

# Infrared Spectra of U.S. Automobile Original Topcoats (1974–1989): I. Differentiation and Identification Based on Acrylonitrile and Ferrocyanide C≡N Stretching Absorptions

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**ABSTRACT:** A survey of U.S. automobile original topcoats (1974–1989) for binder and pigment compositions has been conducted using infrared spectroscopy. Data were obtained from panels of the Reference Collection of Automotive Paints for single layer topcoats, excluding basecoat/clearcoat finishes. This paper describes the occurrence in these topcoats of acrylonitrile, a copolymer used in some acrylic melamine enamels, and iron ferrocyanide, an inorganic pigment used in some blue and green paints. Both of these components produce characteristic C≡N stretching fundamentals, which occur in a spectral region devoid of other significant absorptions. Because of this, they are usually easy to detect and assign, and since the spectra of most U.S. automobile original topcoats do not contain these peaks, their presence can serve as useful markers for identifying certain topcoats when used in conjunction with microscopic data. Of particular significance for hit-and-run cases, acrylonitrile absorptions occur predominantly for some topcoats used on certain Ford/Chrysler/Jeep/American Motor vehicles manufactured before 1985, with the majority of these used on Fords from the 1970s. Polyurethane isocyanate N=C=O stretching absorptions, which also occur in this same spectral region, were not detected for any of the topcoats of this study.

**KEYWORDS:** forensic science, criminalistics, paint analysis, U.S. automobile paints, spectroscopic analysis, infrared spectroscopy, acrylonitrile absorptions, ferrocyanide absorptions

A forensic examination of automobile paint may involve either a comparative analysis of two paint samples or an attempt to identify a given paint to establish the type of vehicle from which it originated. In the former case, one wishes to know if the two samples could share a common source, and if the analytical data support this supposition, some indication of the likelihood that they in fact do. Except in those instances where a physical match can be established between known and questioned samples, this judgment requires statistical knowledge of the occurrence of various automobile paint systems for both original finishes (domestic and imports) and repaints. Such a data base would include information about colors, type of finish (nonmetallic or metallic), luster and texture, layer structures, paint compositions, and so forth.

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Although some work has been done to address these needs (1–14), complete statistics for all of these are not available and the forensic scientist must usually work with more limited information.

The second type of paint examination occurs as part of a hit-and-run investigation where the submitting law enforcement agency wishes to know the type of vehicle involved. In this case, a recovered paint chip is compared to various reference panels to try to identify the paint. A comprehensive data base for automobile paints would again be useful since it could serve to narrow the list of possibilities rapidly, or permit, in certain cases, an unambiguous match without the need to analyze in detail a large number of reference samples.

For either type of examination, the first step in an analysis scheme normally involves a microscopic examination. Following this, chemical compositional data may be sought to further characterize the paint. One of the common methods that has been used for this is infrared spectroscopy (4,5,7–10,15–40), which is particularly well-suited for obtaining information about paint binders and pigments. Binders and pigments were used by Rodgers et al. for example, to classify automobile paints using infrared spectral data collected with a high pressure diamond anvil cell (DAC) accessory (21). Cartwright and Rodgers (4) further proposed a means of storing this information to serve as a data base for identification purposes. Percy and Audette (9) established an infrared data base for some automobile repaints, while Norman et al. (10) used infrared spectroscopy for the classification of automobile paint primers in a collaborative study. Audette and Percy proposed a classification system for automobile paints using infrared and other data (7), and later presented (8) this information for Chrysler vehicles (1960–1979). While many U.S.-manufactured automobiles were included in these surveys, all were concerned primarily with vehicles in Canada.

This infrared spectral data survey, which is presented in several parts, provides binder and pigment data for vehicles manufactured in the U.S. during a recent 16 year period. Data were obtained from panels of the Reference Collection of Automotive Paints for all available topcoats from 1974, when the Reference Collection began, to 1989, the last year for which actual topcoats (rather than color representations) were included in the Reference Collection. This study is concerned with single layer topcoats, and basecoat/clearcoat finishes are not included.

To facilitate the identification of unknown automobile paints, this survey has focused on some spectral features that may be used to rapidly and unambiguously classify topcoats. This first paper describes the occurrence of two paint components which, because their characteristic infrared absorptions occur in a region (2300–

2000  $\text{cm}^{-1}$ ) where few other fundamental transitions take place, produce distinct, easily recognized peaks. These peaks arise from the  $\text{C}\equiv\text{N}$  stretching absorptions of acrylonitrile, a copolymer used in some acrylic melamine enamel finishes, and iron ferrocyanide (Iron Blue, Prussian Blue), an inorganic pigment used in some blue and green topcoats.

In the past, these nitrile and cyano absorptions may not have been fully exploited for their differentiating capability by some forensic scientists, due in part to use of a high pressure diamond anvil cell (DAC) accessory (4,5,10,20–25,32,33). Because of interfering diamond absorptions, peaks in the 2400–1900  $\text{cm}^{-1}$  region cannot be detected when using this accessory on a dispersive spectrometer. In 1984, the low pressure DAC (also known as the miniature DAC) was introduced for use with either a beam condenser or an infrared microscope. Since the anvil windows of this low pressure cell are thinner than those of the high pressure DAC, nitrile and cyano absorptions can usually be observed when using this accessory with a Fourier transform infrared (FT-IR) instrument, especially if only a single anvil is used for sampling (41,42).

