference spectrum shown in Fig. 6c. The major absorptions of Thioindigo Bordeaux (Fig. 6d) can be seen in this subtraction result, which additionally contains a relatively strong residual binder carbonyl stretching absorption (1732 cm^{-1}) and a triplet of broad low frequency absorptions (5) of ferric oxide (Fig. 6e).

The spectrum of a brown (*maroon*) metallic enamel, 74F0009, which also contains Thioindigo Bordeaux and ferric oxide is depicted in Fig. 7b. The difference spectrum obtained by subtracting from Fig. 7b the spectrum of 74L0004 (Fig. 7a), a blue metallic enamel, is shown in Fig. 7c. Residual binder features are weaker for this subtraction result and all of the significant absorptions of Thioindigo Bordeaux (Fig. 7d) can be observed, including the weak ones in the low frequency region which are superimposed on the broad ferric oxide features[19]; the relative peak intensities

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[15] Personal communication, General Motors Corp., Feb. 1998.

[16] See Footnote 4.

[17] Personal communication, Ciba-Geigy Corp., Jan. 1996. The lead chromate pigments are an example of solid solutions involving inorganic compounds. Chrome Yellow (5) consists of a solid solution of lead chromate and lead sulfate, while Molybdate Orange is a solid solution of lead chromate, lead molybdate, and lead sulfate (17). Chrome Yellow has a bright yellow color and Molybdate Orange is orange-red, but lead molybdate itself is nearly colorless, having a slight pale yellow shade (5). It is thus clear that the interactions in solid solutions may be complex and subtle.

[18] Personal communication, Ciba-Geigy Corp., March 1998.

[19] As discussed previously (5), there are noticeable differences in the shapes and frequencies of the ferric oxide triplet absorptions as observed in the spectra of different commercial products of this pigment (21), and also in spectra of various topcoats. The differences between the absorptions of ferric oxide observed for nonmetallic and metallic finishes are particularly evident, as may be seen from a comparison of these features in Figs. 6c and 7c.
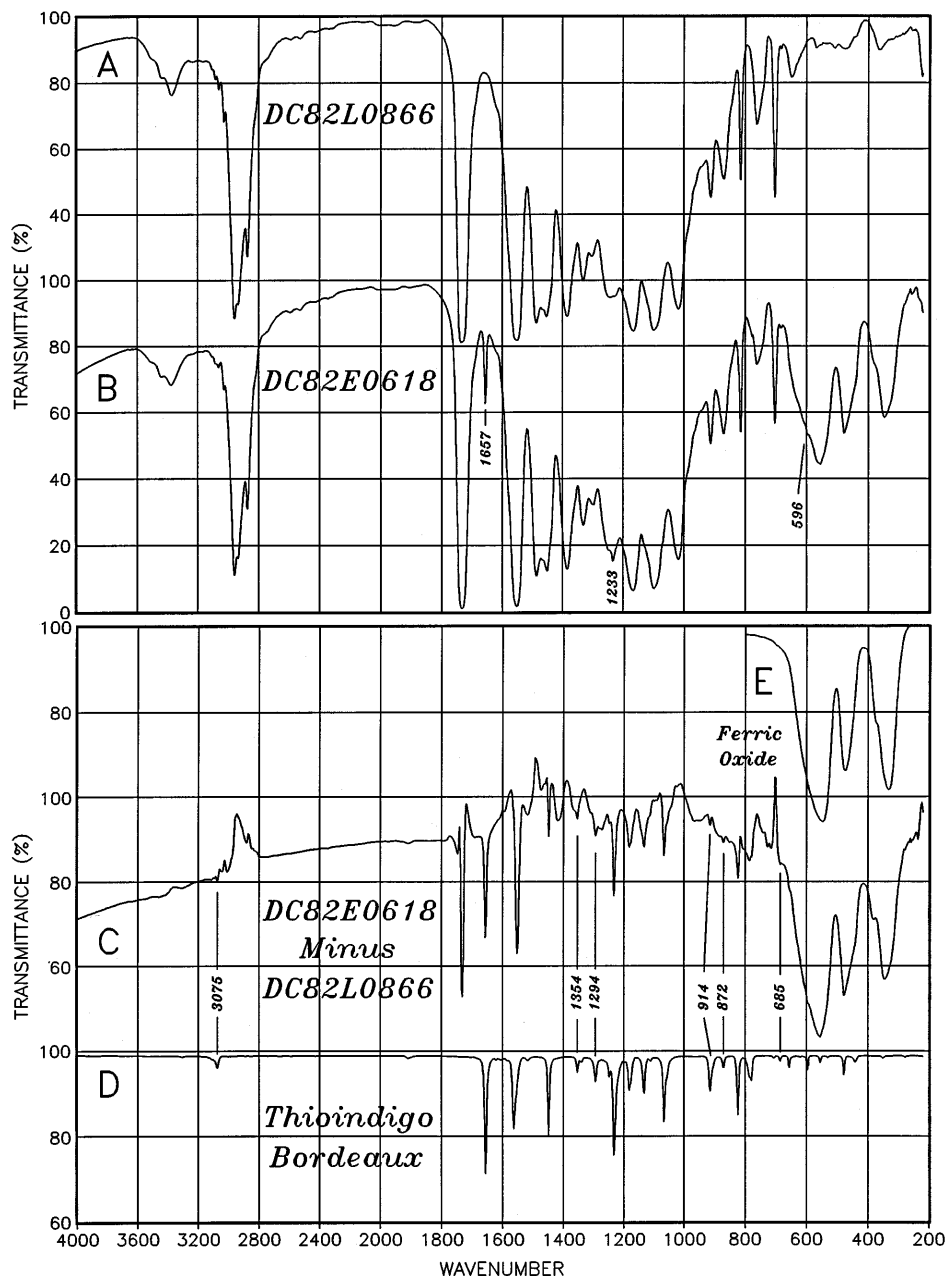
FIG. 6—*Spectra of: (a) a blue metallic enamel, DC82L0866; (b) a red nonmetallic enamel, DC82E0618, that contains Thioindigo Bordeaux and ferric oxide; (c) subtraction results—spectrum (b) minus spectrum (a); (d) Thioindigo Bordeaux; and (e) ferric oxide.*

