

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*

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ABSTRACT: A number of unidentified absorptions, which appeared to be due to specific color-imparting pigments, were observed in infrared spectra of some U.S. automobile original topcoats (1974–1989) from the Reference Collection of Automotive Paints. In previous work of this study, several inorganic pigments were identified which were responsible for some of these. Unlike the inorganic pigment absorptions, which were usually broad and few in number, the remaining unidentified absorptions were sharp and numerous, indicative of organic compounds. Because these peaks are narrower than most binder absorptions, spectral subtraction can be a useful means to help delineate pigment peaks obscured by binder features. Using this technique, several organic pigments have been identified. In cases in which the pigment peaks are prominent, the specific pigment responsible can usually be identified based on the peaks observed between binder absorptions or superimposed upon them, without having to use spectral subtraction. This is possible even when absorptions of two or more pigments are present. This paper discusses the analysis of benzimidazolone pigments, which were identified in some yellow, orange, red, and brown nonmetallic single layer Reference Collection topcoats, and a few brown metallic ones. Absorptions of these particular pigments were not observed in spectra of any Reference Collection topcoats produced before 1977. Use of the benzimidazolones—especially Benzimidazolone Orange—increased in the 1980s because they were common replacements for lead chromate pigments, which were phased out of use in U.S. automobile original finishes during this period.

KEYWORDS: forensic science, criminalistics, paint analysis, infrared spectroscopy, pigment identification, benzimidazolones, Benzimidazolone Orange, Benzimidazolone Yellow 3G, Benzimidazolone Yellow 4G, Benzimidazolone Brown

As part of a more general study involving the classification of U.S. automobile original (OEM) topcoats (1974–1989) based on binder and pigment compositions, a number of pigments which were used in these paints have been identified. Infrared spectroscopy was used for these analyses and the single layer finishes

(monocoats) comprising this work are from the Reference Collection of Automotive Paints. In Part I (1) of this series, the identification of iron ferrocyanide (Prussian Blue), a blue inorganic pigment, was discussed and its occurrence in Reference Collection topcoats was tabulated. Part II (2) of this study described the analysis of five other color-imparting inorganic pigments, along with three inorganic extender pigments used to modify luster. In the present work, the identification of organic pigments is discussed. A number of such pigments have been identified and they consist of several different types which are used for a wide range of colors in both metallic and nonmetallic finishes. The results of this study are therefore presented in several parts. This paper describes the analysis of benzimidazolone pigments, which were identified in some yellow, orange, red, and brown nonmetallic topcoats, and also in a few brown metallic ones.

Although it is not unusual to observe significant absorptions of inorganic pigments in paint infrared spectra, this is not always the case with many organic pigments. This disparity reflects fundamental differences in the absorption properties of these pigments in the visible and infrared regions: in general, inorganic pigments have high infrared absorption coefficients and low (3) visible absorption coefficients, whereas the opposite is true for organic pigments.² Only small amounts of organic pigments may thus be used for some paints and the pigment absorptions may be entirely obscured by binder features (this is one of the reasons why it is not unusual for two paints with quite different colors to have similar infrared spectra). For some organic pigments used in certain types of paint, however, much higher concentrations are required and significant pigment absorptions may be observed. Such paints include red automobile topcoats, and to a lesser extent, orange and yellow ones. In particular, heavy pigment loads are common for red organic pigments used in nonmetallic automobile finishes compared to blue organic pigments: The pigment-to-binder weight percent of the former may be 25% or higher, whereas values of

²Inorganic compounds are generally stronger infrared absorbers because they tend to be considerably more polar than organic compounds. The colored inorganic pigments are predominantly comprised of transition metal ion complexes or salts, and these owe their visible absorption properties to electronic transitions involving valence electrons of the *d* orbitals. Radiative transitions between *d* orbitals are nominally forbidden, but due to perturbations of these orbitals by various ligands, such transitions may become “weakly allowed.” The chromophores of organic pigments, on the other hand, are all highly conjugated unsaturated systems and visible absorptions result from π electron transitions. These are allowed transitions and organic pigments generally have quite intense absorptions in the visible region.

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a few percent or less are typical for the latter.³ Significantly, it is also for red, orange, and yellow nonmetallic colors that the use of organic pigments has increased in the last decade due to the phaseout of lead chromate pigments, which were commonly used (2) for such automobile original finishes before the mid to late 1980s.

For some inorganic pigments, the far-infrared region below 700 cm^{-1} was found to be important for identification (2). To determine if this is also the case for organic pigments, as well as to better characterize combinations involving both organic and inorganic pigments, spectral data for this work were collected between 4000 cm^{-1} and 220 cm^{-1} .

Experimental

Instrumentation

Infrared spectra were acquired at a resolution of 4 cm^{-1} on a Digilab FTS-7 Fourier transform infrared (FT-IR) spectrometer equipped with cesium iodide (CsI) optics and a deuterated triglycine sulfate (DTGS) detector. A low pressure diamond anvil cell (DAC) was used with a Digilab 5X beam condenser for the analysis of topcoats and pigments. Some topcoats were also analyzed using a plate with a 1-mm circular aperture, mounted in the beam condenser, and all of the pigments were also sampled as powders diluted with CsI using a Digilab diffuse reflectance (DRIFTS) accessory. DRIFTS sample cups having a diameter of 3 mm were used for this. For the spectra depicted in this work, 1000 scans were averaged when using the beam condenser, and 100 were used with the DRIFTS accessory. The spectrometer, DAC, aperture plate, beam condenser, and acquisition parameters used for data collection have been described in more detail elsewhere (2).

A few topcoats were also analyzed in a high pressure DAC mounted in an Analect 4X beam condenser. These spectra were collected at a resolution of 4 cm^{-1} using a Laser Precision Analytical RFX-40 FT-IR spectrometer, and 1000 scans were averaged. This system is likewise described in more detail elsewhere (1).

U.S. Automobile Topcoats

All of the topcoats discussed in this work are from the Reference Collection of Automotive Paints (Collaborative Testing Services,

³DuPont Automotive Products, personal communication, June 1995. Part of the reason for this is the higher pigment strengths (3) of the phthalocyanine pigments, which are commonly used (4–8) for blue and green topcoats, compared to those of many of the red automotive pigments. Another factor results from differences in opacities of red and blue pigments. Red pigments absorb the shorter wavelengths of visible light (blue light) and anomalous dispersion results in an index of refraction which is higher on the long wavelength side of the absorption. These pigments thus have (9) relatively high indices of refraction for yellow, orange, and red wavelengths—the light by which red paints are viewed. In contrast, higher indices of refraction occur in the near-infrared region for blue pigments, which absorb red light. The higher indices of refraction make the pigments more opaque, because this causes the pigment particles to scatter more light. Red pigments are therefore more opaque (for red light) than blue pigments (for blue light), and light penetrates more deeply into a blue paint. This causes blue paints to be considerably darker than red ones (5), especially if the pigments are used alone without titanium dioxide (titanium dioxide increases scattering which makes the paint brighter because more light is diffusely reflected). Less blue pigment is therefore required to impart color than is the case with red pigments. It should be noted that this wavelength-dependent behavior is the opposite of that which occurs in a non-colored paint. For these, the shorter wavelengths of light are scattered more (which is the usual case) and red light penetrates more deeply into the paint than blue light (5).

Inc., Herndon, Virginia). Topcoats will be referred to by their nine character identification codes, which have been described previously (1).

Pigments

The following pigments were used (pigment *Color Index* (10) designations are given in parentheses because the cited common names may not be universally used, or the same common name may be used for two or more different pigments; trade names are given in italics): Benzimidazolone Orange (Pigment Orange 36), Sun Chemical Corp. *Sunfast® Orange 36* and Hoechst Celanese *Novoperm® Orange HL-70*; Benzimidazolone Orange (Pigment Orange 62), Hoechst Celanese *Novoperm Orange H5G-70*; this pigment will hereafter be referred to as “Benzimidazolone Orange 62” to distinguish it from Pigment Orange 36; Benzimidazolone Yellow 3G (Pigment Yellow 154), Hoechst Celanese *Hostaperm® Yellow H3G*; Benzimidazolone Yellow 4G (Pigment Yellow 151), Hoechst Celanese *Hostaperm Yellow H4G*; Benzimidazolone Yellow 6G (Pigment Yellow 175), Hoechst Celanese *Hostaperm Yellow H6G*; Benzimidazolone Red (Pigment Red 175), Hoechst Celanese *PV Fast Red HFT*; Benzimidazolone Brown (Pigment Brown 25), Hoechst Celanese *Hostaperm Brown HFR-01*; Benzimidazolone Red 2B (Pigment Red 208), Hoechst Celanese *Novoperm Red HF2B*; and Benzimidazolone Carmine (Pigment Red 185), Hoechst Celanese *PV Carmine HF4C*. Spectra of some inorganic pigments are also discussed in this work, and these particular pigments have been described previously (2).

Sampling

Thin slices of topcoats were produced using a sharp scalpel and they were pressed with a roller to produce a more uniform thickness. The slices were mounted in the DAC or they were placed over the 1-mm circular aperture (which consisted of a hole in a lead disk originally intended for holding micropellets). The aperture method was used for all of the spectra presented in this paper, and these slices were prepared so that their strongest absorptions had transmittance values between 1 and 10%. For most data, the absorption intensities were adjusted using spectral expansion to give the strongest peak a transmittance value between 2 and 5%, with the baselines adjusted to have their highest values near 100%.

Reference pigment spectra were measured in the DAC, either neat or diluted with CsI. For DRIFTS analyses, some CsI was first ground to a fine powder and a portion of this was used as a reference. To the remainder was added a small amount of neat pigment (approximately 10% by volume) and the two were mixed together using a spatula, but they were *not* ground. All of the reference pigment spectra which are depicted in this work were taken using DRIFTS.

Spectral Calculations

Spectral calculations were performed using Spectra Calc™ software. Spectral subtractions, additions, expansions, and baseline adjustments were conducted with data in the absorbance modes. For spectral subtraction, a subtrahend factor was chosen which produced minimal residual binder features in the difference spectrum. Following a subtraction, the baseline of the difference spectrum was usually adjusted (by adding or subtracting a constant absorbance value) so as to produce a transmittance spectrum having its highest point near 100%. Difference spectra, however, were not expanded and their baselines were not flattened, except in a

few cases in which this was done for small portions of such spectra where strong broad residual inorganic pigment absorptions occurred. These portions were flattened using a multiple point baseline correction which was performed on data in the transmittance format.

Reflectance spectra of pigments obtained using the DRIFTS accessory were first converted to an absorbance-type spectrum using the Kubelka-Munk equation (11), then these were converted to a transmittance format using a conventional absorbance-to-transmittance conversion. All of the DRIFTS data which are depicted are presented in the transmittance format.

Elemental Analyses

Most of the elemental analyses were conducted using X-ray fluorescence (XRF) spectrometry. A Kevex 0700 XRF spectrometer equipped with a rhodium primary target and various secondary targets was used. The operating system of this spectrometer, which originally consisted of a Kevex 7000, was replaced with an IXRF Systems Inc. unit. Topcoats were analyzed as slices mounted under a thin strip of adhesive tape. Data collected for a similar strip of tape without any sample were subtracted from each topcoat spectrum. For most of the spectra which are presented, the rhodium primary target was used as the excitation source with the X-rays attenuated with the smallest diameter collimator. An X-ray tube voltage of 30 kV was used at a current of 0.15 mA. Some topcoats were additionally analyzed with titanium or tin secondary targets using voltages of 25 kV and 40 kV, respectively, at currents of 2 mA. The instrument chamber was evacuated, and data were collected for 20,000 s (total live time).

Scanning electron microscope/energy dispersive X-ray (SEM/EDX) analyses of some topcoats were performed on a Leica S430 SEM equipped with an Oxford Isis® X-ray analysis unit. The latter has a light element detection capability which allows elements with atomic numbers greater than those of boron ($Z > 5$) to be analyzed. For collection of elemental data, the SEM was operated with an excitation voltage of 20 kV, with a working distance of between 20 and 25 mm. A take-off angle of 40 degrees was used and the topcoat slices, which were attached to an aluminum stub with graphite filled adhesive tape, were coated with carbon.

Analysis of Organic Pigment Absorptions

The colored inorganic pigments which were previously identified (1,2) in Reference Collection topcoats are all transition metal compounds, mostly oxides, having simple infrared spectra comprised of one to three main absorptions. The absorptions are often quite broad, and with the exception of the ferrocyanide $C\equiv N$ stretching fundamental, they occur primarily below 1000 cm^{-1} . In contrast, the organic pigments, with their extended conjugated chromophores, are all relatively large compounds having rich infrared spectra. These pigment absorptions are typically quite narrow and they occur over a wide spectral range. Some of the pigment absorptions overlap binder absorptions whereas others occur in "window" regions between binder features. These regions differ somewhat for acrylic lacquers and acrylic melamine enamels, the two main binders used in Reference Collection topcoats, and examples involving both types will be presented where applicable.

Even when pigment peaks overlap binder absorptions, they still may be discernable because they tend to be sharper than most binder features and may be manifested as apparent fine structures on the broader binder absorptions. Because of this difference in absorption breadths, spectral subtraction can be a useful means to

clarify spectra and help identify pigment peaks obscured by binder absorptions. Ideally for a given topcoat, the spectrum of the same paint without the pigment of interest should be used for subtraction. Because this was not practical, spectra of similar topcoats lacking observable absorptions of the pigment of interest were used instead. In most cases, blue, green, or gray metallic topcoats were the primary choice for this because their spectra are generally free of pigment peaks. Such topcoats having the same first four characters in their designation codes as the topcoats of interest were usually used; these four characters (1) represent manufacturer, type of paint, and the year it was first produced. In cases in which appreciable absorptions of titanium dioxide were present along with those of the organic pigment, spectra of white or beige nonmetallic topcoats having similar binder compositions and similar amounts of titanium dioxide were sought.

For illustrative purposes, difference spectra having the least intense residual binder features are presented. It is important to remember that these spectra are therefore *not* typical. With some pigments, the subtraction results obtained for several different topcoats—each with its own set of subtrahend spectra—were screened to produce the particular difference spectrum shown. The variations which occurred between results were helpful in interpreting data, because pigment peaks could be more easily distinguished from residual binder features produced by binder differences. Although spectral subtraction may be a useful tool for identifying unknown pigments in "known" topcoats, this method is probably less useful for actual case samples because the binder composition itself is usually in question and the choice of an appropriate subtrahend spectrum becomes much more of a problem.

Because the goal of this work was to be able to identify organic pigments from spectra of intact topcoats without having to use subtraction, this project proceeded in several phases. The first phase used spectral subtraction to help identify commonly-encountered unknown pigments in topcoats containing primarily only one pigment (the latter assumption was made following examination of spectra of a large number of different topcoats of a particular color, all of which contained a certain set of nonbinder absorptions). The second phase examined the feasibility of identifying these same pigments based on the more limited number of pigment absorptions which are normally observed in topcoat spectra. Because this entailed an assessment of the degree to which one could attribute a less than "full" spectrum to certain pigments or pigment types, it was desirable to know how spectra of some closely-related compounds might differ, especially for absorptions occurring in certain spectral regions. Spectra of pigments used in automobile finishes and similar to the one of interest were considered to be particularly important for this comparison. Finally, the applicability of this method for interpreting spectra of topcoats containing various combinations of pigments was examined.

Reference Spectra of Pigments

As an initial screening process, the difference spectra which were obtained by the above procedures were compared to spectra of organic pigments depicted in the first (12) and fourth (13) editions of *An Infrared Spectroscopy Atlas for the Coatings Industry*. The two editions were used because the same pigments are not necessarily found in both, and the first edition has spectral data to 200 cm^{-1} whereas the fourth has data to 400 cm^{-1} . Not all of the unknown pigments were identified by this means, but even when they were not, it was usually possible to obtain some

idea of the type of pigment involved from the similarities in absorption patterns. All of the commercially-available automotive pigments of this type were then sought, and their spectra were compared to the difference results.

Organic Pigments Used in Automobile Finishes

A number of different chromophores are used for organic pigments, and various pigment properties, including color or shade, light-fastness, solubility, thermal stability, and so forth, are determined in part by the different substituents and structural modifications of the basic chromophore (3,6). Organic pigments thus occur as members of a family and there are almost always several different related commercially-available pigments all based on the same type of chromophore. Of these, only a few—if any—are suitable for use in original automotive finishes because of the rigorous performance criteria which such compounds must meet. These pigments must have excellent light-fast characteristics, be able to withstand the temperatures used in the baking process, be insoluble in the various solvents used, fulfill consumer desire for vivid "glamorous" colors, and satisfy other product-specific considerations. If a particular pigment type is indicated, it is thus likely that one can at least narrow the list of possibilities—if not identify the specific member—based on just a portion of the complete spectrum, because the number of possibilities is rather limited.

As noted, when a particular pigment was indicated or identified in this study, all of the available automotive pigments of that type were collected, including those intended for use primarily in refinishes (these may have different heat stability properties from those used in original finishes because they are usually subject to a lower temperature—or no—baking process). Some non-automotive pigments of the same family may also have been used, especially if only one or two of that type were used for automobiles, to provide a better measure of the distinguishing characteristics of the pigment absorptions.

A number of sources and references were used to determine which organic pigments have been, or are currently used, in automobile finishes. They include *Surface Coatings Vol. 1* (3), *Automotive Coatings* (4), *Organic Pigments* (6), *Automotive Paints and Coatings* (8), and information provided by automotive paint and pigment manufacturers (14,15).

Results and Discussion

The structures of the benzimidazolone pigments which are discussed in this work are given in Fig. 1. These compounds, which are classified as monoazo pigments, all contain the benzimidazolone and phenylazo moieties but they consist of two types. Compounds I–V, which are yellow or orange, contain an acetoacetyl portion whereas compounds VI–IX, which are red or brown, contain a 2-hydroxynaphthoic acid amide group. Infrared spectra of the nine are depicted in Fig(s). 2 and 3 for the 3500–2700 cm^{-1} and 1800–200 cm^{-1} regions. The first seven of these pigments (I–VII) are used for automobile finishes and their absorption frequencies are listed in Table 1.

The method of describing topcoat color for this work is similar to that used previously (2): the generic colors (red, orange, and so forth) are those used in the Reference Collection, whereas more specific descriptions of shade (e.g., *maroon*) are given in italics. New topcoat colors added to the Reference Collection after 1982 were not given generic color designations, but these were assigned to a color category based on comparisons to previous panels.