The low pressure DAC has been shown to be well-suited for the analysis of paint (30,31), and it is likely to gain increasing use in forensic science due to its lower cost (in comparison to its high pressure counterpart), durability, and ability to be used with both a beam condenser and an infrared microscope. The latter accessory (with or without a DAC), in particular, has become a popular method for the forensic analysis of paint (27–29,34,36–40). In view of these trends, the potential discriminating features of nitrile and cyano absorptions can now be more fully used by forensic scientists conducting paint examinations.

### The Reference Collection of Automotive Paints

The Reference Collection of Automotive Paints (Collaborative Testing Services, Inc., Herndon, Virginia) consists of panels with topcoats used on automobiles manufactured in the United States from 1974 to 1989. Each panel is identified by a nine-character code that specifies manufacturer, type of paint, the year the topcoat was first produced or added to the Reference Collection, and five characters for a color designation. The fifth character originally consisted of a letter to indicate a general color category, but beginning in 1983, it was no longer used and this space was left blank. The last four digits are the specific color code, with each four-digit number representing a different color. Since most colors have more than one source, there are usually two or more panels having the same four-digit color code. A summary of the specific information given by the nine-character code is presented in Table 1. A booklet, *Reference Collection of Automotive Paints Technical Data* (43), is included with the Reference Collection, which lists the specific vehicles on which a particular topcoat was used.

The last number assigned to a Reference Collection color was 1708, but 213 numbers were not used. Of the 1495 that were, 465 are colors for which all of the available panels have a basecoat/clearcoat finish. For 17 colors, there are no panels in the Reference Collection. The remaining 1013 colors (1708–213–465–17) each have at least one panel with a single layer finish; for the vast majority of these colors, all of the panels have a single layer finish, but there are 27 colors that have panels with both single layer and basecoat/clearcoat finishes. Information about the 2991 single layer topcoats in the Reference Collection comprising these 1013 colors is given in Table 2.

TABLE 1—Nine character coding system used to identify Reference Collection of Automotive Paint panels.\*

Character Position	Information Conveyed	Code Used	Specific Manufacturing Data		
1	Paint supplier	A	Almatex (Canadian Celanese)		
		B	PPG of Canada (Canadian Pittsburgh Industries)		
		C	Jones-Dabney—U.S. Celanese (now part of BASF Inmont)		
		D	DuPont		
		F	Ford (Now part of DuPont)		
		K	Glasurit America (Formerly Cook; now part of BASF Inmont)		
		L	C.I.L. (Canadian Industries, Ltd.)		
		N	BASF Inmont		
		P	PPG Industries		
		X	Not specified		
		2	Paint type	A	Acrylic solution lacquer
				B	Acrylic dispersion lacquer
				C†	Acrylic enamel
D	Polyester enamel				
F	Urethane enamel				
H	Basecoat/clearcoat acrylic enamel				
N	Non-aqueous dispersion enamel (NAD)				
3,4 5	Year made Generic color‡	W	Water-based enamel		
		X	Not specified		
		74–89	1974 to 1989		
		A	White		
		B	Gray		
		C	Black		
		D	Pink		
		E	Red		
		F	Brown		
		G	Orange		
6–9	Number (Specific color)	H	Yellow		
		J	Olive		
		K	Green		
		L	Blue		
		M	Violet		
		N	Purple		
		0001–1708	Assigned sequentially as the color was placed in the Collection		

\*From (43).

†Prior to 1987, basecoat/clearcoat acrylic enamels were labeled C. Starting in 1987, all base coat/clear coat acrylic enamels were labeled H.

‡This code was used prior to 1983 and was based on the Inter-Society Color Council—National Bureau of Standards method of designating colors.

For a number of colors, there are topcoats that are not in the Reference Collection. The designation codes for these particular topcoats have a suffix of either "S" or "M" in the *Technical Data* booklet. These suffixes indicate, respectively, "have samples but insufficient amount to include in Collection; available on an as-needed basis," and "known to have been used but no samples currently available" (43). Samples in the former category were sought from the Collaborative Testing Services to include in this survey, but they are no longer available.<sup>2</sup> They include topcoats

<sup>2</sup>Collaborative Testing Services, Inc., personal communication, May 1994.

TABLE 2—Single layer U.S. automobile original topcoats (1974–1989) that were surveyed for the presence of nitrile and cyano infrared spectral absorptions.

Source or Status in the Reference Collection of Automotive Paints Technical Data Booklet	Number	
	Nonmetallic	Metallic
Panels from the Reference Collection of Automotive Paints:		
Single layer topcoat colors for which there are panels in the Collection	399	614
Topcoats listed in the Technical Data booklet for these colors	1437	1842
Topcoats in Collection but not listed*	+10†	+5‡
Topcoats listed as unavailable§	-94	-157
Topcoats listed as unavailable but actually in Collection	+2	+3¶
Topcoats missing from Collection**	-9‡‡	-9§§
Topcoats with basecoat/clearcoat finishes	-17	-22¶¶
Topcoats examined from Collection	1329	1662
Panels from the FBI Laboratory National Automotive Paint File:		
Single layer topcoat colors	1	6
Topcoats of these colors	1	7
Total number of colors represented	400	620
Total number of topcoats examined	1330	1669

\*These fifteen topcoats are not listed in the *Technical Data* booklet, but each has the same color as other panels in the Collection having that particular color designation number.

†DA78A0042, NB86 0044, PA75E0202, DC82C0407, NC82CO407, PC85 0562, FN81H0762, FN86 1138, DC86 1173, and FN86 1292.

‡DA75K0187, LN78K0288, NW83 0782, PB83 0995, and NB86 1188.

§These all have the suffix "M" or "S" after their designation codes in the *Technical Data* booklet; none are available from the Collaborative Testing Services.

||PA79L0584 and PB83 0986.

¶PN80L0579, PA79L0585 and NW81L0802.