are also consistent. The absorption frequencies of Thioindigo Bordeaux are presented in Table 1, and of the 38 peaks listed, 26 are observed in the difference spectrum. Except for one peak, all 26 have frequency values within 2 cm^{-1} of those of the pigment itself.

Pigment Absorptions Observed in Topcoat Spectra—The absorptions of Thioindigo Bordeaux observed in the spectra of various Reference Collection monocoats are relatively weak (Figs. 6b, 7b, 8c, 9b and 9c), and a large number of pigment peaks are not usually evident. For the spectra of most acrylic melamine enamels, the two strongest pigment peaks at 1655 and 1233 cm^{-1} (Fig. 7d) can usually be observed, and depending on the amount of pigment present, additional very weak peaks at 1294, 1132, 1067, 914, 872, 596 and 478 cm^{-1} (Figs. 6b, 7b, 8c, 9b and 9c) may

also be seen. Other peaks which might be observed are included in the list of Table 1.

The 1655 cm^{-1} Thioindigo Bordeaux absorption should usually be the first to be sought when examining a topcoat spectrum because it is the strongest pigment feature and it occurs in the window region previously mentioned. A few other organic pigments that were used in Reference Collection monocoats may also have a relatively strong absorption near 1655 cm^{-1}, but they can be differentiated from Thioindigo Bordeaux (and from each other) based on other weaker absorptions. The spectra of two enamels of Reference Collection color 0509 (*maroon* nonmetallic) illustrate this point for finishes that may not be easily distinguished based on color alone. DC78F0509 (Fig. 8c) contains ferric oxide and Thioindigo Bordeaux, while LC78F0509 (Fig. 8b) contains ferric
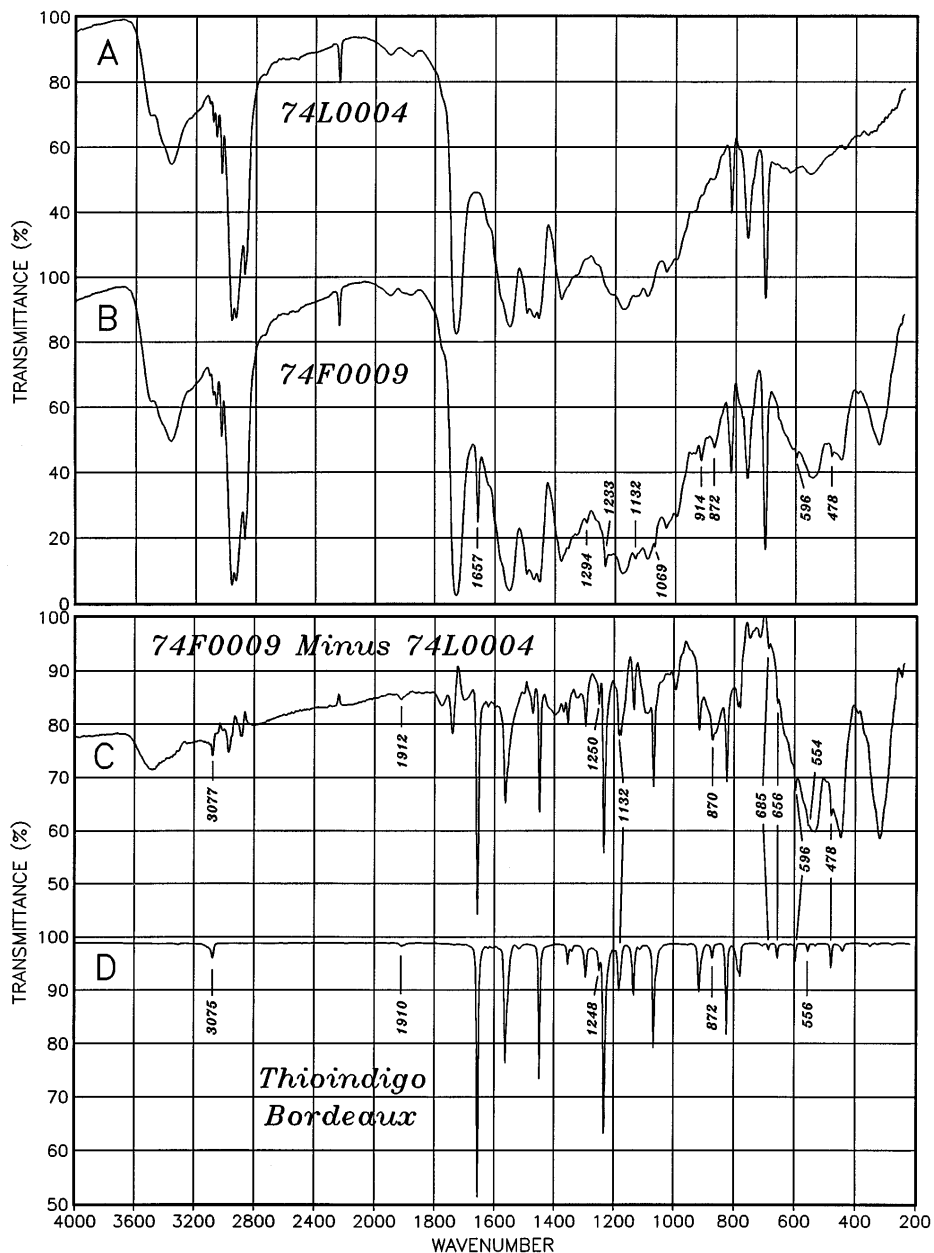
FIG. 7—*Spectra of: (a) a blue metallic enamel, 74L0004; (b) a brown metallic enamel, 74F0009, that contains Thioindigo Bordeaux and ferric oxide; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Thioindigo Bordeaux.*