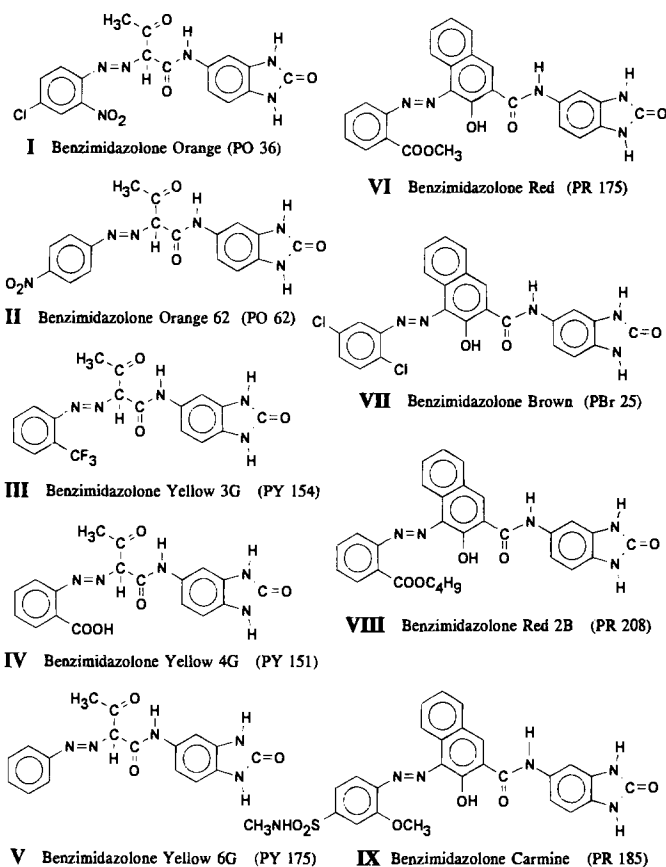


FIG. 1—Structures of the benzimidazolone pigments which are discussed in this work. The Color Index designation of each pigment is given in parentheses (PO = pigment orange, PY = pigment yellow, PR = pigment red, and PBr = pigment brown).

Binder Spectral Window Regions

Spectra of five topcoats that contain primarily absorptions of binder alone, or binder and titanium dioxide, are depicted in Fig(s). 4a, 5a, 6a, 7a, and 8a. For an acrylic melamine enamel binder, the main spectral windows include (Fig. 4a): the region above 3100 cm^{-1} , 1710–1600 cm^{-1} (between the strong carbonyl and melamine absorptions), and 900–200 cm^{-1} excluding the regions where the relatively sharp absorptions (16) of melamine (815 cm^{-1}) and styrene (760 cm^{-1} and 700 cm^{-1}) occur. Although strong binder features are observed between 1400 cm^{-1} and 900 cm^{-1} , pigment peaks can also usually be seen superimposed on the broader binder absorptions, when significant amounts of pigment are present (see for example Fig(s). 4b and 6b).

The spectral windows are wider for acrylic lacquer binders, and they include (Fig. 5a): the region above 3000 cm^{-1} , 1710–1520 cm^{-1} , and most of the region below 1000 cm^{-1} . The stronger pigment peaks may also be observed between, or superimposed on, the two binder absorptions at 1450 cm^{-1} and 1370 cm^{-1} (see Fig. 5b). When appreciable amounts of titanium dioxide are used with either type of binder, most of the region below 800 cm^{-1} is lost as a window, but very weak pigment features can sometimes still be seen superimposed on the very broad titanium dioxide absorption (see Fig(s). 6b, 7b, and 8b).

Benzimidazolone Orange

The spectrum of an orange nonmetallic acrylic melamine enamel topcoat (NN80G0633) which contains prominent pigment absorptions is depicted in Fig. 4b. As a comparison, the spectrum of

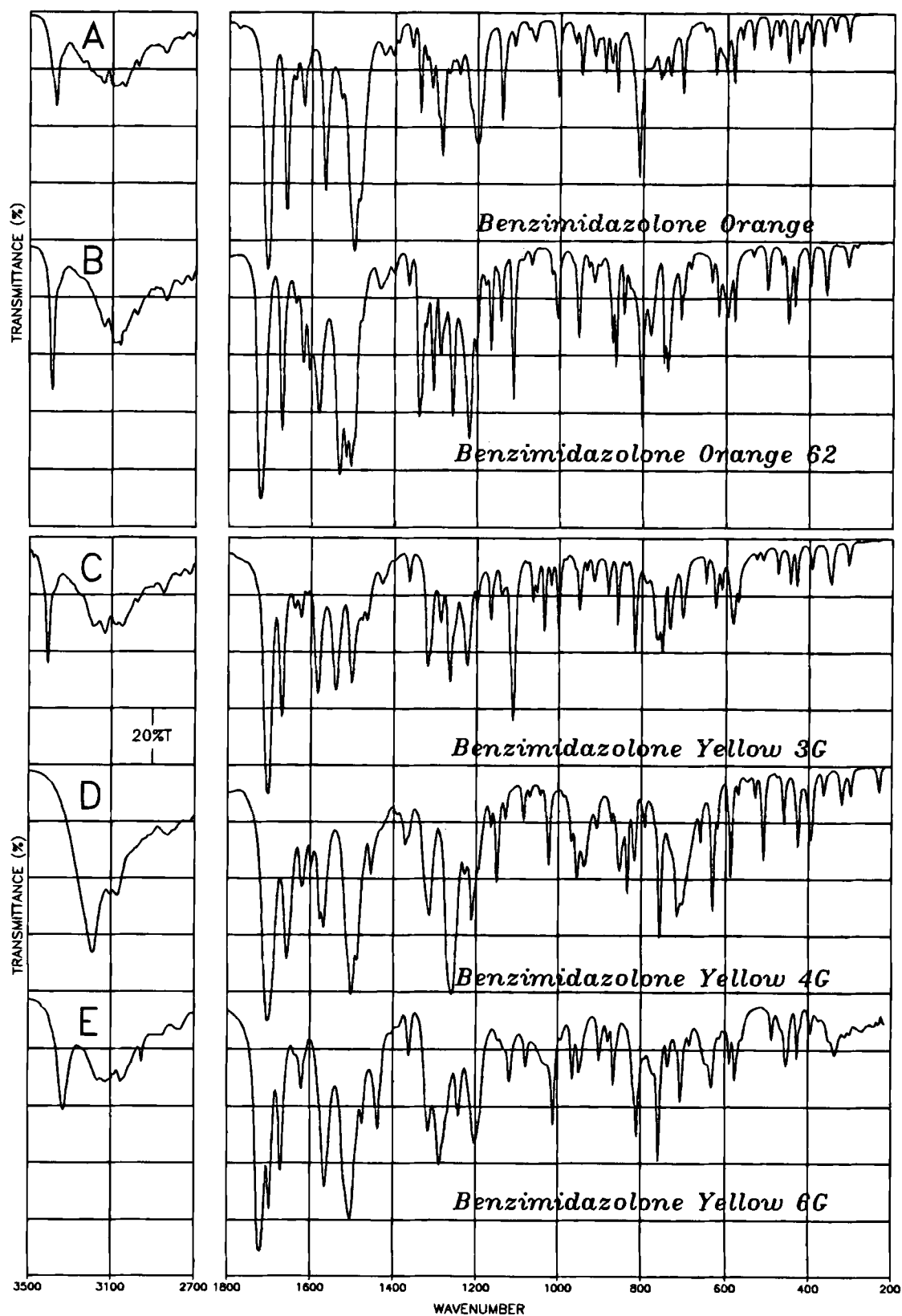


FIG. 2.—Spectra of five benzimidazolone automotive pigments: (a) Benzimidazolone Orange; (b) Benzimidazolone Orange 62; (c) Benzimidazolone Yellow 3G; (d) Benzimidazolone Yellow 4G; and (e) Benzimidazolone Yellow 6G.

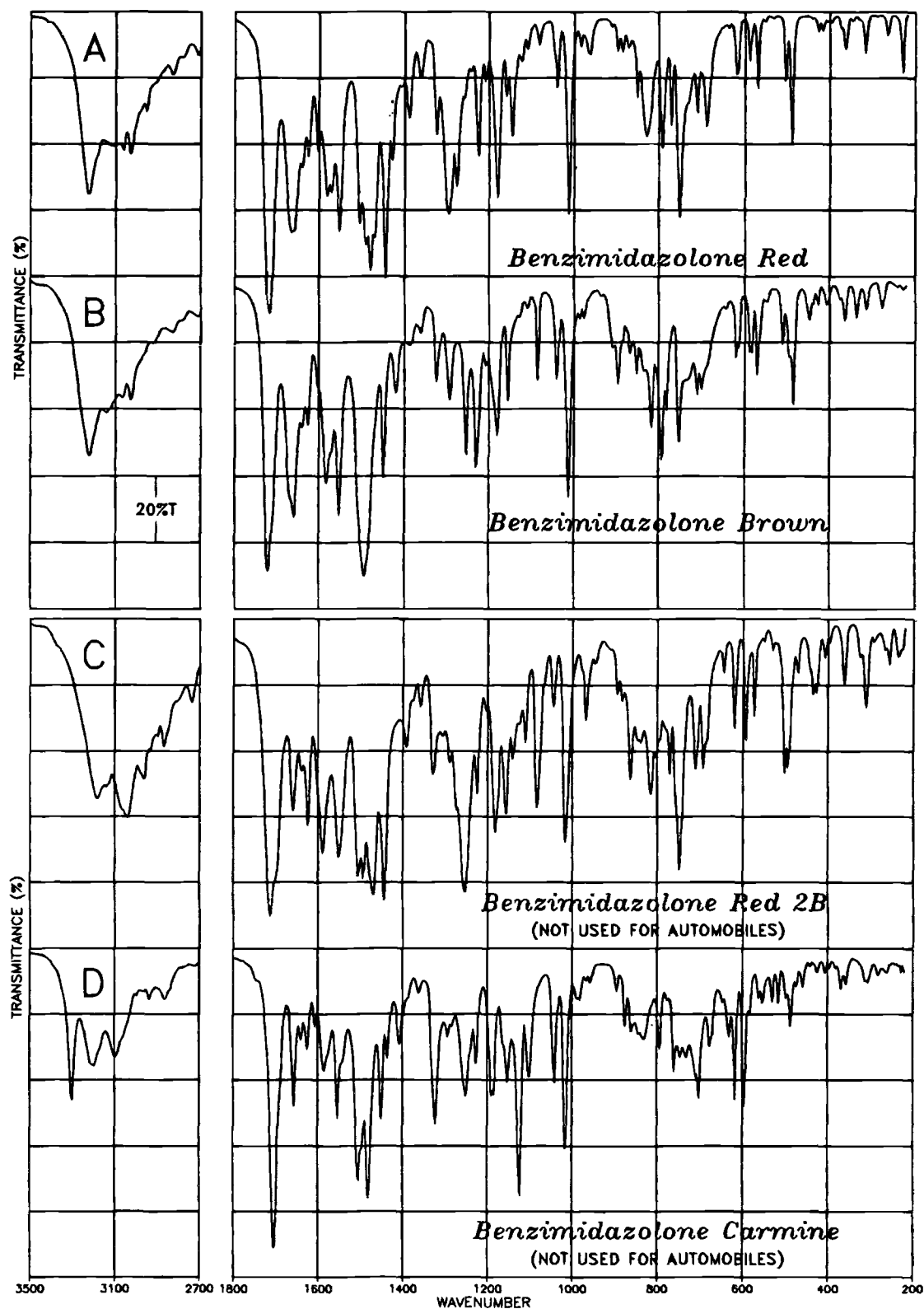


FIG. 3—Spectra of four benzimidazolone pigments: (a) Benzimidazolone Red; (b) Benzimidazolone Brown; (c) Benzimidazolone Red 2B; and (d) Benzimidazolone Carmine. The first two are automotive pigments.

TABLE 1 - *Infrared absorption frequencies of benzimidazolone automotive pigments.*

Pigment ^a	Infrared Absorption Frequencies ^b	Comments
Benzimidazolone Orange (I) <i>Figs. 2a, 4d, 9b</i>	3372m, 3300-2800vb: (3243, 3204, 3142, 3042, 2976, 2841, 2768, 2716), 2010vw, 1933vw, 1844vw, 1775vw, 1705vs, 1659s, 1640vw, 1618w, 1566m, 1530vw, 1499s, 1482sh, 1425w, 1404w, 1391vw, 1358w, 1339m, 1323vw, 1310w, 1294sh, 1285m, 1269vw, 1242w, 1200m, 1142m, 1111w, 1076vw, 1061w, 1005m, 963w, 947w, 916w, 891w, 876w, 862w, 810m, 760w, 752sh, 735w, 706w, 652vw, 627w, 602w, 583w, 563w, 536w, 496w, 475w, 451w, 428w, 421sh, 395w, 368w, 341w, 309w	Identified in some orange, red, and brown nonmetallic Reference Collection topcoats.
Benzimidazolone Orange 62 (II) <i>Figs. 2b, 9d</i>	3389m, 3300-2700vb: (3136, 3061, 2980, 2839, 2768, 2722, 2688), 2446vw, 2224vw, 2014vw, 1975vw, 1904vw, 1856vw, 1796vw, 1721vs, 1670s, 1638w, 1618w, 1605w, 1582m, 1532s, 1516s, 1505s, 1433w, 1402vw, 1366w, 1341m, 1323vw, 1306m, 1289w, 1260m, 1219s, 1202w, 1181vw, 1167w, 1142w, 1113m, 1090vw, 1069w, 1018vw, 1005w, 953w, 930vw, 916vw, 903vw, 872m, 864m, 845w, 829sh, 802s, 781w, 748m, 739m, 708w, 685vw, 635w, 617w, 594w, 579w, 534vw, 500w, 467vw, 449w, 434w, 397w, 359w, 307w, 285vw	For use in nonmetallic automotive paints. A newer pigment which was not identified in any Reference Collection topcoats.
Benzimidazolone Yellow 3G (III) <i>Figs. 2c, 6d, 10b</i>	3478vw, 3407m, 3300-2700vb: (3187, 3133, 3079, 3050, 2976, 2851, 2776, 2726), 2004vw, 1962vw, 1927vw, 1894vw, 1862vw, 1811vw, 1701vs, 1670s, 1640w, 1624w, 1609vw, 1584m, 1541m, 1503m, 1476vw, 1464w, 1427w, 1364w, 1317m, 1287w, 1265m, 1223m, 1200w, 1165w, 1140w, 1111s, 1078vw, 1063w, 1053w, 1036m, 1018w, 1001m, 984vw, 961sh, 951w, 934w, 914w, 882w, 858m, 839vw, 816m, 789w, 762m, 750m, 733w, 704w, 648w, 625w, 611w, 583m, 571w, 527vw, 511vw, 476w, 446w, 430w, 394w, 347w, 305w	Identified in some yellow nonmetallic Reference Collection topcoats and also in one orange nonmetallic Reference Collection topcoat.
Benzimidazolone Yellow 4G (IV) <i>Figs. 2d, 8d, 10d</i>	3187s, 3104sh, 3071sh, 2041vw, 1964vw, 1937vw, 1910vw, 1848vw, 1823vw, 1701vs, 1657s, 1620w, 1599w, 1578m, 1568m, 1501s, 1487sh, 1454w, 1391vw, 1371w, 1314m, 1260s, 1227vw, 1211m, 1165vw, 1150w, 1128vw, 1084w, 1069vw, 1044vw, 1022w, 986vw, 968sh, 955w, 937w, 907w, 872vw, 853w, 833w, 816w, 791w, 756m, 716m, 704sh, 660w, 631m, 619vw, 586w, 569vw, 548vw, 529vw, 509w, 459w, 426w, 395w, 365w, 320w, 299w, 230w	Identified in one yellow nonmetallic Reference Collection topcoat. Used mostly for automobile refinishes.
Benzimidazolone Yellow 6G (V) <i>Fig. 2e</i>	3327m, 3300-2700vb: (3163, 3125, 3052, 2951, 2853, 2772), 2022vw, 1983vw, 1858vw, 1721vs, 1697s, 1670m, 1636vw, 1620w, 1564s, 1503s, 1474w, 1437m, 1362w, 1316m, 1289m, 1242w, 1204m, 1146vw, 1117w, 1078w, 1011m, 991vw, 964w, 949w, 901w, 880vw, 866w, 810m, 770vw, 758m, 737w, 706w, 685vw, 644sh, 633w, 613vw, 588w, 577w, 488w, 453w, 428w, 394w, 376vw, 349sh, 336w, 312vw, 301vw, 270vw	Mostly used for industrial paints but may be found in automotive paints.
Benzimidazolone Red (VI) <i>Fig. 3a</i>	3414vw, 3227m, 3200-2700vb: (3063, 3028, 2953, 2832, 2710), 2025vw, 1960vw, 1821vw, 1717vs, 1665s, 1640sh, 1624w, 1601w, 1582m, 1572m, 1553s, 1505m, 1489s, 1479s, 1470sh, 1445s, 1429w, 1389w, 1364w, 1325w, 1294m, 1277m, 1260sh, 1244vw, 1225w, 1209vw, 1181m, 1159w, 1146w, 1223vw, 1109vw, 1082vw, 1040w, 1013s, 984vw, 963w, 910vw, 897vw, 885vw, 872vw, 851w, 829m, 793m, 772m, 752s, 710w, 689w, 637vw, 621w, 588w, 569w, 505w, 490m, 426vw, 417vw, 395vw, 363w, 345vw, 316w, 264w, 230w	For use in basecoat layers of basecoat/clearcoat automotive finishes. Intended primarily for metallic finishes.

TABLE 1 - *Continued*

Pigment ^a	Infrared Absorption Frequencies ^b	Comments
Benzimidazolone Brown (VII) <i>Figs. 3b, 13b</i>	3223s, 3200-2700vb: (3142, 3067, 3027, 2832, 2710), 2025vw, 1969vw, 1954vw, 1927vw, 1904vw, 1865vw, 1821vw, 1721vs, 1659s, 1640w, 1626w, 1582s, 1553s, 1493vs, 1449s, 1420w, 1387vw, 1362vw, 1325m, 1292m, 1254s, 1231s, 1208vw, 1181m, 1155m, 1128vw, 1109vw, 1086m, 1040m, 1013s, 986vw, 976vw, 936vw, 907sh, 895m, 866w, 851w, 833sh, 816m, 793m, 781w, 752m, 710m, 700m, 644vw, 621w, 615w, 588w, 583w, 571m, 546vw, 511w, 494sh, 484m, 448w, 440sh, 426w, 407w, 376sh, 365w, 338w, 314w, 278w	Identified in two dark brown metallic Reference Collection topcoats.

^aThe figure number(s) in which the spectrum of this pigment appears is given in italics.