\*\*These eighteen topcoats were found to be missing from the Reference Collections of four different forensic laboratories in the U.S., so they may not be in other Collections as well.

‡‡CN78A0033, NW81A0044, NC79H0456, NC79A0466, NC79L0470, NC83 0618, PN83 0755, DC82 1031, and NC82 1031.

§§PA78L0276, PN78L0299, DN78F0397, NC79L0503, AN81B0578, CN81B0578, FN81B0578, KN81B0578, and PN81B0578.

|||PC87 0001, DD87 0090, CC77L0356, DH87 0407, NH87 0548, PC85 0830, NC87 1049, DC87 1055, NH87 1242, PC87 1242, PN86 1267, NC87 1267, PC86 1305, NH87 1305, NH88 1352, PN87 1366, and NH88 1442.

¶¶DC87 0950, PB87 1000, FD84 1065, KD84 1065, KC85 1065, NN86 1065, DD87 1065, DH89 1065, PC85 1158, PB87 1182, PN86 1294, DC86 1309, NC86 1309, PC86 1309, NH87 1309, NC86 1319, PC86 1319, PB86 1323, DC87 1359, PB87 1369, PB87 1375, and DB88 1480.

of the 17 colors for which there are no panels in the Reference Collection. Since these particular missing topcoats were considered to be the most important for identification purposes, they were sought from the FBI Laboratory which maintains its own reference collection, the National Automotive Paint File (44). Panels for 12 of the 17 colors (13 topcoats total) were in this collection, and portions of these panels were obtained for this study. Eight of these topcoats, representing seven colors, were found to consist of single layer finishes and they are included in the survey (Table 2).

Of the 1020 colors of this survey, 620 (61%) are metallic and 400 (39%) are nonmetallic. The metallic/nonmetallic distinction not only provides a rapid visual classification that more or less equally divides automobile topcoats, but there are often significant compositional differences between metallic and nonmetallic topcoats, especially in regard to pigments (45). This distinction thus

serves as a logical basis for classification of topcoats and will be used throughout this study for presentation of spectral data.

## Experimental

Infrared spectra were collected using three different FT-IR instruments: an Analect FX-6200 and a Laser Precision Analytical RFX-40, both with broad-band mercury cadmium telluride (MCT) detectors, and a Digilab FTS-7. The FX-6200 (46) and RFX-40 (42) have been described previously. The FTS-7 was equipped with cesium iodide (CsI) optics and a deuterated triglycine sulfate (DTGS) detector; more information about this system is given elsewhere (45). Spectral resolutions of  $4\text{ cm}^{-1}$  were used with the RFX-40 and FTS-7 spectrometers, and a  $5.3\text{ cm}^{-1}$  resolution was used with the FX-6200; for all of the spectra shown in this work, a  $4\text{ cm}^{-1}$  resolution was used. Depending upon the particular instrument, sample, and accessory used, 100 to 1000 scans were collected and averaged.

Analect FXA-530 diffuse reflectance (DRIFTS) accessories were used on both the FX-6200 and RFX-40 instruments, with the accessory mirrors rotated between 15 and 20 degrees to minimize specular reflectance (32,33). A high-pressure DAC (High Pressure Diamond Optics, Inc.) with an Analect 4X beam condenser system was also used in the collimated beams of both of these instruments. A Laser Precision Analytical XAD Plus infrared microscope, equipped with a narrow-band MCT detector, was used with the RFX-40 instrument. More details of this microscope are given elsewhere (42,47). Low-pressure (miniature) DACs (High Pressure Diamond Optics, Inc.) were used with the infrared microscope and with a Digilab 5X beam condenser mounted in the FTS-7 instrument.

For direct sampling with the DRIFTS accessories, panels were situated horizontally so that their surfaces were at the focal points of the accessory mirrors. The reflectance from a flat mirror was used as a reference background, and increased instrument gains (32,33) were used to compensate for the low reflectances of the panels.

For sampling with the DACs, thin slices of panel topcoats were obtained using a sharp scalpel. For use with the beam condenser systems, enough sample was prepared so as to cover the entire anvil face and the slices were pressed flat with both anvils. With the low pressure DAC used on the FTS-7 instrument, some slices were sampled between both anvils, whereas with others, a single anvil—with the slice pressed against it—was used. For use on the infrared microscope, the slices were placed on an anvil so as to cover only a portion of the face, and all sampling was performed using a single anvil. The clear portion of the anvil was used to obtain a background reference.

Some topcoat slices were sampled with the infrared microscope or the Digilab beam condenser without use of a substrate. These slices were first flattened with a roller, then they were either suspended in the plane of the stage with a piece of tape attached to the edge of the slice (for the microscope), or they were held over a 1 mm circular aperture mounted in the beam condenser.

## Screening of Topcoat Panels

Each of the panels was first tested to determine if it consisted of a single layer topcoat or a basecoat/clearcoat finish. To accomplish this, the panel was viewed with a stereomicroscope while an edge of the finish was cut with a scalpel. Each panel having a single layer topcoat was then subject to a direct DRIFTS sampling (32,33) to screen for the presence of nitrile and cyano stretching absorptions. All of the topcoats for which such absorptions were

detected, as well as many others, were then further sampled using transmittance methods.