oxide and a different organic pigment. This unidentified pigment has an absorption at 1663 cm^{-1}, a shoulder peak at 1701 cm^{-1}, and very weak peaks at 1262, 909, 743 and 409 cm^{-1} (the observation of this particular set of absorptions with similar relative intensities in the spectra of many finishes having different shades suggests that all of the peaks arise from a single pigment, rather than from two or more pigments). A superficial comparison of the two spectra (Figs. 8b and 8c) might lead one to conclude that both finishes contain the same organic pigment, but a closer examination indicates that this is not the case.

Spectra of Thioindigo Bordeaux and the acrylic lacquer previously discussed (DB76L0195, Fig. 3a) were added in proportions to simulate a pigment load similar to that observed for enamels. The 1655 and 1562 cm^{-1} pigment absorptions are seen clearly in this addition result (Fig. 3c), while the 1449, 1233 and 1067 cm^{-1}

peaks overlap binder absorptions and are manifested as sharp spikes on the ends of these broader binder features. The very weak 3075 cm^{-1} peak of Thioindigo Bordeaux (Fig. 7d) is usually obscured by styrene absorptions in an enamel spectrum, but it can be observed in a lacquer spectrum (at 3073 cm^{-1} in Fig. 3c). Additional weak or very weak absorptions may also be observed at 824, 783/779, 656, 596, 556 and 442 cm^{-1} (Fig. 3c). Note, however, that some of these may overlap the very weak absorptions of some lacquers (compare to Fig. 3d), and that broad absorptions of ferric oxide (Fig. 6e) or some other inorganic pigment are also likely to be present in such spectra.