^bGiven in wavenumbers. The relative intensity of each absorption is given after its frequency. The abbreviations are: vs = very strong (this is used for the strongest absorption in the spectrum), s = strong, m = medium, w = weak, vw = very weak, sh = a shoulder peak; and vb = very broad. Most of the pigments have a very broad absorption above 2500cm⁻¹ and the frequency range in which this occurs is listed; this is followed by a colon, and in parentheses are listed the fine structure peaks which are superimposed on this broad feature.

a similar blue metallic topcoat (NN80L0637) lacking noticeable pigment absorptions is shown in Fig. 4a. Many of the pigment peaks, which occur throughout the spectrum, are labeled with their frequencies. The results of a spectral subtraction of NN80G0633 minus NN80L0637 (spectrum of Fig. 4a subtracted from that of Fig. 4b) are depicted in Fig. 4c. The observed absorptions of this difference spectrum match those of Benzimidazolone Orange (I), shown in Fig. 4d. Many of the absorptions below 1400 cm⁻¹ are weak, but they may be seen better in expanded views of the subtraction result and the pigment spectrum depicted in Figs. 9a and 9b, respectively. Essentially all of the absorptions of Benzimidazolone Orange may be seen in the difference spectrum and the wavenumber values⁴ are all within 2 cm⁻¹ of each other, except in one case in which a difference of 4 cm⁻¹ occurs. This very close correspondence in peak frequencies—and in most cases relative peak intensities—can be compared to the differences which occur for the absorptions of the related structures shown in Fig(s). 2 and 3; the differences between Fig(s). 3a and 3c are particularly noteworthy, because the corresponding structures—VI and VIII—differ only in the length of a side chain.

For the difference spectrum of Fig. 4c, only minor residual binder features occur. The observed pigment absorptions appear to be largely unaffected by the binder and a significant amount of minor and subtle detail can be seen in the difference spectrum, including the presence of very weak peaks, shoulder peaks, and band asymmetries (compare Fig(s). 9a and 9b). Note the presence of four very weak overtone/combination bands between 2050 cm⁻¹ and 1750 cm⁻¹ in Fig(s). 4c and 4d; only two of them are evident in the spectrum of Fig. 4b.

The rather surprising quality of this difference spectrum probably reflects not only the efforts to find the best matching subtrahend

spectrum, but also the physical and chemical characteristics of a paint. Such a mixture provides a relatively good system for this type of analysis in view of the analyte/host matrix relationships which are involved: The binder-pigment interactions are likely to be minimal because the pigments are highly insoluble and relatively inert, and the pigment particles are homogeneously dispersed in the binder film.

Figure 5b depicts the spectrum of an orange nonmetallic acrylic lacquer topcoat (NA80G0689) which contains Benzimidazolone Orange, whereas the spectrum of a similar yellow metallic topcoat (NA80H0690) lacking significant pigment absorptions is shown in Fig. 5a. Subtraction results for NA80G0689 minus NA80H0690 are shown in Fig. 5c, and the Benzimidazolone Orange spectrum is shown below in Fig. 5d. Expanded views for the region below 1400 cm⁻¹ are depicted in Fig(s). 9c and 9b. For this difference spectrum, a residual binder feature having a split "first derivative" type appearance (indicative of a binder peak shift) is observed in the carbonyl stretching region, as are some other minor residual binder features. Except for a couple of weak peaks which are obscured, however, all of the pigment peaks are present in the difference spectrum and with one exception, the wavenumber values are within 2 cm⁻¹. From a comparison of the subtraction results for NN80G0633 (Fig. 9a) and NA80G0689 (Fig. 9c) to the spectrum (Fig. 9d) of Benzimidazolone Orange 62 (II), it is clear that this second orange benzimidazolone pigment can be readily eliminated as the source of these absorptions.

Benzimidazolone Yellow 3G

Most of the topcoats which were found to contain Benzimidazolone Orange did not appear to have much rutile. In contrast, almost all of the topcoat spectra for which absorptions of the yellow benzimidazolone pigments were identified also had strong absorptions of rutile (Fig. 6e). The spectrum of a yellow nonmetallic enamel (DC82H0913) which contains Benzimidazolone Yellow 3G (III) and rutile is depicted in Fig. 6b. The subtrahend

⁴The FT-IR instrument used in this work does not add a zero fill to the interferogram, so with a spectral resolution of 4 cm⁻¹, the data points of the spectrum are spaced approximately 2 cm⁻¹ apart. With the exception noted, all of the peak frequencies are therefore within one data point of each other.

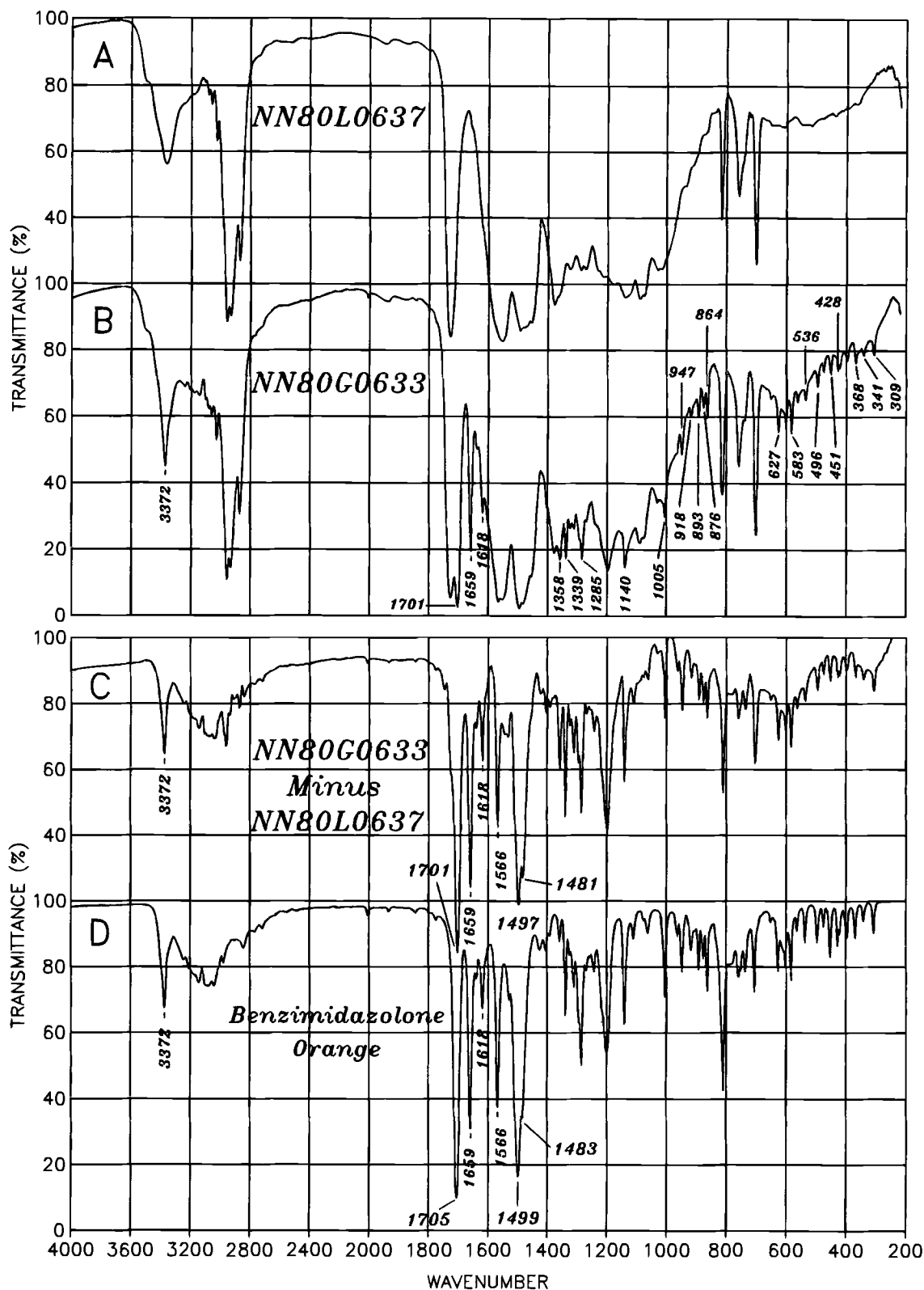


FIG. 4—Spectra of: (a) a blue metallic enamel topcoat, NN80L0637; (b) an orange nonmetallic enamel topcoat, NN80G0633, which contains Benzimidazolone Orange; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Benzimidazolone Orange.

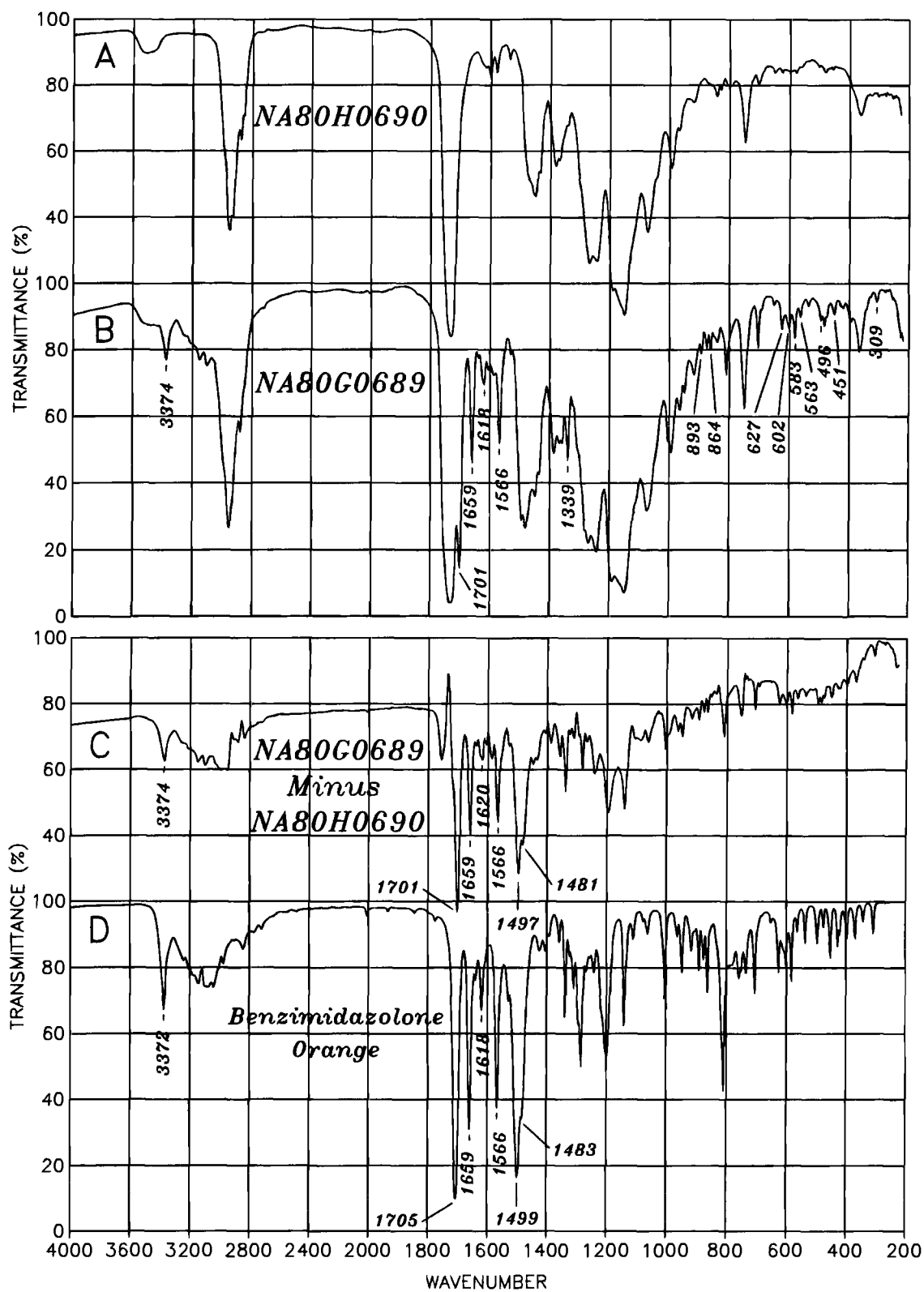


FIG. 5—Spectra of: (a) a yellow metallic acrylic lacquer topcoat, NA80H0690; (b) an orange nonmetallic acrylic lacquer topcoat, NA80G0689, which contains Benzimidazolone Orange; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Benzimidazolone Orange.

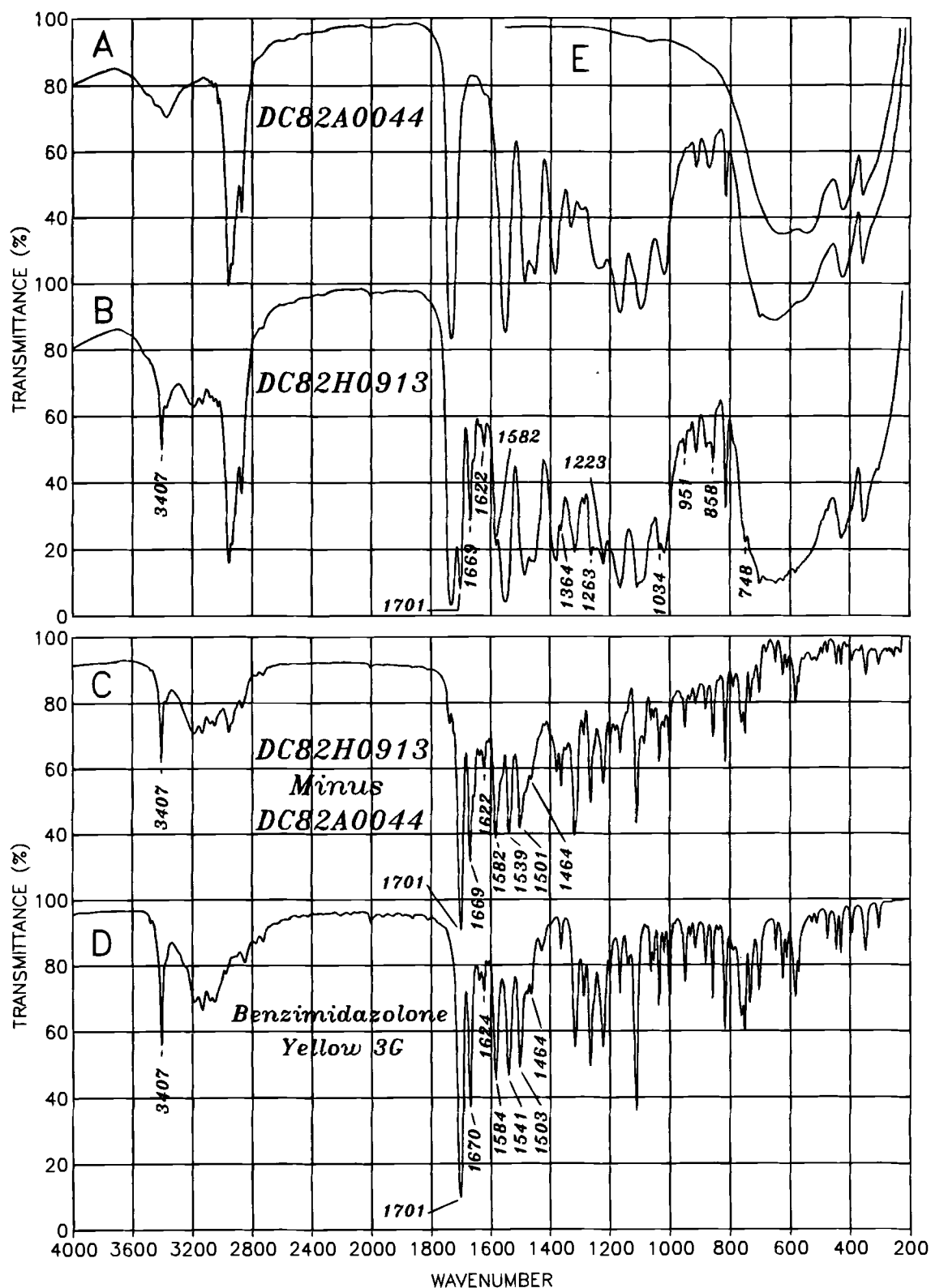


FIG. 6—Spectra of: (a) a white nonmetallic enamel topcoat, DC82A0044, which contains rutile; (b) a yellow nonmetallic enamel topcoat, DC82H0913, which contains Benzimidazolone Yellow 3G and rutile; (c) subtraction results—spectrum (b) minus spectrum (a); (d) Benzimidazolone Yellow 3G; and (e) rutile, diluted with CsI and sampled in the DAC.

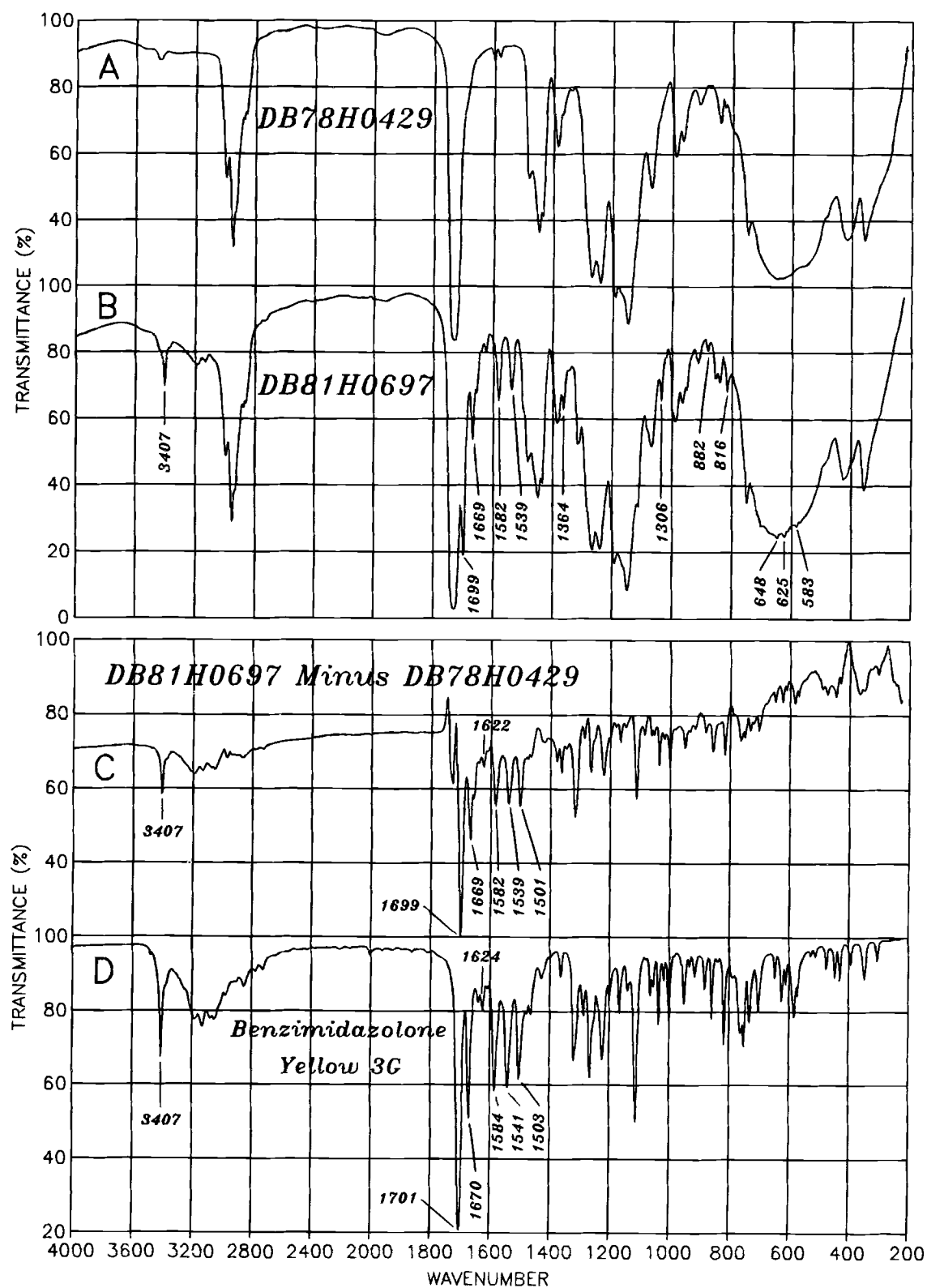


FIG. 7—Spectra of: (a) a yellow nonmetallic acrylic lacquer topcoat, DB78H0429, which contains rutile; (b) a yellow nonmetallic acrylic lacquer topcoat, DB81H0697, which contains Benzimidazolone Yellow 3G and rutile; (c) subtraction results—spectrum (b) minus spectrum (a); and (d) Benzimidazolone Yellow 3G.