### Acrylonitrile in Acrylic Melamine Enamel Automobile Topcoats—A Brief Review

The binder of an acrylic melamine (thermosetting) enamel consists of an acrylic backbone comprised of various copolymers, cross-linked with butylated or isobutylated melamine-formaldehyde (21,48–51). The specific composition of the acrylic copolymers used and the ratio of backbone to cross-linking components determine, in large part, the properties of the finish, such as hardness, flexibility, durability, adhesion, and chemical resistance. Typical acrylic copolymers used for automobile topcoats include methyl methacrylate, butyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, acrylonitrile, and a hydroxyl monomer such as hydroxyethyl acrylate. The latter monomer is used to provide sites along the backbone for melamine cross-linking. Most acrylic melamine enamels also contain a styrene copolymer. Acrylonitrile is normally used in an acrylic melamine enamel to impart hardness, mar resistance, and solvent and grease resistance.

A variety of paint vehicle dispersal methods have been used for acrylic melamine enamel finishes used in automobile topcoats. They include water-based systems, conventional solvent-based enamels, and non-aqueous dispersions (NAD). Unlike a solvent-based enamel in which the paint vehicle ingredients are soluble in the organic solvent used, the components of an NAD are largely insoluble and are dispersed as small particles in the solvent (similar to the situation for a latex paint—except that the medium is not water). Acrylonitrile is often used in an NAD to make the acrylic resin less soluble so that it can be more easily suspended rather than solvated. In comparison to a solvent-based acrylic enamel, the advantages of an NAD finish include the ability to use less-expensive and less-polluting solvents and a greater ease of application. The latter is possible in part due to the higher solids concentration of an NAD, which permits two coats to be used instead of the three normally required for a topcoat. NAD enamels for automobile finishes were introduced in 1968 (52) and by 1973, they were widely used by some U.S. automobile paint suppliers (53).

## Results and Discussion

### Recognition and Occurrence of Acrylonitrile Absorptions

The acrylonitrile  $C\equiv N$  stretching fundamental occurs as a sharp weak to very weak peak at  $2239\text{ cm}^{-1}$  ( $2240\text{--}2238\text{ cm}^{-1}$  range) in the spectrum of an acrylic melamine enamel automobile finish (Figs. 1b and 1c). Although weak, this peak can usually be recognized since—as noted—it occurs in a region devoid of other significant absorptions. Figures 1a and 1b illustrate how this absorption can serve to differentiate between some closely related paints. Depicted are spectra of two Cook NAD nonmetallic white enamels having identical colors and manufactured in successive years; the spectra are quite similar and the main difference is due to the nitrile absorption.

A list of the U.S. original nonmetallic topcoats (1974–1989) which have an acrylonitrile  $C\equiv N$  stretching absorption in their spectra is given in Table 3; a similar list for metallic topcoats is given in Table 4. As expected, all of these topcoats have acrylic melamine enamel binders, and they span essentially the entire range of colors (Tables 3 and 4). To better gauge the relative absorption intensities of the nitrile peaks, all of the relevant spectra are depicted with the highest points of their baselines near 100%

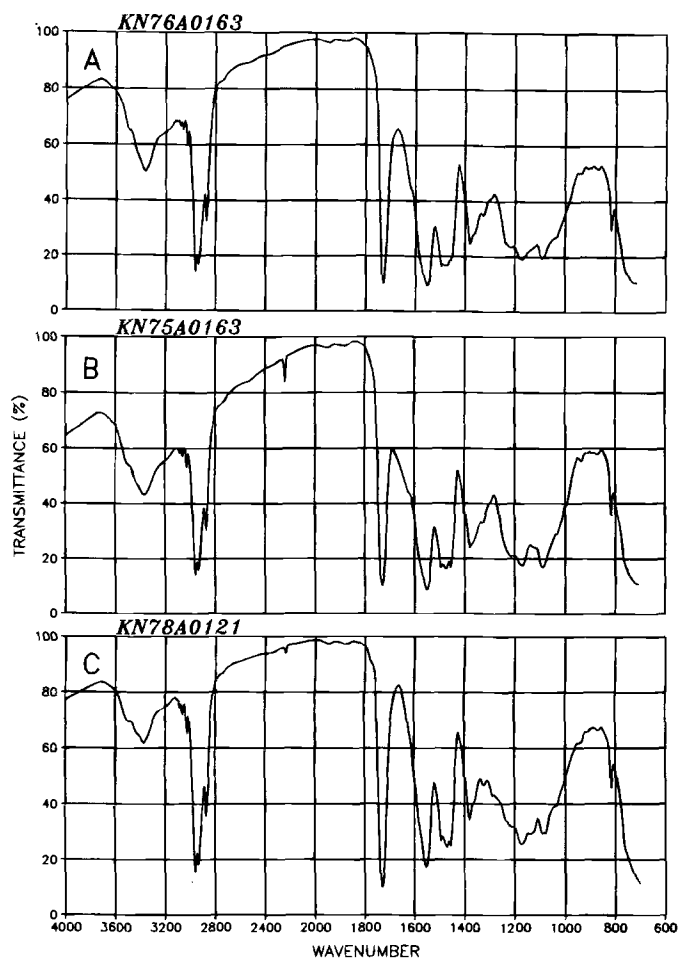


FIG. 1—Infrared microscope spectra of three nonmetallic topcoats sampled without substrates: (a) KN76A0163; (b) KN75A0163; and (c) KN78A0121.

transmittance and with their strongest absorptions between 5% and 10% transmittance. For the majority of acrylonitrile topcoats, the nitrile peak intensities fall within the range depicted by Figs. 1b and 1c, and most of these have an intensity similar to that of Fig. 1b. For the absorption intensity columns of Tables 3 and 4, no entry is listed for these latter topcoats, which might be considered to be “normal” acrylonitrile topcoats. Topcoats having nitrile peak intensities comparable to Fig. 1c are listed as “weak,” and these tend to be more prevalent among the metallic finishes. A few topcoats, together with a group of recent DuPont nonmetallic enamels, have even weaker peaks (Fig. 2c), and these are listed as “very weak.” For weak nitrile peaks, a useful comparison can sometimes be made to the two neighboring styrene overtone/combination bands (33) that occur between  $2000$  and  $1800\text{ cm}^{-1}$  (see Figs. 1 and 2—note that these peaks are *not* observed for Fig. 2c). Nitrile peaks weaker than the styrene bands are listed as “very weak,” whereas those having intensities comparable to them are listed as “weak.”