Use in U.S. Automobile Original Monocoats (1974 to 1989)—Based on the Reference Collection survey noted earlier, absorptions of Thioindigo Bordeaux were identified in the spectra
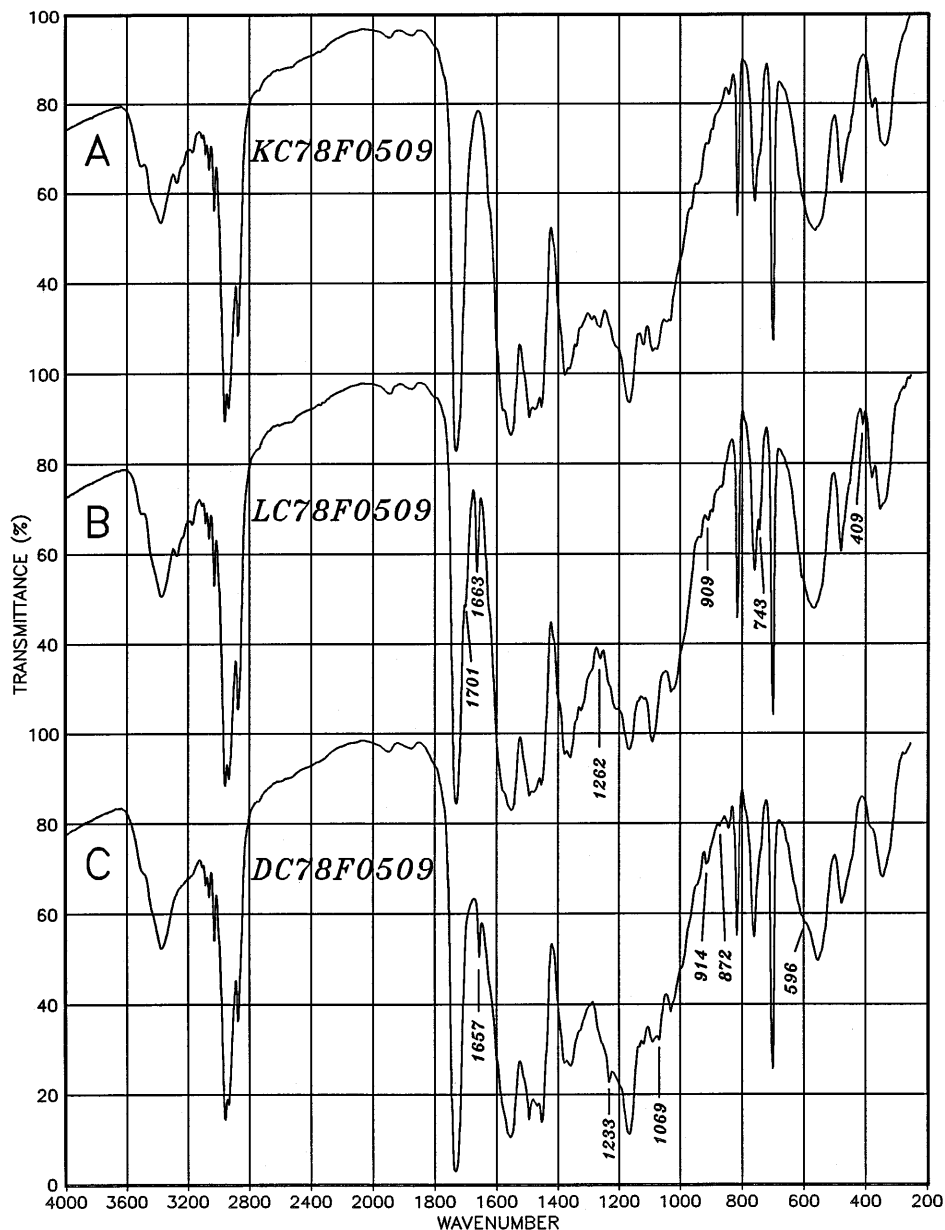
FIG. 8—*Spectra of three brown nonmetallic enamels of color 0509: (a) KC78F0509, that contains ferric oxide; (b) LC78F0509, that contains ferric oxide and an unidentified organic pigment; and (c) DC78F0509, that contains ferric oxide and Thioindigo Bordeaux.*

of three red nonmetallic enamels of color 0618, DC79E0618 (Fig. 9b), AC81E0618 (Fig. 9c), and DC82E0618 (Fig. 6b), and two brown nonmetallic enamels, NN78F0473 and DC78F0509 (Fig. 8c). As discussed, a brown metallic enamel, 74F0009 (Fig. 7b), was also found to contain this pigment. All six of these enamels have *maroon* shades and they all contain ferric oxide in addition to Thioindigo Bordeaux.

Thioindigo Bordeaux was a more common automotive pigment in the 1950s and 1960s, but in the 1970s, it was largely replaced by Quinacridone Violet because of the greater color intensity and durability of the latter pigment.[20] As its occurrence (albeit limited) in Reference Collection monocoats might indicate, this pigment was used primarily in nonmetallic finishes.[21] Although Thioindigo

Bordeaux is currently still marketed by BASF, it is no longer used much in automotive paints.[22]

Pigment Compositional Differences for Topcoats Having Similar Colors—As mentioned earlier, two enamels of color 0509, DC78F0509 and LC78F0509, contain ferric oxide and different organic pigments (Fig. 8). A third enamel of this color, KC78F0509, also contains ferric oxide, but absorptions of organic pigments are not evident in its spectrum (Fig. 8a).

Four enamels of color 0618 illustrate the use of Thioindigo Bordeaux and Quinacridone Violet to produce finishes having similar shades. DC79E0618 (Fig. 9b) and DC82E0618 (Fig. 6b) contain Thioindigo Bordeaux and ferric oxide, while NN83 0618 (Fig.