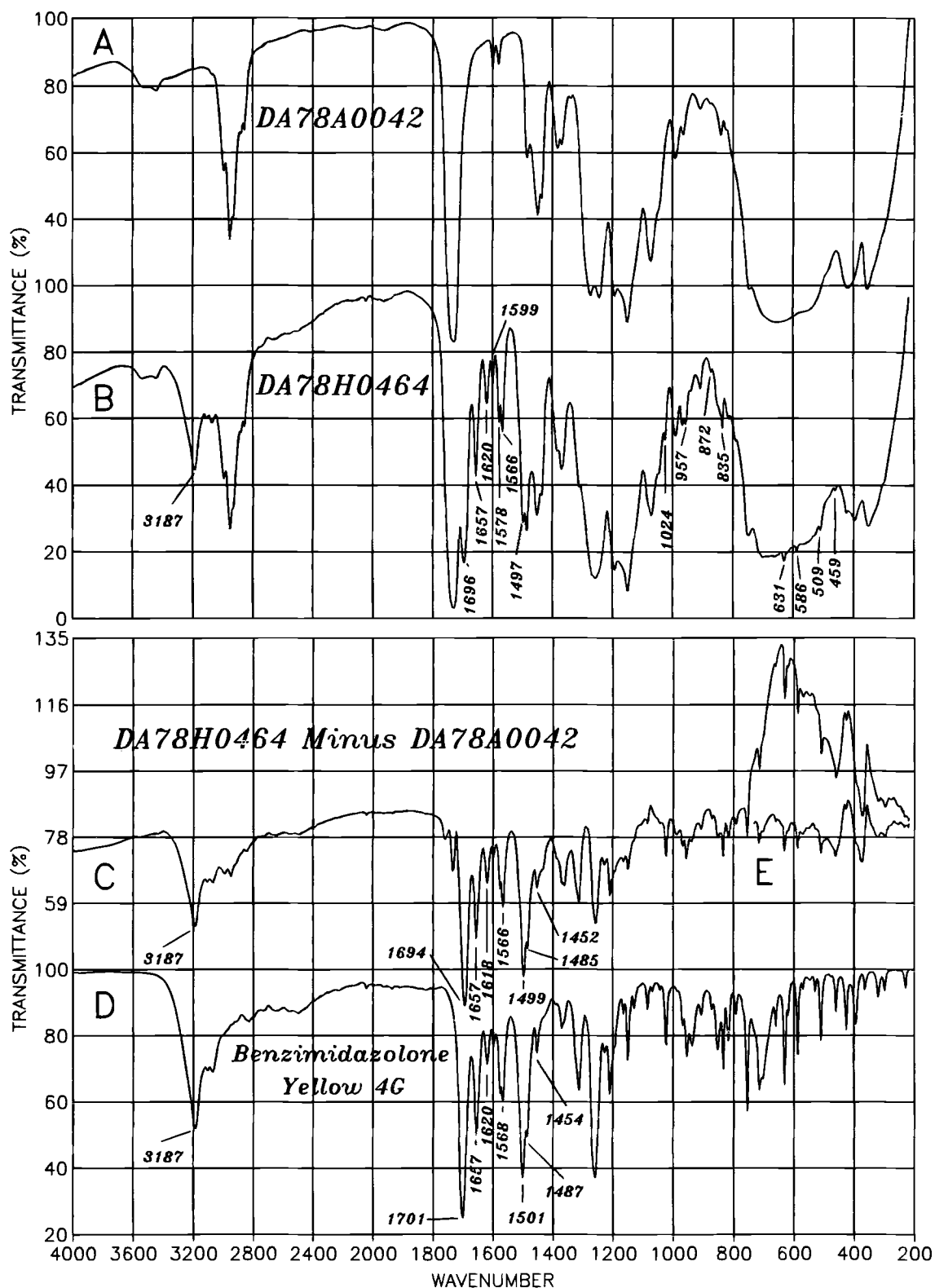


FIG. 8—Spectra of: (a) a white nonmetallic acrylic lacquer topcoat, DA78A0042, which contains rutile; (b) a yellow nonmetallic acrylic lacquer topcoat, DA78H0464, which contains Benzimidazolone Yellow 4G and rutile; (c) subtraction results—spectrum (b) minus spectrum (a); (d) Benzimidazolone Yellow 4G; and (e) a portion of the spectrum of (c) after its baseline was flattened using a three point baseline correction.

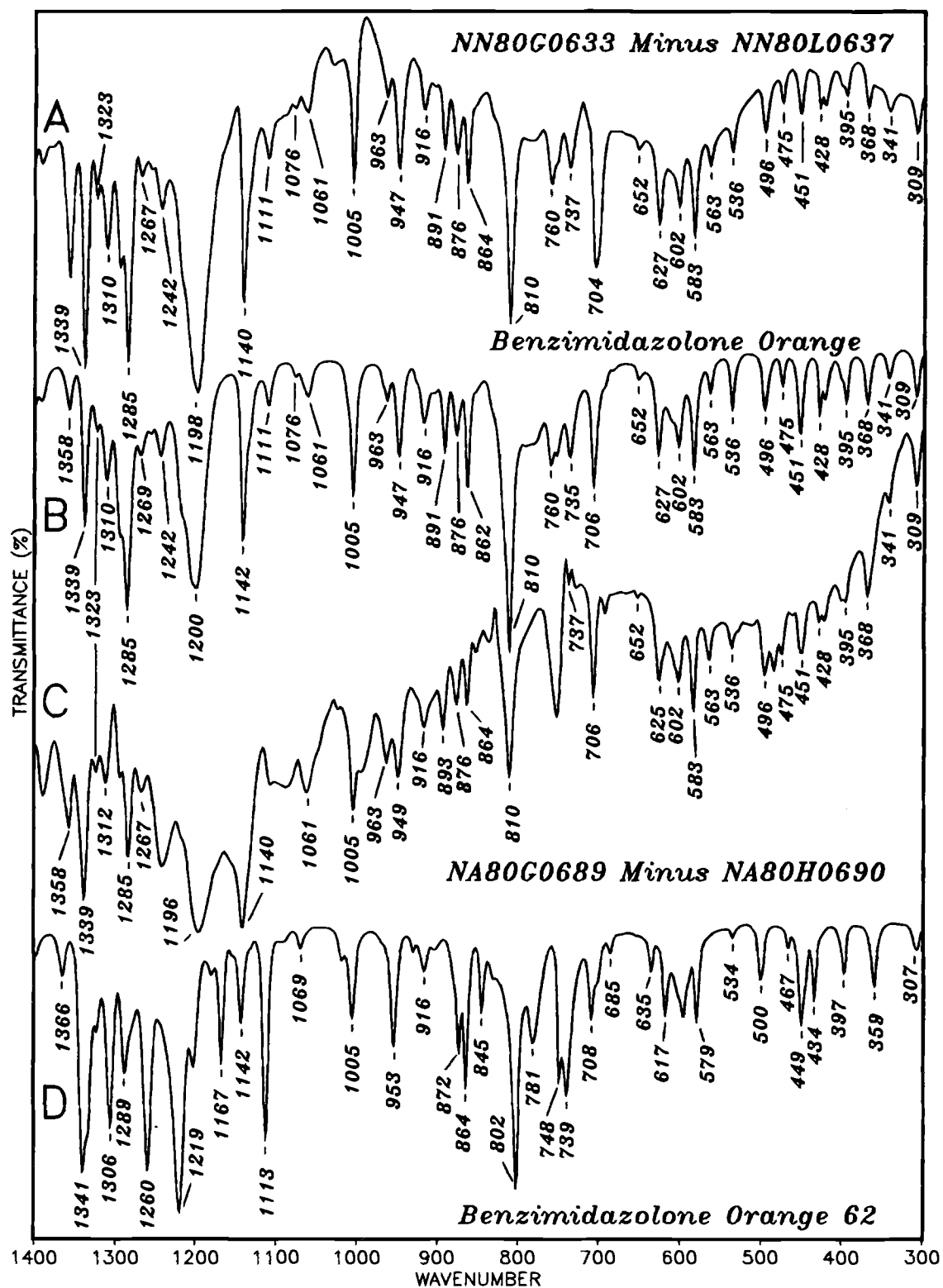


FIG. 9—Spectra in the 1400–300 cm^{-1} region: (a) difference spectrum of NN80G0633 minus NN80L0637 (an expanded view of Fig. 4c); (b) Benzimidazolone Orange; (c) difference spectrum of NA80G0689 minus NA80H0690 (an expanded view of Fig. 5c); and (d) Benzimidazolone Orange 62.

spectrum, taken of a white nonmetallic enamel (DC82A0044) having a similar binder and a similar amount of rutile, is shown in Fig. 6a. The difference spectrum (Fig. 6c) matches that of Benzimidazolone Yellow 3G (Fig. 6d); expanded views of these spectra are shown in Fig(s). 10a and 10b. Again, essentially all of the Benzimidazolone Yellow 3G absorptions are seen for the subtraction results and their peak frequencies all are within 2 cm^{-1} of each other.

The relative intensities of the lower frequency absorptions of Fig. 6c are diminished somewhat compared to those of the pigment (Fig. 6d), and this appears to be true for some of the other subtraction results as well. This diminution arises from differences in the spectral measurement processes which occur with transmittance and DRIFTS analyses. For DRIFTS (11), the lower frequencies of the sampling radiation are scattered less than the higher ones; these frequencies therefore penetrate deeper into the powder and experience a greater average pathlength. Pigment reference spectra, which were all obtained using DRIFTS, may thus have greater relative intensities for the low frequency absorptions. DRIFTS spectra may also exhibit some other relative intensity differences (11) between strong and weak absorptions compared to transmittance spectra (the reason for using DRIFTS for these pigments is discussed later). Another source of apparent variations between peak intensities is the logarithmic scale of the transmittance presentation. All of the aforementioned factors produce systematic differences that affect the entire spectrum; individual peak variations are usually caused by residual binder features.

The spectrum of a yellow nonmetallic acrylic lacquer (DB81H0697) which contains Benzimidazolone Yellow 3G is shown in Fig. 7b, together with the subtrahend spectrum (Fig. 7a, taken of a *beige* nonmetallic topcoat, DB78H0429), the difference spectrum (Fig. 7c), and Benzimidazolone Yellow 3G (Fig. 7d). An expanded view of the difference spectrum is shown in Fig. 10c. Except for a couple of weak peaks which are obscured, all of the pigment peaks can be seen in the difference spectrum with frequency values within 2 cm^{-1} of those of the pigment reference spectrum.

In addition to weak residual binder features, including the "split carbonyl" near 1730 cm^{-1} , the difference spectrum of Fig. 7c has two inverted peaks with maxima at 404 cm^{-1} and 274 cm^{-1} . These are not residues of rutile fine structure absorptions, which occur at 422 cm^{-1} and 357 cm^{-1} (see Fig. 6e), but are manifestations of the presence of a small amount of hydrous ferric oxide in the *beige* topcoat (DB78H0429) of the subtrahend spectrum, and its absence in DB81H0697. The two main absorptions of hydrous ferric oxide, a yellow inorganic pigment, occur at 405 cm^{-1} and 278 cm^{-1} (Fig. 11d). In prior work of this study, it was found that the spectra of 15 to 20% of Reference Collection yellow nonmetallic topcoats contained identifiable absorptions of hydrous ferric oxide (2). The actual fraction of yellow topcoats which contain this pigment, however, is probably much higher because a large number of other topcoats—especially those having pale yellow, *beige*, or *off-white* shades—also appeared to contain small quantities of hydrous ferric oxide (presumably used for tinting). The spectra of such topcoats had, to varying degrees, indications of hydrous ferric oxide absorptions, but these were not deemed sufficiently distinct to include these topcoats in this conservative count (determination of minimum "degree of distinctiveness" criteria for inclusion in such a survey is necessarily arbitrary when the measurement in question falls within a continuum of ranges—as appears to be the case for the amount of this pigment which is used in topcoats).

At first glance, the spectrum of DB78H0429 (Fig. 7a) appears to have little indication of the presence of hydrous ferric oxide, but from a comparison to the spectrum of DB81H0697 (Fig. 7b), a shoulder protrusion near 280 cm^{-1} and a more rounded low frequency shoulder for the rutile 430 cm^{-1} absorption may be seen for DB78H0429. These subtle differences are inconspicuous, but they do become more apparent in the difference spectrum.

Benzimidazolone Yellow 4G

The spectrum of a yellow nonmetallic acrylic lacquer (DA78H0464) which contains rutile and another benzimidazolone yellow pigment, Benzimidazolone Yellow 4G (IV), is depicted in Fig. 8b. The subtrahend spectrum (Fig. 8a) was taken of a white nonmetallic topcoat, DA78A0042, which also contains rutile; note, however, that relative to binder absorptions (such as the acrylate ester pair between 1300 cm^{-1} and 1100 cm^{-1}), the rutile absorption for this spectrum is stronger compared to that of Fig. 8b. This results in a broad negative peak for the difference spectrum shown in Fig. 8c. This region was flattened using a three point baseline correction, and this flattened portion is depicted in Fig. 8e. The absorptions of this difference spectrum match those of Benzimidazolone Yellow 4G (Fig. 8d); expanded views are depicted in Fig(s). 10d–10f. All of the pigment absorptions, except for a couple of weak ones in the rutile-absorbing region (Fig. 10f), may be seen in the difference spectrum, and the wavenumber values of all except one are within 2 cm^{-1} of those of the pigment reference spectrum. Benzimidazolone Yellow 4G was not identified in any Reference Collection topcoats having acrylic melamine enamel binders.

Benzimidazolone Brown

Benzimidazolone Brown (VII) is a red-brown pigment which is used for metallic finishes. Because the metal flakes normally provide much of the hiding power for such finishes, the pigment concentrations which are used for these topcoats are often less than those used for nonmetallic ones. Consequently, the intensities of organic pigment absorptions which are observed in the spectra of metallic topcoats are usually weaker than those observed for nonmetallic topcoats having similar colors.

The spectrum of a dark brown metallic topcoat, DC82F0915, which contains Benzimidazolone Brown is depicted in Fig. 12b. For comparison, the spectrum of a similar blue metallic topcoat (DC82L0866) which lacks observable pigment peaks is depicted in Fig. 12a. The spectrum of Fig. 12b has several weak peaks (labeled with their frequencies) which are not observed for Fig. 12a. Subtraction results for DC82F0915 minus DC82L0866 are shown in Fig. 13a, and this difference spectrum may be compared to the spectrum of Benzimidazolone Brown (Fig. 13b). As might be expected, residual binder features are more prominent for this subtraction result because the pigment peaks are weak compared to binder absorptions. The majority of the Benzimidazolone Brown peaks can still be observed, however, and with one exception, their frequencies are within 2 cm^{-1} of those of the pigment spectrum. Even for this subtraction result, many of the very weak peaks and subtle features of the pigment absorptions can be discerned (compare Fig(s). 13a and 13b).