A number of topcoats were found to have such very weak nitrile peaks in their spectra that they would not normally be detected unless they were actively sought. The nitrile stretching frequencies for most of these occur between  $2235$  and  $2230\text{ cm}^{-1}$ , although there are a few with frequencies near  $2239\text{ cm}^{-1}$  similar to that of acrylonitrile. The latter include KN76F0171 (metallic), NW75L0179 (metallic), NW75H0182 (nonmetallic), NW75K0187

TABLE 3—U.S. automobile original nonmetallic topcoats (1974–1989) that have an acrylonitrile nitrile stretching absorption in their infrared spectra.

Topcoat	Abs. Int.*	Color†	Vehicle Type‡ and Year	No. Paints§/Pigments¶
74A0002		White	AMER 71–74	1 RU vs
74E0003		Red	AMER 73–75	1 MO s
74L0007		Blue	AMER 73,74	1 RU s
74H0008	w	Yellow	AMER 73,74	1 RU s LC w
74G0019		Orange	AMER 74,75	3Y FO w MO w
74L0021		Blue	CRPL DODG 74,75	3Y RU s
74E0024		Red	CRPL DODG 72–75	3Y MO m
74H0029		Yellow	CRPL DODG 72–75	3Y RU s HF?
74A0033		White	CRPL DODG 72–75	9YM RU vs
74H0035		Yellow	CRPL DODG 73,74	1 RU vs
74H0037		Yellow	CRPL DODG 74,75	3Y RU vs
FN76C0090	w	Black	FORD LIME 76,77	25YB
DC89 0090	vw	Black	FORD LIME 89	25YB
74E0094		Red	FORD LIME 72–76	2N MO m
FN78E0094		Red	FORD 78,79	2N MO m
74E0095		Red	FORD 74,75 LIME 75	7Y MO w OR w
74L0103		Blue	FORD LIME 74,75	1 RU vs
74H0120		Yellow	FORD LIME 74,75	1 RU s HF w
FN78A0121		White	FORD 78–80	12Y RU vs
KN78A0121	w	White	FORD 78–80	12Y RU vs
74A0123		White	FORD LIME 74,75	19YM RU vs
FN76A0123		White	FORD LIME 76–79	19YM RU vs
KN76A0123	w	White	FORD LIME 76,77	19YM RU vs
KN78A0123	w	White	FORD LIME 78–80	19YM RU vs
FN80A0123		White	FORD LIME 80–82	19YM RU vs
FN76H0157		Yellow	FORD LIME 76–78	3Y RU s LC w
FX75H0159		Yellow	FORD LIME 75	5N RU s
FN76H0159		Yellow	FORD LIME 76,77	5N RU s HF?
KN76H0159		Yellow	FORD LIME 76	5N RU s
BN75A0163	w	White	AMER 75	7Y RU vs
KN75A0163		White	AMER 75	7Y RU vs
BN76A0163		White	AMER JEEP 76	7Y RU vs
BN75L0164		Blue	AMER 75	2N RU s
DN75L0164		Blue	AMER 75	2N RU s
DN75H0168		Yellow	AMER 75	2N TI m HF s
LN75H0168		Yellow	AMER 75	2N TI m HF s
LN75K0174		Green	AMER 74,75	2N RU m
BN75F0175	w	Brown	AMER 74,75	2N TI w HF m
BN77E0222		Red	AMER JEEP 77	5Y MO s
BN76H0225	vw	Yellow	AMER JEEP 76,77	4N RU s LC?
BN78H0225		Yellow	AMER JEEP 78	4N RU s LC?
FN76B0242		Gray	FORD LIME 76–79	4N RU m
FN76E0243		Red	FORD LIME 76	6N MO s
KN76E0243		Red	FORD LIME 76	6N MO s
FN78E0243		Red	FORD 78,79	6N MO s
FN76L0246		Blue	FORD LIME 76	4N RU s
FN76G0248		Orange	FORD LIME 76	4N LC s
FN76H0249		Yellow	FORD LIME 76–79	8N RU vs
KN78H0249	w	Yellow	FORD LIME 78,79	8N RU vs
FN76F0250		Brown	FORD 76–78 LIME 76,77	7Y RU m HF vw
FN76H0251		Yellow	FORD LIME 76	4N RU m HF w
FN78H0251		Yellow	FORD LIME 78,79	4N RU m HF w
FN76H0253		Yellow	FORD 76	2N RU vs LC w
BN77L0285		Blue	AMER 77	4Y RU s
BN78G0293		Orange	AMER JEEP 78	4Y MO s
FN77L0309		Blue	FORD LIME 77,78	2N RU vs FE vw
FN77G0312		Orange	FORD LIME 77	6Y LC m RU w
FN77H0313		Yellow	FORD LIME 77	3N RU vs HF vw
FN78L0356		Blue	LIME 78	2YB FE vs
FN78E0400		Red	FORD LIME 78	2N MO m
FN78L0401	w	Blue	FORD LIME 78	3N FE vs
FN78L0402		Blue	FORD 80 LIME 78,79,82	6YM RU s
FN78F0405		Brown	LIME 78,79	1 RU s
FN78H0408		Yellow	FORD LIME 78,79	6Y RU vs
FN78K0410		Green	FORD LIME 78	2N RU s
FN78K0411		Green	FORD 78,79 LIME 78	2N HF m
FN78F0414		Brown	FORD LIME 78,79	6N RU s HF w
KN78F0414		Brown	FORD LIME 78,79	6N RU s HF w
FN78G0415		Orange	FORD LIME 78,79	3N MO s
FN78A0416		White	FORD 78–80	7Y RU vs