[20] Personal communications, Ciba-Geigy Corp., Feb. 1996, and DuPont Automotive Products, Oct. 1997.

[21] Personal communication, Sun Chemical Corp., June 1997.

[22] Personal communications, Ciba-Geigy Corp., Feb. 1996; Hoechst Celanese Corp., April 1996; BASF, June 1997; and DuPont Automotive Products, Oct. 1997.
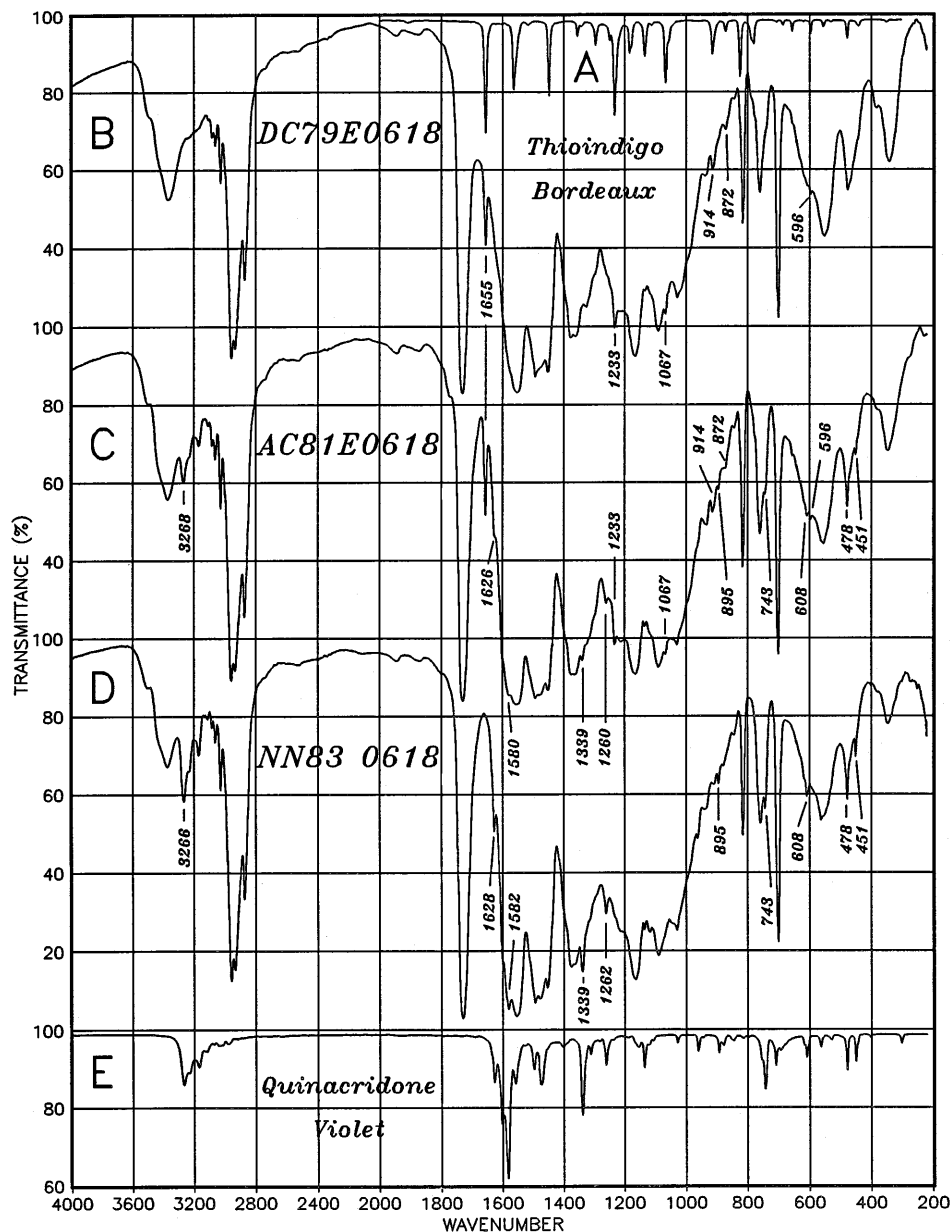
FIG. 9—*Spectra of two pigments and three red nonmetallic enamels of color 0618: (a) Thioindigo Bordeaux; (b) DC79E0618, that contains Thioindigo Bordeaux and ferric oxide; (c) AC81E0618, that contains Thioindigo Bordeaux, Quinacridone Violet and ferric oxide; (d) NN83 0618, that contains Quinacridone Violet and ferric oxide; and (e) Quinacridone Violet.*

9d) contains Quinacridone Violet (7) and ferric oxide. Spectra of Thioindigo Bordeaux and Quinacridone Violet are depicted in Figs. 9a and 9e, respectively, and their absorptions (labeled with frequency values) as present in the spectra of DC79E0618 (Fig. 9b) and NN83 0618 (Fig. 9d) can be compared. A fourth topcoat of color 0618, AC81E0618 (Fig. 9c), contains both Thioindigo Bordeaux and Quinacridone Violet, along with ferric oxide.