Other Benzimidazolone Automotive Pigments

The four benzimidazolone pigments which were identified in Reference Collection topcoats, along with three others (II, V, and

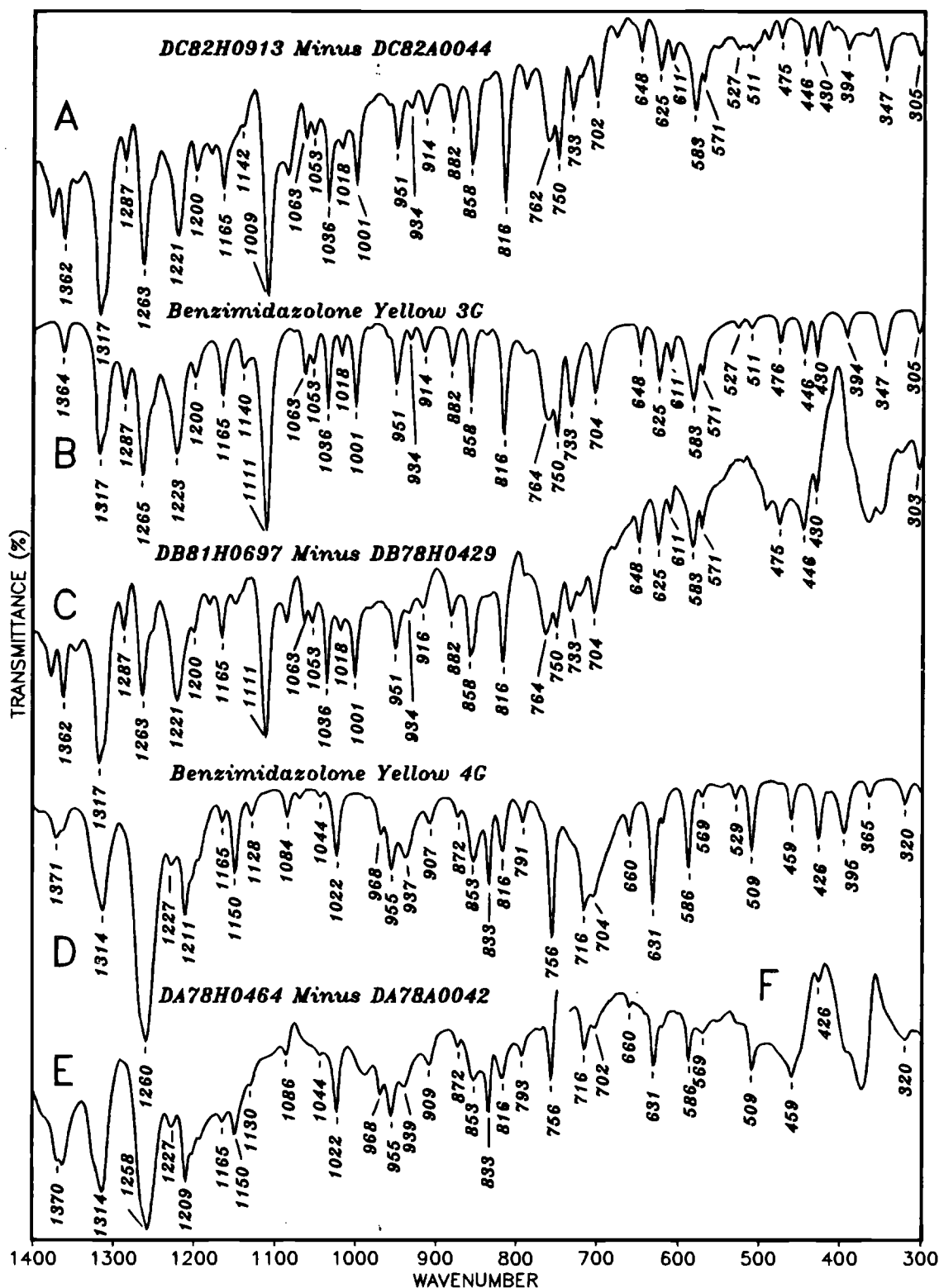


FIG. 10—Spectra in the $1400\text{--}300\text{ cm}^{-1}$ region: (a) difference spectrum of DC82H0913 minus DC82A0044 (an expanded view of Fig. 6c); (b) Benzimidazolone Yellow 3G; (c) difference spectrum of DB81H0697 minus DB78H0429 (an expanded view of Fig. 7c); (d) Benzimidazolone Yellow 4G; (e) difference spectrum of DA78H0464 minus DA78A0042 (an expanded view of Fig. 8c); and (f) a portion of this same spectrum with its baseline flattened (an expanded view of Fig. 8e).

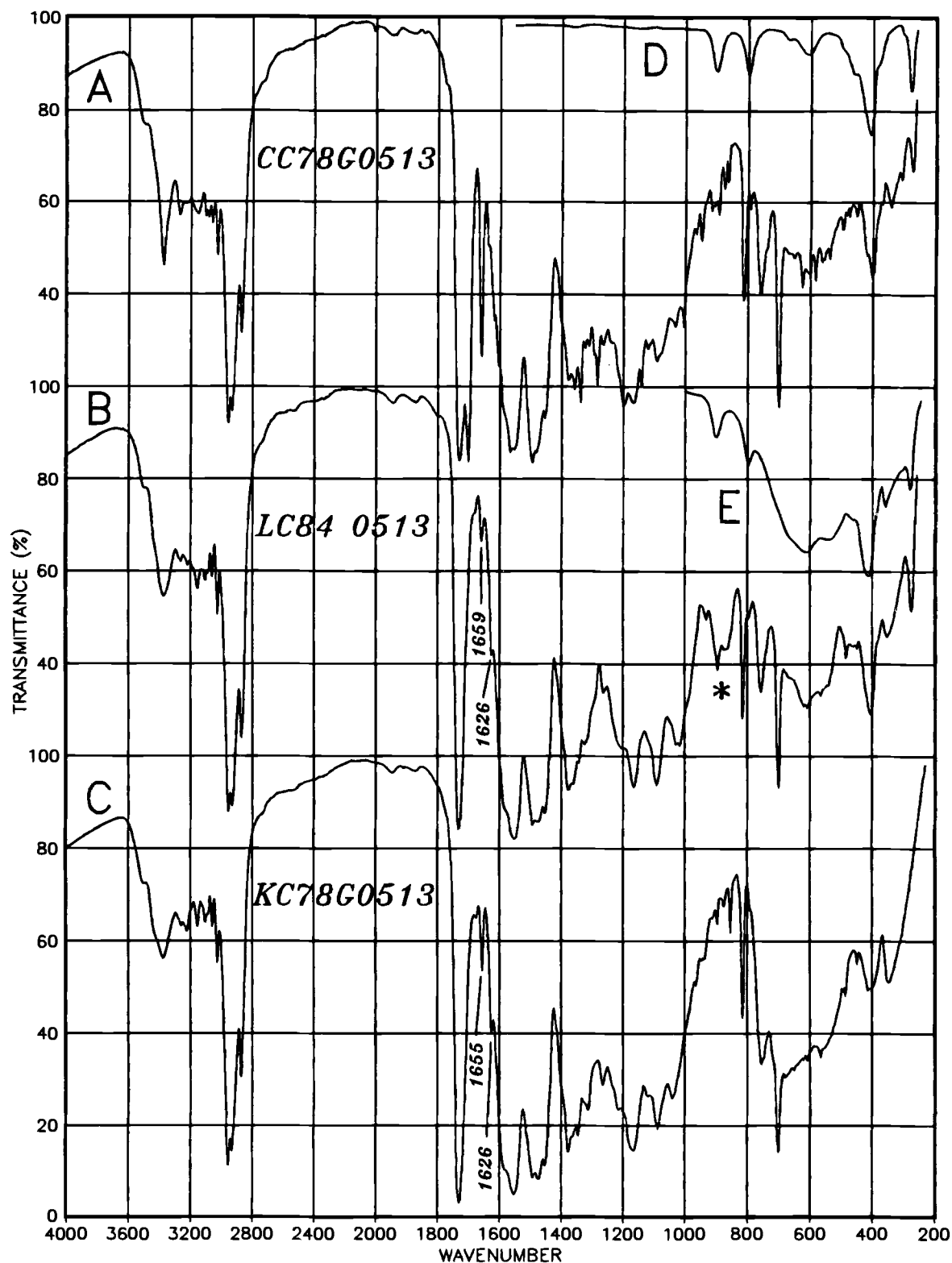


FIG. 11—Spectra of three orange nonmetallic enamel topcoats of color 0513 which all contain rutile: (a) CC78G0513, which also contains Benzimidazolone Orange and hydrous ferric oxide; (b) LC84 0513, which also contains a lead chromate pigment (the absorption of which is marked with an asterisk), hydrous ferric oxide, and a small amount of an unidentified organic pigment; and (c) KC78G0513, which also contains a small amount of an unidentified organic pigment. (d) A portion of the spectrum of hydrous ferric oxide (diluted with CsI and sampled in the DAC). (e) Addition of the absorptions of rutile (Fig. 6e) and hydrous ferric oxide.

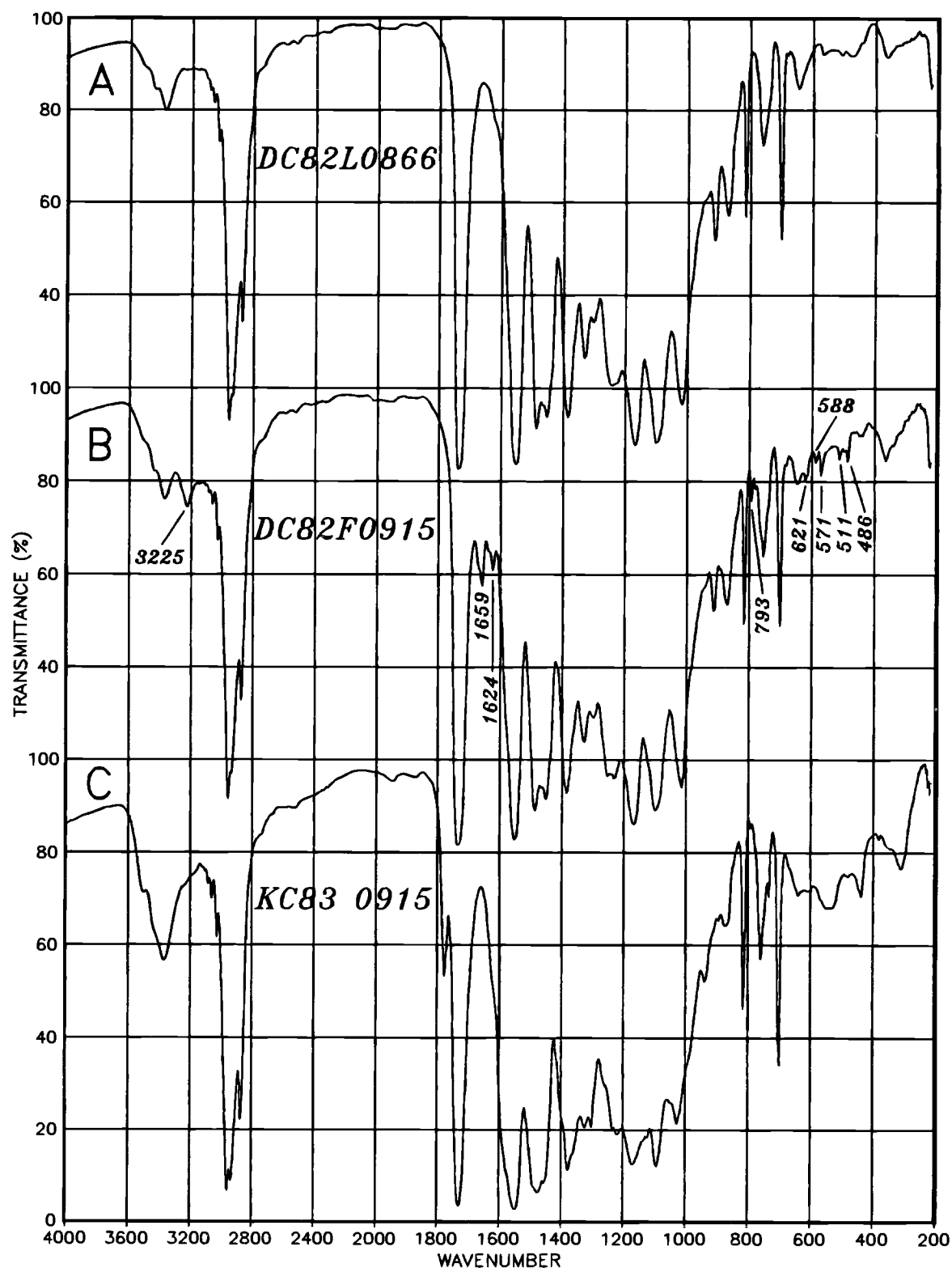


FIG. 12—Spectra of: (a) a blue metallic enamel topcoat, DC82L0866; (b) a brown metallic enamel topcoat, DC82F0915, which contains Benzimidazole Brown; and (c) a brown metallic topcoat, KC83 0915, which has the same color as DC82F0915.

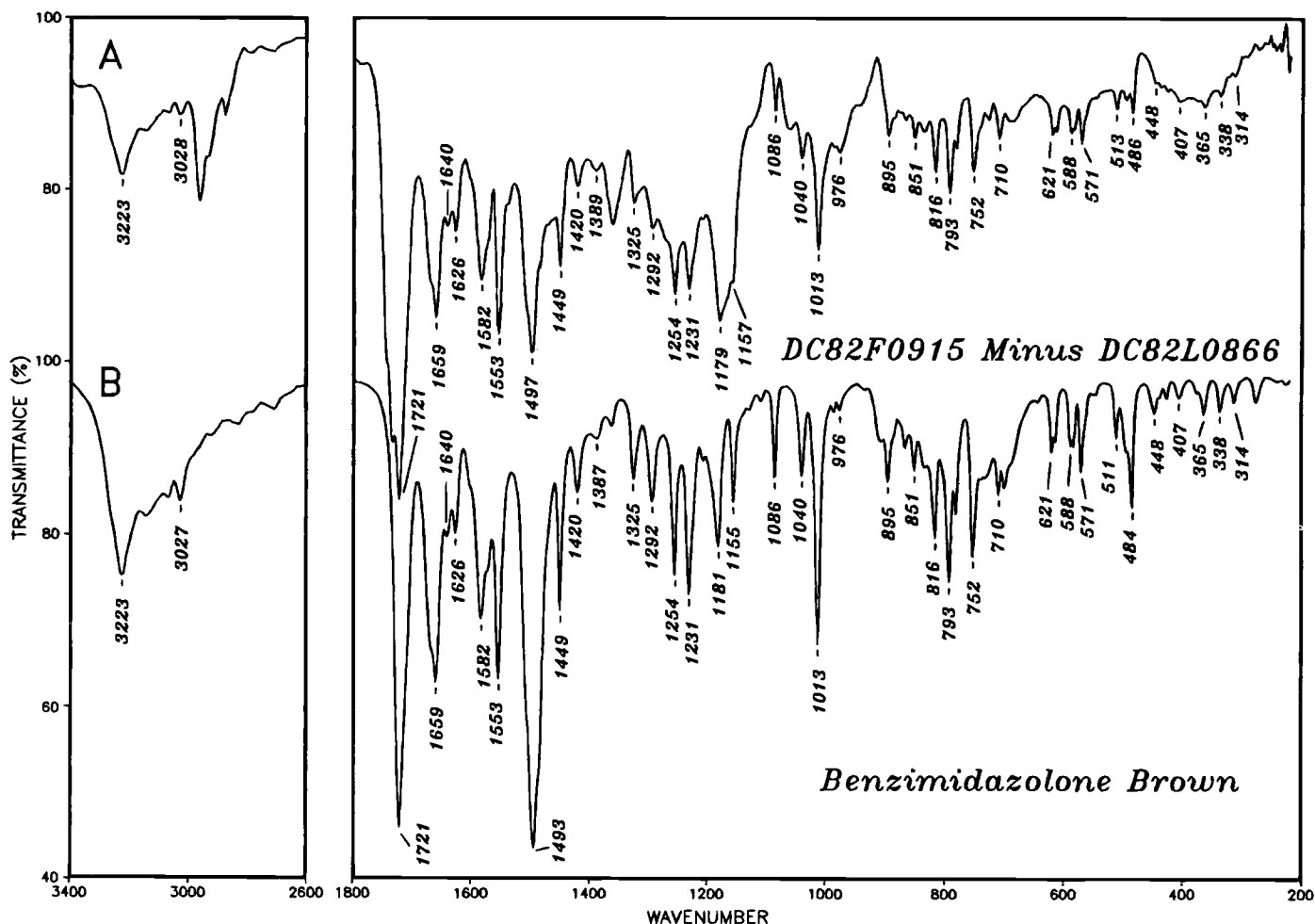


FIG. 13—(a) A difference spectrum resulting from the subtraction of the spectrum depicted in Fig. 12a (DC82L0866) from that shown in Fig. 12b (DC82F0915); and (b) the spectrum of Benzimidazolone Brown.

VI), are currently marketed for use in automotive paints (14). Benzimidazolone Orange 62 (II) is a newer pigment, which may be one of the reasons it was not found in Reference Collection topcoats. It is intended for use in nonmetallic finishes. Benzimidazolone Yellow 6G (V) may be used in automotive topcoats (14), but most of its current sales are for use in industrial paints.⁵ Benzimidazolone Red (VI) is not durable enough for single layer systems, but may be used for basecoat layers of basecoat/clearcoat finishes (6); it is intended⁶ for use primarily in metallic finishes because of its high transparency. Because basecoat/clearcoat finishes were not examined in this study, whether Benzimidazolone Red was used in Reference Collection topcoats is not known. All seven of the benzimidazolone pigments may also be used for automobile refinishes (14).

Recognition and Differentiation of Benzimidazolone Pigment Absorptions in Topcoat Spectra

For each of the benzimidazolone pigments which were identified in Reference Collection topcoats, the most characteristic and recognizable pigment absorption is usually the highest frequency peak above 3100 cm⁻¹ (see Fig(s). 2 and 3). For Benzimidazolone

Orange and Benzimidazolone Yellow 3G, these consist of sharp features at 3372 cm⁻¹ and 3407 cm⁻¹, respectively, which can be observed in spectra of both acrylic melamine enamels (Fig(s). 4b and 6b) and acrylic lacquers (Fig(s). 5b and 7b). Although enamel binders also have a weak broad absorption in this same region (Fig(s). 4a and 6a), the pigment peaks are sharper and can be seen superimposed on the broader binder features. The 3372 cm⁻¹ and 3407 cm⁻¹ peaks are usually quite noticeable because there are few other⁷ paint components which produce such sharp peaks in the spectral region above 3300 cm⁻¹, an area normally characterized by broad absorptions.

Benzimidazolone Yellow 4G and Benzimidazolone Brown have broader features at 3187 cm⁻¹ (Fig(s). 8b and 8d) and 3223 cm⁻¹ (Fig(s). 12b and 13b), respectively, which can also be easily observed for both lacquers and acrylic melamine enamels, although the former pigment does not appear to have been used for any Reference Collection enamels. Unlike the other three benzimidazolone pigments, which were identified as a result of analyzing certain spectra with unknown absorptions, peaks of Benzimidazolone Brown were specifically sought in spectra of metallic topcoats.

⁷The spectrum of talc has a sharp absorption at 3678 cm⁻¹, and while common in primers (16), this inorganic extender pigment occurs in appreciable quantities in only a few black nonmetallic Reference Collection topcoats having semigloss finishes (2).

⁵Hoechst Celanese Corp., personal communication, July 1996.

⁶Hoechst Celanese Corp., personal communication, April 1996.

For this, spectra were first examined for the possible presence of the 3223 cm^{-1} peak, and observation of this feature did, in fact, lead to the identification of this pigment. The high frequency peak should thus be one of the first features to look for when attempting to determine if a benzimidazolone pigment is present.