TABLE 3—Continued

Topcoat	Abs. Int.*	Color†	Vehicle Type‡ and Year	No. Paints§/Pigments¶
FN84 0416		White	FORD 84	7Y RU vs
DC86 0466	vw	White	GNMO 86–88	15Y RU vs
DC86 0467	vw	Black	GNMO 86–88	14Y
FN78L0475		Blue	FORD 78,80	8Y RU m
FN84 0475		Blue	FORD 84	8Y RU m FE vw
FN84 0476		Yellow	FORD 84	8Y CY vs
FN78H0477		Yellow	FORD 78,79 LIME 79	2N RU s LC w HF?
FN78K0478		Green	FORD 78,79	3N RU s
FN78K0479		Green	FORD 78–80	7Y RU m HF w
FN84 0479		Green	FORD 84	7Y RU m HF w
FN78K0480	w	Green	FORD 78,79	1 RU m LC w
FN78F0482	w	Brown	FORD 78	3N LC w FO w
FN79L0562		Blue	FORD LIME 79–81	7Y RU vs
FN79L0563		Blue	FORD LIME 79,80	3NM RU m
FN79K0567		Green	FORD 79,80 LIME 79	3N RU s
FN79H0580		Yellow	FORD 79,80 LIME 80	4NM RU vs
FN80G0639		Orange	FORD 80,81 LIME 80	5YM CY s RU m
FN80H0641		Yellow	FORD LIME 80,81	7YM RU vs
FN83 0642		Brown	FORD 83	2Y FO w OR m
DC86 0824	vw	Blue	GNMO 86,88	12YM
FN82H0840	vw	Yellow	FORD LIME 82–84	4NM RU vs
DC89 1049	vw	(White)	FORD LIME 89	13YB RU s
DC89 1260	vw	(Blue)	FORD LIME 89	6Y RU m
DC89 1270	vw	(Gray)	FORD 89	4Y RU m
DC89 1292	vw	(Gray)	FORD LIME 89	5Y RU s
DC88 1351	vw	(Red)	FORD 88	4N FO w OR w
DC89 1351	vw	(Red)	FORD 89	4N FO w OR w
DC89 1352	vw	(Brown)	FORD LIME 89	5YB FO w OR w
DC89 1360	vw	(Brown)	FORD LIME 89	2Y RU m
DC88 1442	vw	(Gray)	FORD LIME 88	4NB RU m
DC88 1466	vw	(Yellow)	FORD 88	2Y RU s HF?
DC89 1621	vw	(Red)	FORD LIME 89	1 FO w OR m
DC89 1624	vw	(Gray)	FORD 89	2N RU s
DC89 1629	vw	(Red)	FORD 89	2N OR m
DC89 1638	vw	(Red)	FORD 89	1 FO m OR w

\*Absorption intensity of the nitrile stretching peak; no entry is given for those topcoats which have a "normal" intensity for this peak; w = weak, vw = very weak.

†This is the color indicated by the fifth character of the identification code (see Table 1); for colors introduced in 1983 or later, panels were compared to others in the Collection to assign a color and these colors are indicated in parentheses.

‡The abbreviations used (43) are as follows: AMER = American, BUIC = Buick, CADI = Cadillac, CHEV = Chevrolet, CRPL = Chrysler/Plymouth, DODG = Dodge, FORD = Ford, GNMO = GMC, JEEP = Jeep, LIME = Lincoln/Mercury, OLDS = Oldsmobile, PONT = Pontiac.

§The number of different paints used for this color is given; if there is more than one, the possibility of distinguishing between the various vehicles having this color based on the presence of a nitrile stretching peak is indicated: Y means that the presence of a nitrile peak can serve, by itself, to eliminate some vehicles as possible sources; N means that this is not possible based on this criterion alone. B indicates that at least one of the topcoats of this color consists of a basecoat/clearcoat finish. M indicates that at least one other topcoat of this color is not in the Reference Collection.

¶The inorganic pigments which were identified (45) in these topcoats are listed. The abbreviations for the pigments are: CY = Chrome Yellow, FE = iron ferrocyanide, FO = ferric oxide, HF = hydrous ferric oxide, LC = a lead chromate pigment but cannot differentiate between Chrome Yellow and Molybdate Orange, MO = Molybdate Orange, OR = an unidentified organic pigment, RU = rutile (titanium dioxide), and TI = titanium dioxide indicated but cannot differentiate between rutile and anatase (it should be noted, however, that anatase by itself does not appear to have been used in automobile topcoats). A question mark after a pigment indicates that a very weak absorption of that pigment appears to be present. The intensity of the pigment absorption is given after each pigment (if the pigment has more than one absorption, the intensity of the strongest peak is listed). The abbreviations are: w = weak, m = medium, s = strong, and vs = very strong (indicating the strongest absorption in the spectrum).