Elemental Analysis—Elemental analysis data for 74L0004, the light blue metallic enamel which lacks pigment absorptions in its infrared spectrum (Fig. 7a), are depicted in Fig. 4f. This monocoat contains primarily aluminum and titanium, with lesser amounts of sulfur, chlorine, iron, copper and lead.

Data for 74F0009, the brown metallic enamel which contains Thioindigo Bordeaux and ferric oxide (Fig. 7b), are shown in

Fig. 4g. Consistent with the infrared results, a relatively large amount of iron is observed, along with aluminum, chlorine, barium, chromium, zinc, lead, molybdenum, and most likely sulfur and titanium as well. Although not evident from its infrared spectrum (Fig. 7b), 74F0009 contains Molybdate Orange (5) as indicated by the presence of chromium, lead, and molybdenum—and especially—their peak intensity ratios. The Molybdate Orange infrared absorption, however, can be seen clearly in the difference spectrum of Fig. 7c as the broad dip centered near 860 cm^{-1} (5).

Molybdate Orange consists of a solid solution of lead chromate with lesser amounts of lead molybdate and lead sulfate (5,17). The lead L lines and chromium and molybdenum K lines are usually easily observed in XRF spectra of topcoats containing this pigment, but the sulfur K lines cannot be seen because they overlap the

much stronger lead M lines, and the molybdenum L lines also occur in this same region (5–7).

Whether sulfur from a source other than Molybdate Orange is present in 74F0009 is of interest since Thioindigo Bordeaux (V) contains this element (see Fig. 1). XRF spectra of three monocoats which contain Molybdate Orange, NW77E0054, KN79E0561, and NN79E0561, were therefore used for spectral subtraction to determine whether K lines of sulfur—in addition to those from Molybdate Orange—might be revealed. These XRF spectra were collected under the same conditions used for 74F0009, and they have been discussed previously (7). For subtraction, they were normalized so that their lead L line intensities were the same as those of 74F0009 (Fig. 4g, right). In all three cases, a residual peak consistent with sulfur K lines resulted following subtraction. These peaks do not appear to be artifacts since: (1) the three have similar intensities (approximately one-third that of the adjacent chlorine K line); (2) the ratios of the chromium, lead, and molybdenum peaks are essentially identical for all four spectra, so possible differences in the contributions of the lead M and molybdenum L lines are not a factor; and (3) all three residual peaks are shifted by 0.1 keV to lower energies relative to the lead M/molybdenum L/sulfur K composite peak, and this is consistent with the difference between the peak energies of lead M and sulfur K lines.

The data for 74F0009 (Fig. 4g, left) and 74L0004 (Fig. 4f, left) that were obtained using the titanium target are depicted with the same ordinate scales, and a comparison of these indicates that there is much more chlorine in the former topcoat (for Fig. 4g, note also the difference in relative intensities of the lead M/molybdenum L/sulfur K composite peak and the chlorine peak obtained using the two targets; this results primarily from differences in the efficiencies with which lead is excited by the two target X-rays). If the intensity of the sulfur peak resulting from the spectral subtractions is assumed to be fairly accurate, then a comparison to the data of Fig. 4f (right) suggests that there is also much more sulfur (although this may not be evident from the ordinate scale depicted). These results support the conclusion that Thioindigo Bordeaux is present in 74F0009, since this pigment contains both chlorine and sulfur (see Fig. 1), but more definitive comparisons are provided by some other topcoats which do not contain either lead or molybdenum (discussed later). Detection of the sulfur of Thioindigo Bordeaux (or other pigments) is thus hampered when Molybdate Orange, Chrome Yellow (5), other lead chromate pigments, or other sources of lead or molybdenum are also present in topcoats.

The two weak peaks to the left of the chromium K lines of Fig. 4g (right) and the analogous features of Figs. 4a (right) and 4h (right) illustrate another case where overlapping peaks may cause ambiguities, especially when low concentrations are involved. Peaks of three elements which may be found in topcoats, titanium, barium, and vanadium, occur in this region. The Kα and Kβ peaks of titanium overlap the barium Lα and Lβ peaks, respectively, while the vanadium Kα peak overlaps the titanium Kβ/barium Lβ peaks. The barium Lα and Lβ peaks normally have nearly equal intensities, while the titanium Kα peak is approximately six times as intense[23] as that of Kβ (see, for example, the titanium K lines of Figs. 4b and 4f). The intensity ratios of the three peaks of Figs. 4a, 4g, and 4h, however, occur between these values, indicating that more than one peak series is probably present. Barium was

confirmed for 74F0009 (Fig. 4g) and DC78E0618 (Fig. 4h) using excitation with a gadolinium target, which produced the barium K lines depicted as inserts of Fig. 4g, right (shown between 31 and 37 keV) and Fig. 4h. Very weak barium Lγ peaks are also seen in expanded views of the tin target results. The apparent enhancements of the barium Lα peaks for 74F0009 and DC78E0618 are likely due to the presence of small amounts of titanium.