If one of these absorptions is observed in the spectrum of a yellow, orange, red, or brown nonmetallic, or brown metallic topcoat, the second window region on the low frequency side of the carbonyl stretching absorption should be examined. For a nonmetallic topcoat, the 3372 cm^{-1} feature together with a shoulder peak near 1701 cm^{-1} , a peak at 1659 cm^{-1} , and a weak shoulder at 1618 cm^{-1} for an enamel (Fig. 4b), or these three together with another absorption at 1566 cm^{-1} (having an intensity comparable to the 1659 cm^{-1} peak) for a lacquer (Fig. 5b), are strong indications of the presence of Benzimidazolone Orange. If the 3407 cm^{-1} feature is present together with peaks at 1701 cm^{-1} (shoulder), 1669 cm^{-1} (weak), 1624 cm^{-1} (very weak), and 1582 cm^{-1} (shoulder) for an enamel (Fig. 6b), or these plus a peak at 1541 cm^{-1} for a lacquer (Fig. 7b), Benzimidazolone Yellow 3G is indicated. For the spectrum of a nonmetallic lacquer having absorptions at 3187 , 1696 , 1657 , 1620 , 1599 , 1578 , and 1566 cm^{-1} (Fig. 8b), or a nonmetallic enamel with the first three and possibly shoulders at 1620 and 1599 cm^{-1} , the presence of Benzimidazolone Yellow 4G would be indicated. For a brown metallic topcoat, absorptions at 3225 cm^{-1} , 1659 cm^{-1} (with a noticeable high frequency shoulder) and 1624 cm^{-1} (Fig. 12b) are indicative of Benzimidazolone Brown, although these are likely to be weak absorptions. For all of these pigments, the majority of the aforementioned absorptions are fairly sharp, so the frequency values which are measured should normally be within a few wavenumbers of those cited.

For distinguishing between the seven benzimidazolone automotive pigments, the high frequency features and the second window absorptions should serve to limit the possibilities to, at most, two (compare Fig(s). 2a–2e and Fig(s). 3a and 3b). Benzimidazolone Orange and Benzimidazolone Orange 62 have some similarities in the two regions, but the high frequency feature of the latter occurs at 3389 cm^{-1} and the second window absorptions occur at 1721 , 1670 , 1618 , 1605 cm^{-1} (Fig. 2b). The pair consisting of Benzimidazolone Red and Benzimidazolone Brown (Fig(s). 3a and 3b) may be more difficult to differentiate based solely on absorptions in these two regions, but they can be distinguished by observing absorptions in other regions.

If the high frequency and second window benzimidazolone absorptions are present, the weaker peaks in other regions of the spectrum should be examined to see if they further support the assignment. Some of the peaks which one might expect to observe can be seen in Fig(s). 4b, 5b, 6b, 7b, 8b, and 12b, where they are labeled with their frequencies. Because there are likely to be some differences in binder features, all of these may not necessarily be discernable, or others not seen in these particular spectra may be observed. Benzimidazolone Orange, in particular, has a rich spectrum below 700 cm^{-1} (Fig. 2) and although these peaks are weak, many of them can be observed in topcoat spectra, especially for many enamels (see Fig(s). 4a and 4b). A complete listing of frequencies for the benzimidazolone pigments is given in Table 1.

To illustrate how the benzimidazolone absorptions may be differentiated from those of some other automotive pigments *in situ*, spectra of eight topcoats, each of which contains a different organic pigment, are depicted in Fig. 14 for the 3500 – 2900 cm^{-1} and 1800 – 1200 cm^{-1} regions. Yellow, orange, and red nonmetallic topcoats were used, and most of the pigment peaks are labeled with their frequencies. Topcoats having acrylic melamine enamel

binders were used for all of these examples, except for Fig. 14h, because the second window region for these are narrower—and hence potentially less discriminating—than those of acrylic lacquers. Spectra of topcoats containing Benzimidazolone Orange (Fig. 14a), Benzimidazolone Yellow 3G (Fig. 14b), Benzimidazolone Yellow 4G (Fig. 14h), and five other nonbenzimidazolone pigments are shown. The organic pigment of AC84 0912 (Fig. 14c) has absorptions in the second window somewhat like those of Benzimidazolone Orange (Fig. 14a), although the frequencies and relative intensities are not the same; differences are also apparent in other regions. From a comparison of these eight spectra, it can be seen that even when using only these limited regions, discrimination between different organic pigment absorptions is usually not difficult when more than a cursory examination is conducted.

In cases in which heavy pigment loads are used, a dozen or more organic pigment absorptions, located throughout the spectrum, can often be easily observed in topcoat spectra (see for example, Fig(s). 4b and 5b). As the amount of pigment used decreases, correspondingly fewer absorptions are observed, but some of the weaker ones may still be detected by expanding the appropriate spectral regions. Spectra of two *orange-brown* topcoats which contain Benzimidazolone Orange are shown in Fig. 15: FN83 0642 (Fig. 15b) contains more of this pigment than KN80F0642 (Fig. 15d), and the spectrum of the latter has only weak pigment absorptions. These include (Fig. 15d) a peak at 1659 cm^{-1} , a shoulder at 1701 cm^{-1} , what appears to be a “sharpened” binder feature at 3372 cm^{-1} , and very weak peaks at 1339 , 1285 , 947 , 893 , 878 , 864 , 600 , and 583 cm^{-1} , together with a very weak shoulder at 1616 cm^{-1} . All of these support the presence of Benzimidazolone Orange, as does the detection of chlorine (see structure I in Fig. 1) in this topcoat by elemental analysis (discussed later).

The spectrum of a topcoat (NC82H0913) having even weaker pigment absorptions is shown in Fig. 16c. This topcoat has the same color as DC82H0913, which contains Benzimidazolone Yellow 3G (Fig. 6), and it also appears to contain this same pigment based on the 3407 and 1670 cm^{-1} peaks and the low frequency shoulder (which is not conspicuous) of the carbonyl stretching absorption. None of the other pigment peaks can be observed however.

Occurrence of Benzimidazolone Orange, Benzimidazolone Yellow 3G, Benzimidazolone Yellow 4G, and Benzimidazolone Brown in U.S. Automobile Original Topcoats (1974–1989): Earliest Detected Usage Dates

To determine the extent to which the benzimidazolone pigments were used in single layer U.S. automobile original topcoats (1974–1989), a spectral survey was conducted. The benzimidazolones are used mostly for nonmetallic finishes, and because pigment absorptions are generally more prominent in spectra of such topcoats, this survey was concerned primarily with these finishes. Accordingly, spectra of all of the available nonmetallic single layer finishes in the Reference Collection were obtained between 4000 and 220 cm^{-1} . The usage frequencies which are reported are based on the total number of available topcoats which were sampled, and not on the total number listed in the *Reference Collection of Automotive Paints Technical Data* (17) booklet (7% of the more than 800 single layer nonmetallic yellow, orange, red, and brown topcoats listed in this booklet are not in the Reference Collection).

A more limited survey was conducted of metallic finishes. Most of the ones which were tested were from the Reference Collection color comparison set, although a few chemical supplement panels

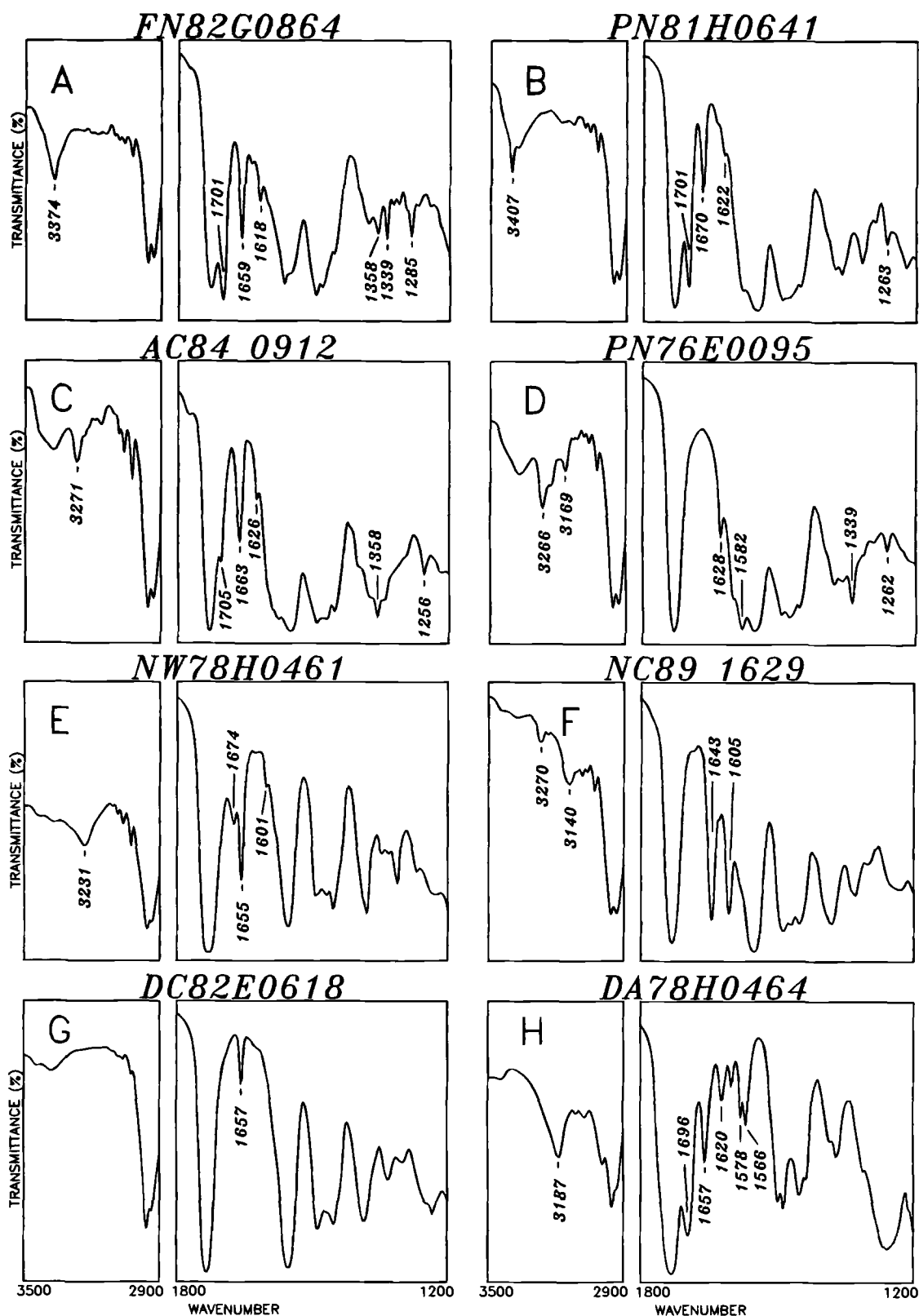


FIG. 14—Spectra in the $3500\text{--}2900\text{ cm}^{-1}$ and $1800\text{--}1200\text{ cm}^{-1}$ regions of eight Reference Collection nonmetallic topcoats, each of which contains a different organic pigment (the color of each topcoat is given in parentheses after its designation code): (a) FN82G0864 (orange), which contains Benzimidazolone Orange; (b) PN81H0641 (yellow), which contains Benzimidazolone Yellow 3G; (c) AC84 0912 (red); (d) PN76E0095 (red); (e) NW78H0461 (yellow); (f) NC89 1629 (red); (g) DC82E0618 (red); and (h) DA78H0464 (yellow), which contains Benzimidazolone Yellow 4G. All of the topcoats have acrylic melamine enamel binders except for DA78H0464, which has an acrylic lacquer binder. Some of the more prominent peaks are labeled with their frequencies.

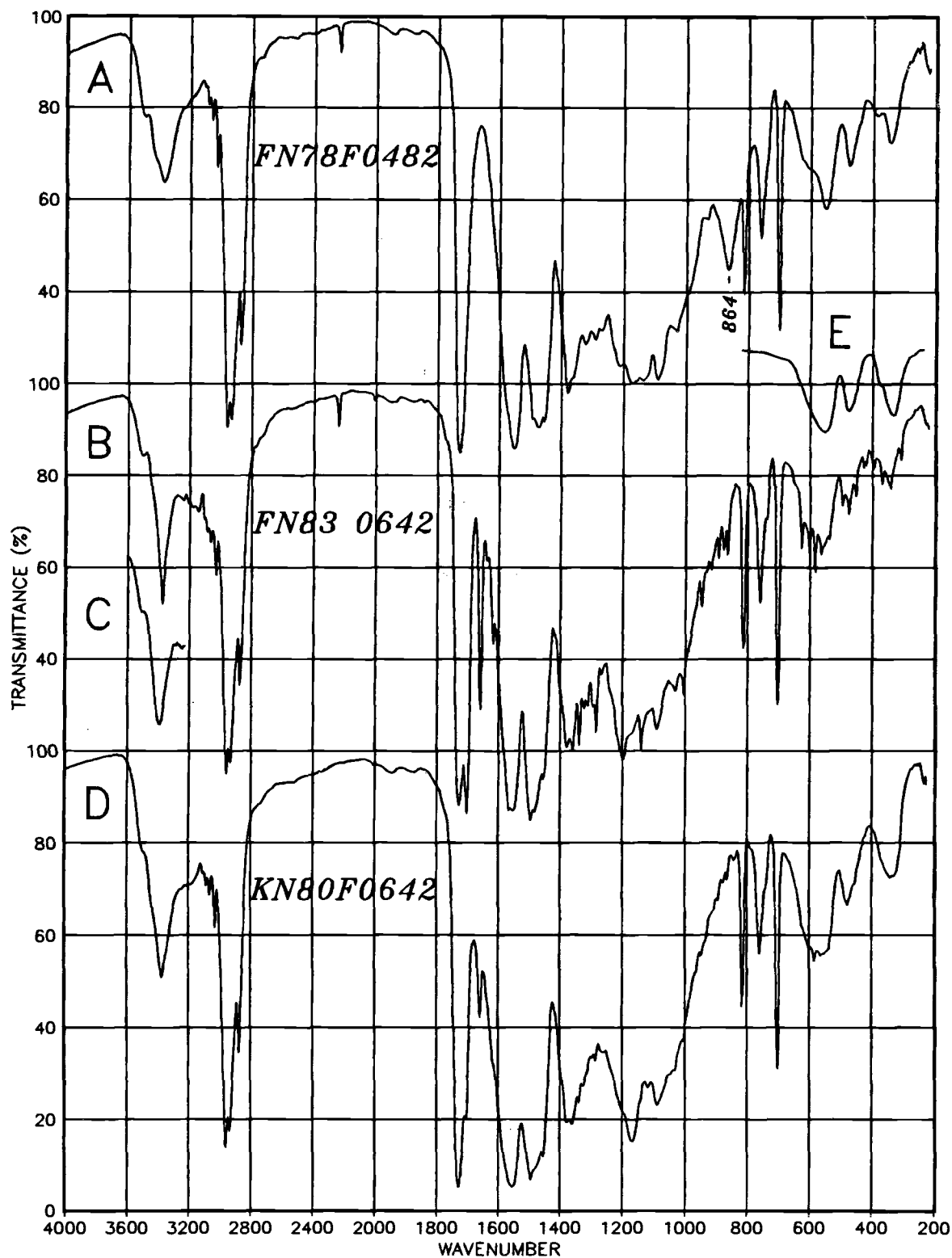


FIG. 15—Spectra of three brown nonmetallic enamel topcoats which contain ferric oxide and which have similar colors: (a) FN78F0482, which also contains Molybdate Orange (the absorption of which is labeled with its frequency); (b) FN83 0642, which also contains Benzimidazolone Orange; (c) a portion of the spectrum of FN83 0642 sampled in the high pressure DAC with a moderate to high pressure applied; and (d) KN80F0642, which has the same color as FN83 0642 and which probably also contains a small amount of Benzimidazolone Orange. (e) A portion of the spectrum of ferric oxide (diluted with CsI and sampled in the DAC).

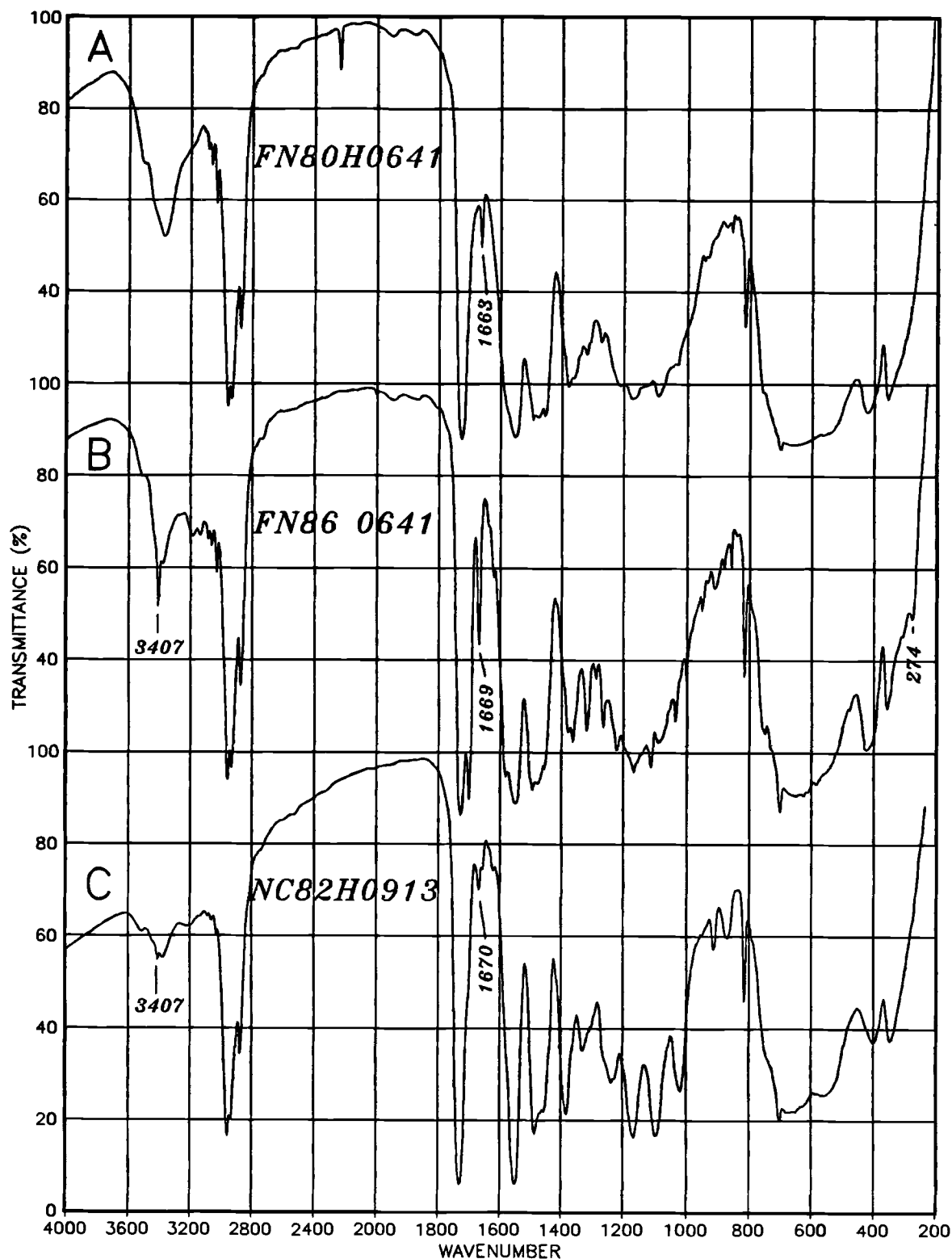


FIG. 16—Spectra of two yellow nonmetallic enamel topcoats of color 0641: (a) FN80H0641, which contains rutile and a small amount of an unidentified organic pigment; and (b) FN86 0641, which contains rutile, Benzimidazolone Yellow, and a small amount of hydrous ferric oxide. (c) Spectrum of a yellow nonmetallic topcoat, NC82H0913, which contains rutile and probably a small amount of Benzimidazolone Yellow.

were also selected. The survey included all of the red and orange metallic color comparison samples, and most of the brown ones as well. The latter consisted of all of those having darker brown colors, excluding many with *light brown*, *tan*, *beige*, or *yellow-gold* shades. A total of over 200 metallic topcoats were analyzed.