(metallic), KN80F0671 (nonmetallic), and DC89 1707 (nonmetallic). The spectrum of NW75K0187 is shown in Fig. 2a; the nitrile peak can be seen more clearly when the entire thickness of this topcoat is sampled (Fig. 2b). As will be described in more detail elsewhere, these very weak absorptions are consistent with the presence of certain very minor paint components unrelated to acrylonitrile, although for those with peaks near 2239  $\text{cm}^{-1}$ , the alternative explanation of small amounts of acrylonitrile cannot be completely ruled out (this is more likely the situation for DC89 1707, as described later). In any case, the vast majority of these peaks are not apt to be confused with the acrylonitrile absorptions of interest here, since they are too weak to be observed. Several nonacrylonitrile topcoats<sup>3</sup> produced in the 1980s, however, have spectra with nitrile peak intensities comparable to that of Fig. 2c;

these can be differentiated from those with acrylonitrile by their lower peak frequencies, which typically occur below 2235  $\text{cm}^{-1}$ .

Acrylonitrile absorptions occur in spectra of 105 of the 1330 nonmetallic topcoats (8%), and 84 of the 1669 metallic topcoats (5%). They occur for topcoats of 82 of the 400 nonmetallic colors

<sup>3</sup>For nonmetallic topcoats, these include: PC82C0041, PC88 0090, NN82F0250, AC84 0465, AC84 0500, AC84 0506, BN83 0562, DB79K0586, NN82B0761, PC85 1049, PC88 1049, NN84 1054, PC85 1054, PN86 1126, PC85 1169, PC85 1170, PC85 1178, PC85 1207, PC88 1260, PC88 1270, PN87 1352, and PC88 1442. All have acrylic melamine enamel binders except for DB79K0586, which is an acrylic lacquer. Extensive transmittance spectra were not obtained for metallic finishes, but two examples of metallic topcoats having these stronger absorptions are NN84 0981 and PN87 1261.

TABLE 4—U.S. automobile original metallic topcoats (1974–1989) which have an acrylonitrile nitrile stretching absorption in their infrared spectra.

Topcoat	Abs. Int.*	Color†	Vehicle Type‡ and Year	No. Paints§ Pigments
74L0004		Blue	AMER 73,74	1
74F0009		Brown	AMER 73,74	1 FO w OR w
74L0010		Blue	AMER 74	1
74L0011		Blue	AMER 74	1
74F0013		Brown	AMER 75	1 FO m OR vw
74K0014		Green	AMER 74	1
74E0017		Red	AMER 74	1 OR w
74B0018		Gray	AMER 74	1
FN76B0092		Gray	FORD LIME 76–79	15Y
FN80B0092		Gray	FORD LIME 80–82	15Y
FN83 0092		Gray	FORD LIME 83	15Y
74L0093		Blue	FORD 75 LIME 74,75	2N
FN76L0093	w	Blue	FORD LIME 76	2N
FN76L0100		Blue	FORD LIME 76	4Y
FN76L0101	w	Blue	FORD 76–79 LIME 76–78	6Y
FN76K0107	w	Green	FORD LIME 76,77	5Y FO w
74F0110		Brown	FORD LIME 73–75	7N FO w OR vw
FN76F0110	w	Brown	FORD LIME 76	7N FO w OR vw
FN78F0110	w	Brown	FORD LIME 78,79	7N FO w
FN76F0113	w	Brown	FORD LIME 76	4Y FO w
74F0116		Brown	FORD 75 LIME 74,75	1 FO w OR w
74L0124		Blue	FORD LIME 73–75	3Y
74K0125	w	Green	FORD LIME 74,75	3N HF m
FN76K0125	w	Green	FORD LIME 76	3N HF m
74F0126		Brown	FORD LIME 72–75	1 OR w
FN76F0127		Brown	FORD LIME 76	4Y FO w
74F0128		Brown	FORD LIME 72–74	1
FC76F0139		Brown	LIME 76	2Y
FX75L0151	w	Blue	FORD LIME 75	2N
FC76L0151		Blue	FORD LIME 76	2N
FC76F0152		Brown	LIME 76	2Y
FC76B0153	w	Gray	FORD 76 LIME 76,77	2Y
FX75L0154		Blue	LIME 75	1
FX75F0155		Brown	FORD LIME 75	1 HF m OR w
FN76K0160		Green	FORD LIME 76–79	9Y
FX75J0161		Olive	FORD LIME 75	1 HF w
FN75F0162¶		Brown	FORD 75,79 LIME 75	5Y OR w FO?
KN75L0165		Blue	AMER 75	4Y
LN75L0165		Blue	AMER 75	4Y
BN75L0166	w	Blue	AMER 75	2N
DN75L0166		Blue	AMER 75	2N
KN75J0169		Olive	AMER 75	2Y HF s
KN75F0171		Brown	AMER 75	3N FO w OR m
BN75B0172		Gray	AMER 75	2N
KN75B0172		Gray	AMER 75	2N
BN76K0217		Green	AMER 76	2N
BN76K0221	w	Green	AMER 76	2N HF w
BN76L0224	w	Blue	AMER 76 JEEP 76	2N
FN76F0247		Brown	FORD LIME 76–79	16Y FO w
FN80F0247		Brown	FORD 80	16Y FO w
FN76L0252		Blue	FORD 76–78 LIME 76	2N
FN76F0254	w	Brown	LIME 76	1 FO w HF vw
FN76J0255		Olive	FORD LIME 76,77	3N HF?
FC76C0256	w	Black	LIME 76,77	1
FC76G0257		Orange	FORD LIME 76,77	1 FO w OR vw
FC76H0258	w	Yellow	FORD 76 LIME 76,77	1
FC76K0259		Green	FORD 76	1
FC76E0260		Red	LIME 76,77	1
FC76K0261		Green	FORD 76 LIME 76,77	1
FN77F0283	w	Brown	AMER 77,78 JEEP 76–78	4N FO m
FN77B0308	w	Gray	FORD LIME 77–79	11YM
FN80B0308	w	Gray	FORD LIME 80,81	11YM
FN77K0311		Green	FORD 77	2N
FN77F0314		Brown	FORD LIME 77	4N FO m
KN77F0314	w	Brown	FORD LIME 77	4N FO m
FN77F0317		Brown	FORD LIME 77,78	4NM
FN77E0319		Red	FORD 77	2N
FN77L0320	w	Blue	FORD LIME 77,78	3N
FN77L0321		Blue	FORD 77,78	2N
FN77K0322		Green	FORD LIME 77–79	2N