For DC89 1359 (Fig. 4a), barium K lines were not observed using a gadolinium target, so the features in question are K lines of titanium. The apparent enhancement of the titanium Kβ peak may be due to the presence of a small amount of vanadium. Normally, the vanadium Kβ peak would also be observed, but in this case, the levels involved are too low to produce a peak which can be distinguished from the background.

One possible source of barium (and sulfur) is barium sulfate. Small amounts of this extender pigment, which is commonly found in undercoats,[24] are sometimes used as diluents in the pigments themselves, where they serve to standardize the strength of the pigment.[25] Barium and sulfur from such a source would normally be present in only small quantities, since the barium sulfate is a minor ingredient in a component which itself is often not a major constituent of the paint.

The aluminum of 74L0004 (Fig. 4f, left) and 74F0009 (Fig. 4g, left) is from the metal flakes used in these two metallic finishes. The difference in the intensities of the aluminum peaks is consistent with the microscopic observation that 74L0004 contains a noticeably greater concentration of metal flakes than 74F0009 (which, in turn, contains significantly more flakes than DC89 1359—compare the left spectra of Figs. 4a and 4g, which are depicted with the same ordinate scales).

Figures 4c, 4d and 4e depict, respectively, XRF data for KC78F0509, LC78F0509 and DC78F0509, the three brown nonmetallic enamels with infrared spectra shown in Fig. 8. From their infrared absorptions, ferric oxide was identified in all three, while DC78F0509 was also found to contain Thioindigo Bordeaux and LC78F0509 also contains an unidentified organic pigment. The XRF results are all depicted with the same ordinate scales to facilitate comparisons between them. The three enamels contain roughly the same levels of iron (Figs. 4c–4e, right) consistent with the relative intensities of the ferric oxide absorptions observed in their infrared spectra (Fig. 8). Additionally, all three enamels contain chlorine, KC78F0509 contains phosphorous, LC78F0509 contains sulfur and phosphorous, and DC78F0509 contains sulfur and a small amount of titanium. A comparison of the titanium secondary target results indicates that there is much more chlorine and sulfur in DC78F0509 than the other two, supporting the conclusion that

[24] Many of the panels in the Reference Collection of Automotive Paints have undercoats, and the undercoat of 74F0009 (Fig. 4g) contains a large amount of barium sulfate, as indicated by its infrared and XRF spectra. To minimize the possibility of contamination during removal of topcoat slices for XRF analyses, care was taken to exclude undercoat material, and slices that included any surface which was adjacent to the undercoat were not used. Because contamination by the undercoat could not be completely ruled out for 74F0009, however, two separate samplings were subject to XRF examinations, and this monocoat—from the Georgia State Crime Laboratory Reference Collection—was also analyzed using a SEM/EDX instrument (personal communication, Tammy Jergovich, Georgia State Crime Laboratory, Feb. 1998). Similar amounts of barium were detected in all three cases. The undercoat of DC79E0618, which was also found to contain a small amount of barium (Fig. 4h), does not contain this element.

[25] Personal communications, Ciba-Geigy Corp., Feb. 1997, and Engelhard Corp., March 1998.

[23] XRF spectra of barium hydroxide and rutile (titanium dioxide) were collected using a tin secondary target. For barium hydroxide, the intensity of the barium Lα peak was 95% of that of the Lβ peak, and for rutile, the intensity of the titanium Kβ peak was 17% of that of the Kα peak.

Thioindigo Bordeaux is present in this finish. The XRF spectrum of Thioindigo Bordeaux obtained with a titanium secondary target is depicted as an insert to Fig. 4e (left), and the sulfur/chlorine peak intensity ratio for DC78F0509 may be seen to be similar to that of the pigment.

XRF data for the three red nonmetallic enamels, DC79E0618, AC81E0618 and NN83 0618, whose infrared spectra are presented in Fig. 9 are shown in Figs. 4h, 4i and 4j, respectively. The infrared results indicated the presence of ferric oxide in all three, and Thioindigo Bordeaux in DC79E0618, Thioindigo Bordeaux and Quinacridone Violet in AC81E0618, and Quinacridone Violet in NN83 0618 (Fig. 9). The XRF data support these assignments; note that Quinacridone Violet (VI) does not contain sulfur or chlorine (Fig. 1). The tin target results (right spectra) are shown with the same ordinate scales, and all three enamels contain roughly the same levels of iron (compare the ferric oxide absorptions of Figs. 9b, 9c and 9d). The titanium target results (left spectra) are also shown with the same ordinate scales, and DC79E0618 (Fig. 4h) and AC81E0618 (Fig. 4i) contain roughly the same levels of sulfur and chlorine, while NN83 0618 (Fig. 4j) contains only a small amount of sulfur. The sulfur/chlorine peak intensity ratios of DC79E0618 and AC81E0618 should also be compared to that of Thioindigo Bordeaux (Fig. 4e left, insert).