For nonmetallic topcoats, the most common benzimidazolone pigment identified was Benzimidazolone Orange. Absorptions of this pigment were detected in spectra of 15% of orange topcoats, and 29% of red ones. Benzimidazolone Orange absorptions were also identified in spectra of a few brown topcoats (see for example Fig(s). 15b and 15d). Absorptions of Benzimidazolone Yellow 3G were observed in spectra of 5% of yellow topcoats, and also in the spectrum (Fig. 17c) of a single orange topcoat, DC89 0312. Absorptions of Benzimidazolone Yellow 4G were only observed in the spectrum of a single yellow topcoat, DA78H0464 (Fig. 8b). According to Hoechst Celanese⁸, Benzimidazolone Yellow 4G is used mostly for refinishes.

Except for Benzimidazolone Brown, absorptions of the other benzimidazolones were not observed in spectra of any metallic topcoats. Benzimidazolone Brown was detected in only two dark brown metallic topcoats, DC82F0915 (Fig. 12b) and NC83 0915. The latter has the same color as DC82F0915, but its pigment absorptions are even weaker than those of Fig. 12b. Absorptions of Benzimidazolone Brown were not detected in the spectrum (Fig. 12c) of KC83 0915, a third topcoat of this color, whereas a fourth, LC82F0915, is not in the Reference Collection. Because a complete survey of metallic topcoats was not conducted, it is not known if these two are the only available Reference Collection finishes containing this pigment. It is clear, however, that Benzimidazolone Brown was not widely used in such finishes (the most common pigment identified in brown metallic topcoats was ferric oxide (2), the absorptions of which occurred in spectra of over 40% of the panels tested).

The first patent application for a benzimidazolone compound was made by Hoechst in 1960, and a pigment of this family first became commercially available in 1969 (6). The results of the spectral survey indicate that benzimidazolones were either not used or were only used in small quantities in the earliest topcoats of the Reference Collection. Absorptions of Benzimidazolone Orange were not detected in spectra of any Reference Collection topcoats produced before 1977, and only a single topcoat produced in 1977 (DC77E0054, which has a red nonmetallic finish) was found to contain this pigment. Absorptions of Benzimidazolone Yellow 3G were not observed in spectra of any Reference Collection topcoats produced before 1978, and as noted, Benzimidazolone Yellow 4G was detected in only a single topcoat produced in 1978. These observations are consistent with marketing information provided by Hoechst Celanese regarding approximate dates when these pigments were likely to have first been used in automobile finishes.⁹ Based on the survey, some limits to the model years of automobiles which could have been the source of a particular *original topcoat* containing these pigments can be established.

Pigment Combinations

In general, organic pigments are less opaque than inorganic ones due to their smaller particle sizes and lower indices of refraction (3). Organic pigments usually produce brighter and more vivid colors than their inorganic counterparts, but they are considerably more expensive. To increase the hiding power of topcoats with

organic pigments, and possibly to decrease costs as well, inorganic pigments are frequently also used, especially for nonmetallic finishes. Several different organic/inorganic pigment combinations have been identified, and certain organic pigments (presumably the less opaque ones) always seem to be used with inorganic pigments. Inorganic pigments—particularly rutile—are also much more likely to be used with organic pigments for the lighter colors.

Organic/inorganic pigment combinations are sometimes quite apparent because the spectra contain both numerous narrow absorptions, occurring over a wide range of frequencies, and a few very broad absorptions in the low frequency region. As already noted, almost all of the topcoats containing Benzimidazolone Yellow 3G and Benzimidazolone Yellow 4G also have large amounts of rutile (Fig(s). 6b, 7b, and 8b). Figure 11a depicts the spectrum of an orange nonmetallic enamel, CC78G0513, which contains Benzimidazolone Orange, rutile, and hydrous ferric oxide. The spectra of hydrous ferric oxide and rutile are shown in Fig(s). 11d and 6e, respectively, and an addition of the absorptions of the two are shown in Fig. 11e. The absorptions of this addition result can be seen in the spectrum of Fig. 11a, and also in the spectrum (Fig. 11b) of another topcoat which does not contain Benzimidazolone Orange.

The spectrum of a brown (*orange-brown*) nonmetallic enamel, FN83 0642, which has absorptions of both Benzimidazolone Orange and ferric oxide is shown in Fig. 15b. The absorptions of ferric oxide (2) alone are depicted in Fig. 15e. As discussed earlier, KN80F0642 (Fig. 15d) also contains a small amount of Benzimidazolone Orange, together with ferric oxide.

Figure 16b depicts the spectrum of a yellow nonmetallic enamel, FN86 0641, which contains Benzimidazolone Yellow 3G, rutile, and a small amount of hydrous ferric oxide (Fig. 11d). Because of the strong rutile absorptions, only the lowest frequency peak of hydrous ferric oxide can be observed (labeled with its frequency in Fig. 16b).

For all of the yellow and orange topcoats in which either Benzimidazolone Orange or the two benzimidazolone yellows were identified, significant amounts of other organic pigments were not evident. In contrast, almost all of the red topcoats which contain Benzimidazolone Orange also have appreciable amounts of other organic pigments present. The identification of combinations of Benzimidazolone Orange with other organic pigments will be described in a subsequent article dealing with these particular pigments, but the compositions are mentioned here because they are so common.

Benzimidazolone Orange occurs more often in red topcoats than in orange ones, and almost all of these red topcoats contain mixtures of Benzimidazolone Orange with either Quinacridone Red Y or Quinacridone Violet. Benzimidazolone Orange and Quinacridone Red Y are used together to produce¹⁰ a "*fire engine red*" shade, and this particular combination of two organic pigments appears to be the most common used in Reference Collection nonmetallic topcoats. A couple of brown nonmetallic topcoats were found to contain a mixture of Benzimidazolone Orange and Quinacridone Violet.

A summary of the various pigment combinations which have been identified in this work is given in Table 2.

¹⁰Personal communications: DuPont Automotive Products, January 1995; CIBA-GEIGY, February 1996; and Hoechst Celanese, February 1996.

⁸See Footnote 5.

⁹See Footnote 5.

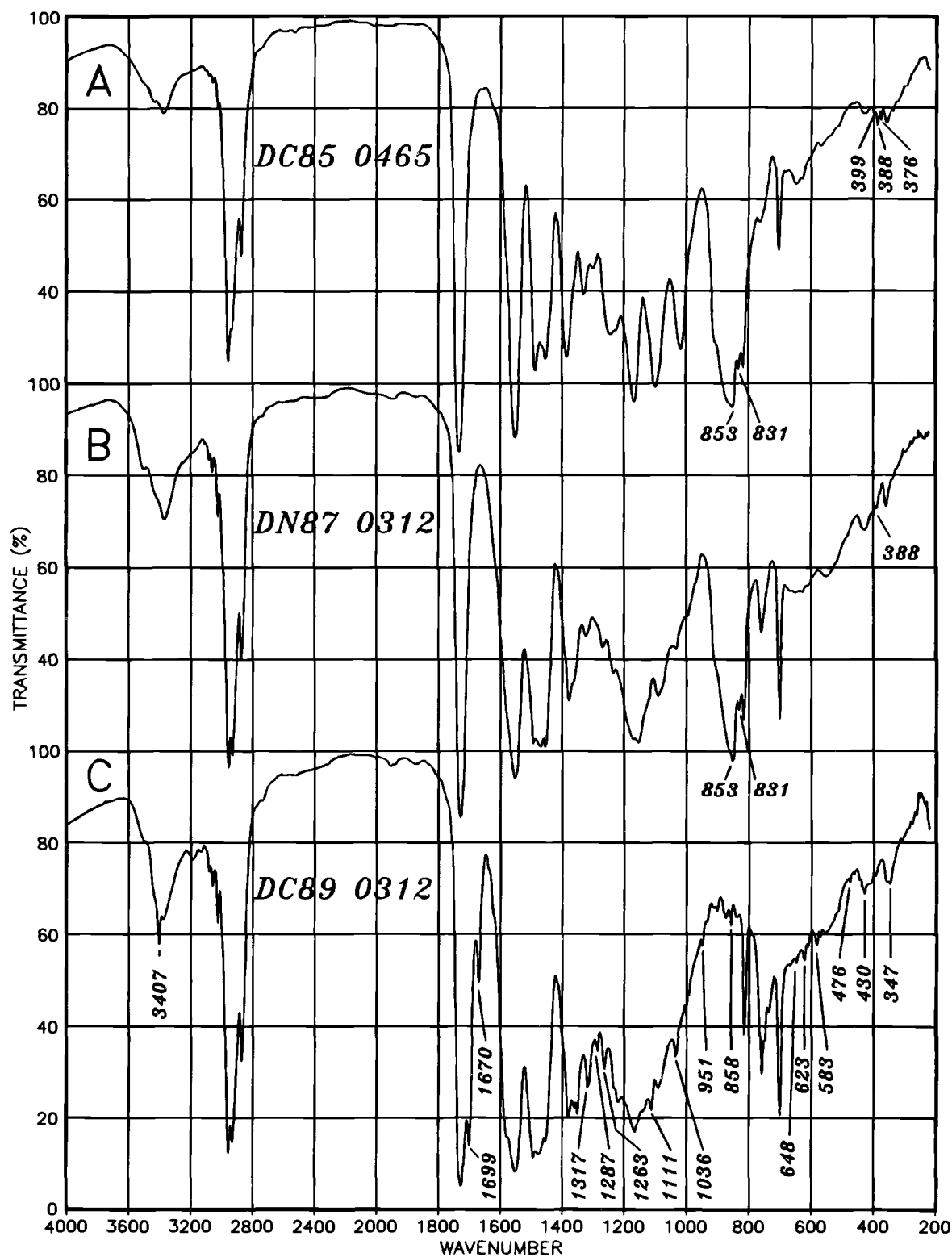


FIG. 17—Spectra of three orange nonmetallic enamel topcoats which have similar colors: (a) DC85 0465 and (b) DN87 0312, which both contain Chrome Yellow; and (c) DC89 0312, which has the same color as DN87 0312; this topcoat contains Benzimidazolone Yellow 3G. All three topcoats also contain rutile.

TABLE 2—*Pigment combinations identified in this study.*

Topcoat	Type	Color	Binder	Pigments Identified	Figure	Comments
DC82H0913	Nonmetallic	Yellow	Acrylic Melamine Enamel	Benzimidazolone Yellow 3G, Rutile	6b	XRF spectrum—Fig. 18m; Rutile spectrum—Fig. 6e
DB81H0697	Nonmetallic	Yellow	Acrylic Lacquer	Benzimidazolone Yellow 3G, Rutile	7b	
DA78H0464	Nonmetallic	Yellow	Acrylic Lacquer	Benzimidazolone Yellow 4G, Rutile	8b	
CC78G0513	Nonmetallic	Orange	Acrylic Melamine Enamel	Benzimidazolone Orange, Rutile, Hydrous Ferric Oxide	11a	XRF spectrum—Fig. 18a; Hydrous Ferric Oxide spectrum—Fig. 11d
LC84 0513	Nonmetallic	Orange	Acrylic Melamine Enamel	Rutile, Lead Chromate, Hydrous Ferric Oxide, Unidentified Organic Pigment	11b	XRF spectrum—Fig. 18b; The Lead Chromate pigment is probably Molybdate Orange
KC78G0513	Nonmetallic	Orange	Acrylic Melamine Enamel	Rutile, Unidentified Organic Pigment	11c	XRF spectrum—Fig. 18c
KC83 0915	Metallic	Brown	Acrylic Melamine Enamel	Ferric Oxide, Unidentified Organic Pigment	12c	XRF spectrum—Fig. 18e; Ferric Oxide spectrum—Fig. 15e
FN78F0482	Nonmetallic	Brown	Acrylic Melamine Enamel, Acrylonitrile	Ferric Oxide, Lead Chromate	15a	XRF spectrum—Fig. 18f; The lead Chromate pigment is probably Molybdate Orange
FN83 0642	Nonmetallic	Brown	Acrylic Melamine Enamel, Acrylonitrile	Benzimidazolone Orange, Ferric Oxide	15b	XRF spectrum—Fig. 18g
KN80F0642	Nonmetallic	Brown	Acrylic Melamine Enamel	Benzimidazolone Orange, Ferric Oxide	15d	XRF spectrum—Fig. 18h
FN80H0641	Nonmetallic	Yellow	Acrylic Melamine Enamel, Acrylonitrile	Rutile, Unidentified Organic Pigment	16a	
FN86 0641	Nonmetallic	Yellow	Acrylic Melamine Enamel	Benzimidazolone Yellow 3G, Rutile, Hydrous Ferric Oxide	16b	
NC82H0913	Nonmetallic	Yellow	Acrylic Melamine Enamel	Benzimidazolone Yellow 3G?, Rutile	16c	
DN87 0312	Nonmetallic	Orange	Acrylic Melamine Enamel	Chrome Yellow, Rutile	17b	
DC89 0312	Nonmetallic	Orange	Acrylic Melamine Enamel	Benzimidazolone Yellow 3G, Rutile	17c	

Topcoats with Similar Colors: Differences in Pigment Compositions

Although the same major pigments are most often used for different topcoats having identical Reference Collection colors, this is not always the case. For red or orange nonmetallic finishes, in particular, it is not unusual for topcoats having similar or identical colors to have different pigment compositions. Even when the same pigments are used, there may be significant differences in the amounts present.

The following examples illustrate some of the differences which can occur (some compositions have already been discussed): (1) Figure 11 depicts spectra of three orange nonmetallic enamels of color 0513—CC78G0513 contains Benzimidazolone Orange, rutile and hydrous ferric oxide; LC84 0513 contains a small amount of an unidentified organic pigment, rutile, hydrous ferric oxide, and a small amount of a lead chromate pigment (the absorption of which is marked with an asterisk in Fig. 11b; Molybdate Orange is indicated because molybdenum was detected for this topcoat using XRF); and KC78G0513 contains a small amount of an unidentified organic pigment and rutile; (2) Figure(s) 12b and 12c depict spectra of two brown metallic enamels of color 0915—DC82F0915 contains Benzimidazolone Brown whereas KC83 0915 contains an unidentified organic pigment and ferric oxide; (3) Figure 15 depicts spectra of three brown nonmetallic enamels having similar colors; all three contain ferric oxide (the shapes and

frequencies of ferric oxide absorptions may vary somewhat—see Reference 2)—FN78F0482 also contains a small amount of Molybdate Orange (the absorption of which is labeled with its frequency in Fig. 15a; molybdenum was detected for this topcoat using XRF); FN83 0642 also contains Benzimidazolone Orange; and KN80F0642 also contains a small amount of Benzimidazolone Orange; (4) Figure(s) 16a and 16b depict spectra of two yellow nonmetallic enamels of color 0641—FN80H0641 contains a small amount of an unidentified organic pigment and rutile, and FN86 0641 contains Benzimidazolone Yellow 3G, rutile, and a small amount of hydrous ferric oxide; (5) Figure(s) 6b and 16c depict spectra of two yellow nonmetallic enamels of color 0913 which contain rutile—DC82H0913 also contains Benzimidazolone Yellow 3G, and NC82H0913 appears to likewise contain a small amount of this same pigment; and (6) Figure 17 depicts spectra of three orange nonmetallic enamels having similar colors, and all three contain rutile—DC85 0465 and DN87 0312 also contain Chrome Yellow, whereas DC89 0312 also contains Benzimidazolone Yellow 3G.

Benzimidazolones as Replacements for Lead Chromate Pigments

Due to concerns about the toxicity of lead-containing pigments, lead chromate pigments were phased out of use in U.S. original finishes in the mid to late 1980s for regular production vehicles;

they continued to be used for certain special order/fleet vehicles until 1994, when all use of lead chromates in U.S. original finishes was discontinued (2). The lead chromate pigments include Molybdate Orange, Chrome Yellow, and silica-encapsulated versions of the two. These pigments are very common in yellow, orange, and red nonmetallic Reference Collection topcoats (2). Organic pigments, including the benzimidazolones, were used as replacements because most inorganic pigments lack the bright colors characteristic (21) of the lead chromates. Benzimidazolone Orange was the main replacement¹¹ pigment for Molybdate Orange, because it has a shade very similar to it. An example of this can be seen in the spectra of Fig. 15: a topcoat produced in 1978 contains Molybdate Orange (Fig. 15a) and two topcoats having colors similar to it, and produced in later years, both contain Benzimidazolone Orange (Fig(s). 15b and 15c). An example illustrating the substitution of Benzimidazolone Yellow 3G for Chrome Yellow is depicted in Fig. 17. The two topcoats produced in 1985 and 1987 contain Chrome Yellow (Fig(s). 17a and 17b), whereas a topcoat having a similar color and produced in 1989 contains Benzimidazolone Yellow 3G (Fig. 17c).

Pressure Sensitivity of the Benzimidazolones

Spectra of several of the benzimidazolone pigments obtained using the DAC differed somewhat from those obtained using DRIFTS. The most pronounced difference was usually a significant broadening of the highest frequency feature, but some of the other absorptions below 1800 cm^{-1} also differed. The spectra of the acetoacetyl compounds appeared to be affected much more than those of the hydroxynaphthoic structures.

This peak broadening was first noted when pigment DAC spectra were compared to difference spectra of Benzimidazolone Orange (such as Fig. 4c), which invariably had much sharper 3372 cm^{-1} absorptions than those of the pigment itself (the 3372 cm^{-1} peak is actually somewhat sharper than it appears in the spectra of many acrylic melamine enamel topcoats because, as noted earlier, these binders have a broad absorption in this same region—compare these features in Fig(s). 4a–4d). The peak broadening was found to be related to pressure and was more pronounced when the pigments were sandwiched between both anvils of the DAC. All of the benzimidazolone pigments were therefore analyzed using DRIFTS, but even with this technique, it was found that some peak broadening occurred if the pigment was ground together with CsI. These compounds were thus diluted with powdered CsI and mixed together without grinding; the resulting DRIFTS data had absorptions which matched the various difference spectra much better than DAC spectra.

Peak broadening has been reported for other materials sampled using the DAC (18–20), and has been attributed to effects associated with changes in crystallinity. In most such cases, the spectral changes are reversible and normal absorptions occur if the same material is analyzed without pressure. For the benzimidazolone pigments, however, the broadening effects are much more pronounced and they appear to be irreversible; other spectral changes occur as well.

The acetoacetyl compounds (I–V), for which these effects were more pronounced, may exist in a number of tautomeric forms which assume various ring conformations stabilized by hydrogen bonds. The structures of I–V depicted in Fig. 1 are shown in the

keto form in one ring conformation, but these compounds may also exist in an enol form (10) and a phenylhydrazone form (21); for the former, the lone hydrogen which is sandwiched between the two acetoacetyl carbonyl groups of I–V is attached to the ketone oxygen, whereas with the latter, it is on the azo nitrogen adjacent to the phenyl group. The spectra of pigments I–III have sharp absorptions above 3300 cm^{-1} (Fig(s). 2a–2c) which are especially prone to pressure broadening. These particular peaks are not observed in spectra of the hydroxynaphthoic pigments (Fig. 3—the 3298 cm^{-1} peak of IX is likely due to the N–H stretching mode of the $-\text{SO}_2\text{NHCH}_3$ group); they are thus logically assigned to the stretching mode of the tautomeric hydrogen, and their high frequencies would indicate that they are not due to the keto form. According to CIBA-GEIGY,¹² the phenylhydrazone form may be an important tautomer which contributes to the color of these pigments, and color changes occur when the pigments are ground (the chromophores for the keto, enol, and phenylhydrazone forms are not the same due to differences in conjugation). Although these effects are apparently not completely understood, pressure-induced changes in the tautomer forms or ring conformations are indicated from the above observations, polymorphism¹³ may also be a factor.

For those topcoats containing Benzimidazolone Orange which were pressed between both anvils of the (low-pressure) DAC, some pigment peak broadening was observed, but it appeared to be less than that which occurred for the pigment itself.¹⁴ It is likely that for pigments *in situ* with only moderate pressures applied to the paint, the binder matrix produces a cushioning effect which serves to protect them partially. Figure 15c depicts the 3372 cm^{-1} peak of Benzimidazolone Orange when FN83 0642, which contains this pigment, was mounted in a high pressure DAC with a moderate to high pressure applied. This peak can be compared to this same spectral feature for FN83 0642 analyzed with no pressure applied (Fig. 15b); the broadening of Fig. 15c probably represents the maximum which is likely to occur because such a pressure is not normally used with this device.

Because of the color changes which may occur with grinding, the benzimidazolone pigments are usually subject to a mild dispersion process during paint manufacture which avoids excess pressure.¹⁵ The possibility should be kept in mind, however, that spectra of certain topcoats may have broader peaks and other spectral differences for these pigment absorptions, either produced by sample preparation or sampling (as illustrated), as a result of the processes used to manufacture the paint, or conceivably even due to photo-induced changes or weathering.

¹²Pigments Division, CIBA-GEIGY Corp., personal communication, February 1996.

¹³See Footnote 12.

¹⁴The spectra of Benzimidazolone Orange and Benzimidazolone Yellow 4G depicted in *An Infrared Spectroscopy Atlas for the Coatings Industry* (12,13) were obtained using KBr or CsI pellets, and there are many differences evident between these and the corresponding DRIFTS spectra obtained in the present study. Information presented in the Sample Preparation section of the *Atlas* suggests that a mechanical grinding device may have been used for preparing the pellets. Our experience with this device indicates that it results in pellet spectra having very pronounced broad hydroxyl stretching absorptions of adsorbed water, and most of the pigment pellet spectra in the *Atlas* have such absorptions. The use of this device would be expected to produce significant pressure effects, and the *Atlas* spectra of the two pigments seem to reflect this. The *Atlas* spectrum of Benzimidazolone Orange (13) does not have a strong absorption of adsorbed water, and the region where the characteristic 3372 cm^{-1} peak occurs can be observed. This normally sharp and conspicuous pigment peak, however, appears as an insignificant broad shoulder.

¹⁵See Footnote 12.

¹¹Personal communications: DuPont Automotive Products, January 1995; Pigment Consultants, Inc., December 1995; and CIBA-GEIGY, February 1996.

Elemental Analyses

Elemental analysis is particularly useful when performed together with infrared spectroscopy for topcoat pigment identification. Although organic pigments do not always contain elements detectable by XRF or many SEM/EDX systems, elemental methods are still quite revealing because, as already discussed, inorganic pigments are frequently used with organic pigments. For those organic pigments which do have detectable elements and which occur in low concentrations, elemental data can corroborate the assignment of weak infrared peaks (as demonstrated earlier). In addition, elements of inorganic and organic pigments are often detected for pigments (or other topcoat components) with concentrations too low to produce observable infrared absorptions (1,2).

To illustrate this complementary nature and the potentiation that may result from using the two methods, elemental data for ten topcoats which were previously discussed are presented in Fig. 18. For eight of these, the elements detected by XRF analyses and the organic and inorganic pigments which were identified by infrared spectroscopy (given in parentheses with figure numbers) are: (1) Figure 18a—CC78G0513, titanium, iron and chlorine, and lesser amounts of nickel and antimony (Benzimidazolone Orange, rutile and hydrous ferric oxide, Fig. 11a); (2) Figure 18b—LC84 0513, iron and titanium, with lesser amounts of lead, chromium, molybdenum (Fig. 18i), and antimony (rutile, hydrous ferric oxide, a lead chromate pigment, and an unidentified organic pigment, Fig. 11b); (3) Figure 18c—KC78G0513, titanium and chlorine, and lesser amounts of chromium, manganese, and antimony (rutile and an unidentified organic pigment), Fig. 11c; (4) Figure 18d—DC82F0915 (metallic), chlorine, aluminum, phosphorus and iron, and small amounts of titanium and nickel (Benzimidazolone Brown, Fig. 12b); (5) Figure 18e—KC83 0915 (metallic), iron, aluminum, titanium and chlorine, and a small amount of nickel (ferric oxide and an unidentified organic pigment, Fig. 12c); (6) Figure 18f—FN78F0482, iron, lead, chromium, calcium, and (Fig. 18j) molybdenum (Molybdate Orange and ferric oxide, Fig. 15a); (7) Figure 18g—FN83 0642, iron and chlorine, and small amounts of chromium, lead, titanium, calcium, and (Fig. 18k) molybdenum (Benzimidazolone Orange and ferric oxide, Fig. 15b); and (8) Figure 18h—KN80F0642, iron and chlorine, with a small amount of calcium (ferric oxide and a small amount of Benzimidazolone Orange, Fig. 15d). A tin secondary target was used for the results depicted in Fig(s). 18i, 18j, and 18k, because this permitted the molybdenum K lines to be observed more easily.

The chlorine detected for CC78G0513 (Fig. 18a), FN83 0642 (Fig. 18g) and KN80F0642 (Fig. 18h) is due (in part at least) to Benzimidazolone Orange (I), while that detected for DC82F0915 (Fig. 18d) can be attributed to Benzimidazolone Brown (VII). Two other topcoats, KC78G0513 (Fig. 18c) and KC83 0915 (Fig. 18e) also contain chlorine, which is a common element for automotive organic pigments. Topcoat KN80F0642 (Fig. 18h) contains much less chlorine, relative to iron, than does FN83 0642 (Fig. 18g); this is consistent with the infrared data—compare the ferric oxide and Benzimidazolone Orange absorptions of Fig(s). 15b and 15d. The analysis conditions which were used for the XRF examples (Fig(s). 18a–18h) were chosen to permit a wide range of element peaks to be easily observed simultaneously, but direct excitation with a rhodium target is *not* an ideal method to determine chlorine because the rhodium L lines occur in the same region as the chlorine K lines. The contributions of the rhodium L lines were removed, for the most part, by subtracting a background spectrum and the presence of chlorine in all of the cited topcoats was also

confirmed by using a titanium secondary target; SEM/EDX results further corroborated the presence of chlorine for two of these.

The molybdenum observed for LC84 0513 (Fig. 18b) indicates that the lead chromate pigment identified for this topcoat by infrared spectroscopy (Fig. 11b) is—or at least contains—Molybdate Orange (which is a solid solution of mostly lead chromate with lesser amounts of lead molybdate and lead sulfate). The lead, chromium, and molybdenum of FN83 0642 (Fig. 18g) are also indicative of the presence of this pigment, although this is not apparent from the infrared spectrum (Fig. 15b; this should be compared to Fig. 15a, which depicts the spectrum of a topcoat which does have a Molybdate Orange absorption). The molybdenum K β line of Fig. 18k appears to be broadened, and there is another weaker peak adjacent to it on the high energy side. These are not peaks of the sample but are caused by differences between the amounts of rhodium K α X-rays reaching the detector from the sample and the background, due to Compton (inelastic) and Rayleigh (elastic) scattered radiation, respectively (they are only apparent for this sample because the molybdenum lines are so weak). All of the topcoats containing lead also contain sulfur, but its presence cannot be determined because the sulfur K lines overlap the lead M lines (the strong peak on the left in Fig. 18f). The L lines of molybdenum also overlap the lead M lines, but most of this peak is due to lead because the amount of molybdenum, relative to lead, is usually 10% (molar ratio) or less (2). The presence of molybdenum in topcoats containing Molybdate Orange may thus be difficult to confirm using a SEM/EDX analysis because the molybdenum K lines are usually not seen. The antimony, nickel and titanium (in part) of CC78G0513 (Fig. 18a), an orange topcoat, may be due to Titanium Nickel Yellow (21), a yellow inorganic pigment which contains these three elements.

Analyses using SEM/EDX were performed on two other topcoats, and similar information is listed for these: (1) Figure 18l—DC82A0044, titanium, aluminum, silicon, sulfur, carbon, nitrogen, and oxygen (rutile, Fig. 6a); and (2) Figure 18m—DC82H0913, these same elements plus fluorine and chlorine (Benzimidazolone Yellow 3G and rutile, Fig. 6b). The light element capability of this instrument permitted detection of the fluorine of Benzimidazolone Yellow 3G (III) for the latter topcoat, although this peak is quite weak (the intensities depicted in Fig. 18m might suggest that there is more chlorine than fluorine present, but considering the detection efficiencies which are involved, it is clear that the opposite is true). Carbon, nitrogen, and oxygen were also detected for the two topcoats, but these are predominantly from the binders (and the coating material, in the case of carbon). It is likely that small amounts of aluminum, silicon, and other lighter elements are also present in some of the topcoats analyzed by XRF, but were not detected due to the insensitivity of this instrument for these elements (the aluminum peaks observed for Fig(s). 18d and 18e are due to *large* amounts of this element because these are spectra of metallic topcoats with aluminum flakes).

Summary and Concluding Comments

Pigment absorptions in automobile topcoat spectra are generally more pronounced for red nonmetallic finishes, and to a lesser extent for orange and yellow nonmetallic and red metallic ones, due to the heavy pigment loads which may be used for these. Organic pigment absorptions can usually be easily distinguished from those of inorganic pigments, because they are narrower and occur throughout the spectrum. Only a few colored inorganic pigments were used in appreciable quantities for U.S. automobile

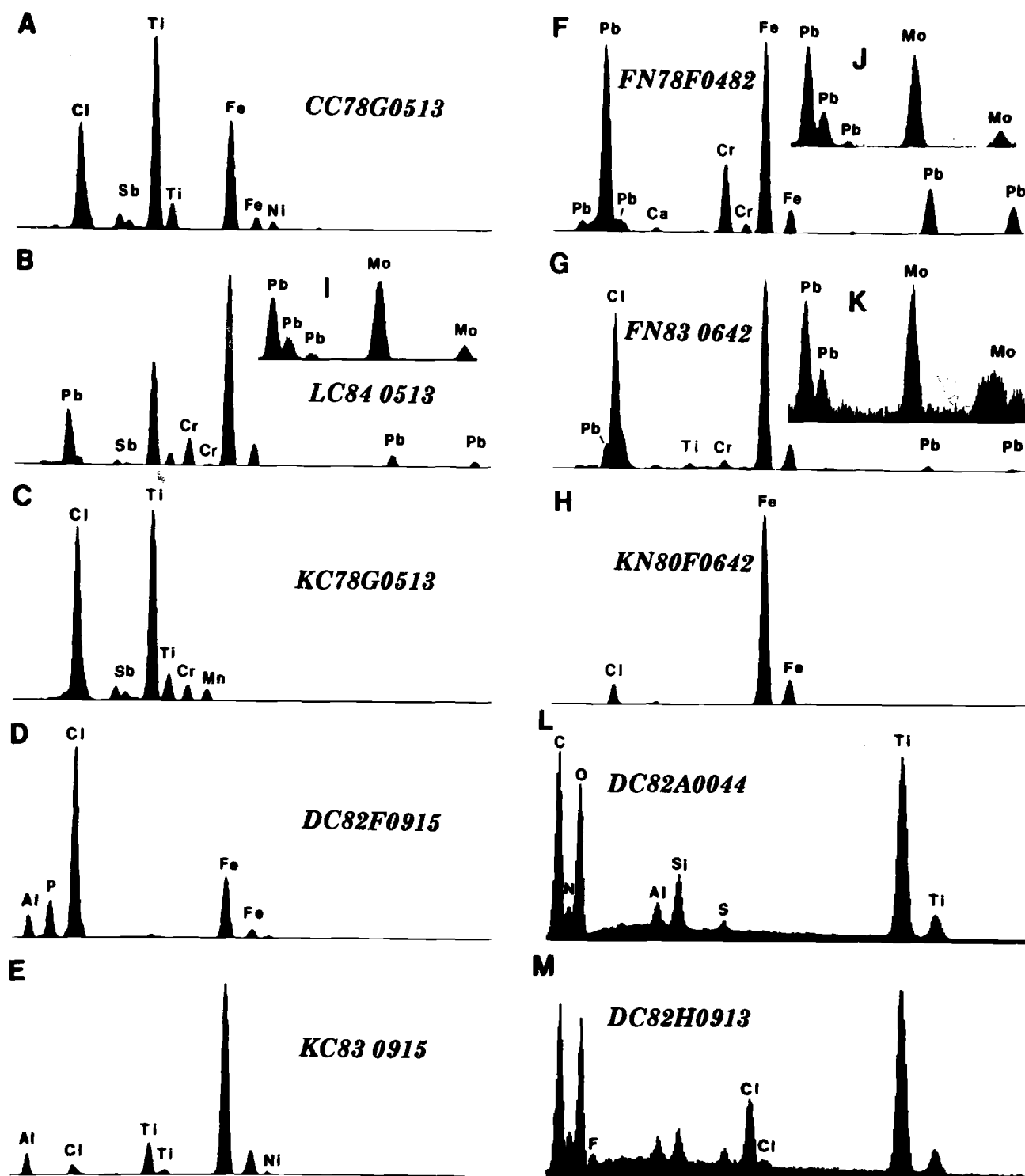


FIG. 18—Elemental analysis data for ten topcoats. XRF spectra between 1 and 13 keV of eight topcoats sampled using excitation from a rhodium primary target: (a) CC78G0513; (b) LC84 0513; (c) KC78G0513; (d) DC82F0915; (e) KC83 0915; (f) FN78F0482; (g) FN83 0642; and (h) KN80F0642. XRF spectra between 14.4 and 19.9 keV of three of these topcoats sampled with a tin secondary target, depicting the lead $L\gamma$ and molybdenum K lines: (i) LC84 0513; (j) FN78F0482; and (k) FN83 0642—this particular spectrum was collected for 100,000 seconds. Background spectra were subtracted from each of the above. SEM/EDX spectra between 0.1 and 6.0 keV of two topcoats: (l) DC82A0044; and (m) DC82H0913; both of these spectra were collected for 1000 seconds.

original topcoats (1974–1989), whereas noticeable absorptions of a large number of different organic pigments are evident in their spectra. Spectral subtractions using subtrahend spectra of closely-matched topcoats were performed to isolate pigment peaks, and several different organic pigments were identified *in situ* by this means. These pigments can often be identified based on the more limited number of pigment peaks observed in topcoat spectra without using spectral subtraction. This is true even when absorptions of other pigments are present, and several different organic/inorganic pigment combinations have been identified.

Seven benzimidazolone pigments are currently marketed for use in automobile topcoats, and four of these were identified in some single layer topcoats from the Reference Collection of Automotive Paints. The pigments and the types of finishes in which they were identified (given in parentheses) are: Benzimidazolone Orange (nonmetallic orange, red, and brown), Benzimidazolone Yellow 3G (nonmetallic yellow and orange), Benzimidazolone Yellow 4G (nonmetallic yellow), and Benzimidazolone Brown (metallic brown). Benzimidazolone Orange is the most common of these, and occurs in 15% of orange nonmetallic topcoats and 29% of red ones. Benzimidazolone Yellow 3G was used in 5% of yellow nonmetallic topcoats, whereas Benzimidazolone Yellow 4G was identified in only a single yellow nonmetallic topcoat. Benzimidazolone Brown also appears to be a relatively rare pigment and was identified in only two dark brown metallic topcoats. The benzimidazolone pigments were not detected in any Reference Collection topcoats produced before the following years: Benzimidazolone Orange, 1977; Benzimidazolone Yellow 3G and Benzimidazolone Yellow 4G, 1978; and Benzimidazolone Brown, 1982 (only a limited survey was taken of metallic topcoats, so this pigment might have been used earlier). Topcoats containing some benzimidazolone pigments may exhibit band broadening and other changes when subject to excess pressure, and this possibility should be considered when such topcoats are analyzed.

Recognition of benzimidazolone and other organic pigment absorptions in topcoat spectra, like any type of pattern recognition process, is an art. Because these absorptions must be "mentally separated" from those of the binder, the key to recognition of pigment peaks is an ability to identify absorptions of binders readily, which for this study consist predominately of acrylic melamine enamels and acrylic lacquers. Spectral differences can occur within binder types and acrylic lacquers in particular may have some weak sharp absorptions; these factors must be considered in this sorting process. Analysts who use infrared spectroscopy for paint examinations on a regular basis and who routinely identify binders by this means are likely to find this an easier task than those who rarely use this technique, or those who use infrared absorption patterns in strictly a comparative mode without attempting to identify binders and pigments.

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