AC81E0618 (Fig. 4i) and NN83 0618 (Fig. 4j) both contain small amounts of zirconium. Zirconium compounds may be used as driers in alkyds, and they are frequently used together with cobalt compounds (17). As discussed previously (7), however, zirconium in an acrylic melamine enamel or acrylic lacquer is probably a contaminant which resulted from wear of the grinding media used in the paint dispersion process. Grinding balls or beads constructed of fused zirconium oxide are often used, and the media must be replaced periodically because of this wear (22).

Thioindigo Bordeaux is the first organic pigment identified to date which contains sulfur. Of the ten organic pigments (including the two discussed here) which have been identified thus far in Reference Collection monocoats, five contain chlorine (Benzimidazolone Orange, Benzimidazolone Brown, Quinacridone Magenta B, DPP Red BO, and Thioindigo Bordeaux), and one contains fluorine (Benzimidazolone Yellow 3G); identification of the latter element requires a special detection system if X-ray methods of analysis are used. The combination of chlorine and sulfur sets Thioindigo Bordeaux apart from the others, and is a particularly useful characteristic for identification in view of the relatively weak infrared absorptions of this pigment which are usually observed in topcoat spectra. It should be remembered, however, that both chlorine and sulfur are quite common elements in topcoats and they may be from components other than pigments.

Additional Considerations

The pigment loads that are used for various inorganic and organic pigments in automotive finishes can vary continuously over a wide range. As illustrated by the monocoats containing DPP Red BO and Thioindigo Bordeaux, the number and intensity of pigment absorptions observed in topcoat spectra may therefore also vary considerably. For a given pigment and pigment load, this number is determined primarily by the spectral window regions of the binder, and the presence or absence of other pigments—particularly rutile and some other inorganic pigments. It is also affected by individual differences between binders of a given type.

One other important limiting factor is the type of detector used to collect spectra. The data presented for the various pigments in

this study represent the maximum number likely to be observed[26] since an extended range CsI instrument was used. Fewer absorptions will be observed using broadband and narrowband mercury cadmium telluride (MCT) detectors, which have low frequency cutoff points near 400 and 700 cm^{-1}, respectively. The absorptions of inorganic pigments tend to be concentrated in the low frequency regions, and the value of an extended range instrument for the identification of some inorganic pigments has been discussed previously (5). Absorptions of organic pigments, on the other hand, occur over much of the mid-infrared region and their most intense absorptions rarely occur below 700 cm^{-1} (often, these absorptions involve stretching modes of carbonyl groups conjugated with the chromophore). The use of MCT detectors for the in situ identification of organic pigments is thus less limiting than for inorganic pigments. The relative importance of the 700 to 200 cm^{-1} pigment absorptions for identification varies, however, depending on the number and distinguishing characteristics of the pigment absorptions observed above this region. The low frequency features become more important when relatively few pigment absorptions are observed, and as noted, most binders do not have strong absorptions below 700 cm^{-1} so this region provides a fairly good window. As was found to be the case with inorganic pigments (5), the 700 to 400 cm^{-1} segment is usually more important than the 400 to 200 cm^{-1} one; an example of this is the differentiation of the DPP pigments previously discussed.

Because the number of organic pigment absorptions observed in a topcoat spectrum may vary, the degree of confidence which can be ascribed to the assignment of a particular set of absorptions to a specific pigment likewise varies. In general, the pigments which are most likely to have absorption patterns similar to that of one of interest are the other pigments in the same family, and of these, there are usually only a few which are used in automotive paints. An examination of the spectra of the benzimidazolones (6), quinacridones (7) and DPPs which are used in automotive paints suggests that in order to distinguish between individual members of these families, a large number of absorptions are not usually required. Most absorptions of organic pigments are quite narrow and their frequencies, as observed in topcoat spectra, are very reproducible. As much as practical, the relative intensities of the observed pigment absorptions should also be considered, remembering that in the transmittance format, a nonlinear scale is involved. Some other practical considerations, such as the colors of the finish and the pigment, and the type of finish (nonmetallic or metallic) in which a particular pigment is used, should also be kept in mind when considering possibilities.

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[26] Although spectral data can be collected below 200 cm^{-1} using FT-IR instruments equipped with appropriate beamsplitters and detectors, it is not possible to cover the entire mid-infrared region and far-infrared region below 200 cm^{-1} simultaneously using a single beamsplitter and detector.

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