TABLE 4—Continued

Topcoat	Abs. Int.*	Color†	Vehicle Type‡ and Year	No. Paints§ Pigments
FN77K0323	w	Green	FORD 77	2N
FN77F0324		Brown	FORD LIME 77-79	3N HF m
FN77F0325	w	Brown	FORD LIME 77,78	3Y FO w
FC77L0328	w	Blue	LIME 77	1
FC77F0330	w	Brown	LIME 77	1 FO w
FN78F0406	w	Brown	FORD 78	1 FO w
FN78B0472	w	Gray	FORD 78	1
FN78F0483	w	Brown	FORD 78	2N FO w
FN78F0489	w	Brown	FORD 78	2N FO w
FN79L0564		Blue	FORD LIME 79-81	11Y
FN79K0565		Green	FORD LIME 79	4N
FN79F0583	w	Brown	FORD 79,80	3N HF m
FN80K0643	w	Green	FORD LIME 80,81	6NM
FN80K0645		Green	FORD LIME 80,81	5NM

\*As in Table 3.

†As in Table 3.

‡The abbreviations are as in Table 3.

§As in Table 3.

||As in Table 3.

¶This panel is labeled FX75F0162 and FX75 is listed under color 0162 in the *Reference Collection Technical Data* booklet for the 1975 supplement. In the 1989 supplement booklet (43) under color 0162, it is listed as FN75.

(21%), and 70 of the 620 metallic colors (11%). Of the 152 colors (total metallic and nonmetallic) for which there are topcoats containing acrylonitrile, 116 have more than one source of paint. In 28 of these cases, two or more topcoats have acrylonitrile peaks. For roughly half of the multiple source colors, the presence of a nitrile peak can serve, by itself, to eliminate from consideration some of the vehicles for which that particular color was used. As an example, three paints, 74G0019, CN76G0019, and LN76G0019—all acrylic melamine enamels—were used for color 0019, but only 74G0019 has a nitrile peak in its spectrum. Topcoat 74G0019 was used on certain 1974 and 1975 American Motors vehicles, while CN76G0019 and LN76G0019 were both used on 1976 Jeeps and certain 1976 American Motors vehicles. The latter 1976 vehicles can be eliminated as possibilities if a paint of color 0019 has a nitrile peak (conversely, in this case, the absence of a nitrile peak for this color can eliminate the former vehicles). The last columns of Tables 3 and 4 list how many paints of that particular color were used; if there were two or more, whether the presence of a nitrile peak can serve to narrow the list of possible vehicles is indicated.

Examination of the manufacturing data (Table 1) for the topcoats of Tables 3 and 4 reveals some clear trends. Not counting the 31 1974 topcoats, for which manufacturing data were not provided, the remaining 158 paints are mostly Ford NAD enamels (90) or other Ford paints (17), and NAD enamels manufactured by Cook (13), PPG of Canada (14), Canadian Industries (3), and DuPont (3). Excluding three 1986 DuPont nonmetallic enamels (DC86 0466, white; DC86 0467, black; and DC86 0824, blue), all of the other acrylonitrile topcoats were used on non-GM vehicles; this includes the 1974 paints, and most of these vehicles were Fords (Tables 3 and 4).

The manufacturing dates of the acrylonitrile topcoats are also not randomly distributed, as may be seen from Fig. 3a. This chart lists the acrylonitrile topcoats by the year that they were first produced. A chart that perhaps better reflects the chronological distribution of vehicles which used acrylonitrile topcoats is shown below (Fig. 3b), where the acrylonitrile topcoats are listed by vehicle model years (for example, FN76A0126 is counted once each for 1976, 1977, 1978, and 1979, since this paint was used

on vehicles of these model years). From these charts, it is evident that acrylonitrile topcoats were produced predominantly during the first half of the time period (1974–1989) covered, and that they were used mostly on vehicles from the 1970s and early 1980s. For metallic finishes, acrylonitrile topcoats were not used on any vehicles after the 1981 model year (Table 4). Excluding a group of DuPont enamels, the last model year for which an acrylonitrile nonmetallic topcoat was used was 1984.

According to Ford Motor Company Paint Operations,<sup>4</sup> which produced most of the acrylonitrile topcoats, the decline in their use was due to a number of factors, including safety/environmental concerns about acrylonitrile. Also, NAD enamels in general were supplanted by newer enamels which produced a superior appearance (especially with regard to gloss) to that possible with the NAD paints.

The 18 1986–1989 DuPont nonmetallic topcoats (Table 3—all have “DC” as the first two characters in their codes) are somewhat unusual not only because of their very weak acrylonitrile peaks (Fig. 2c), but also because they were produced after acrylonitrile usage in other topcoats was discontinued (Fig. 3a). According to DuPont,<sup>5</sup> the small amounts of acrylonitrile in these topcoats are from an NAD resin that comprises roughly 20% of the binder formulation of these high-solids enamels. Further, this NAD resin is the only source of styrene in these enamels, which would account for the lack of significant styrene absorptions, which also seems to be characteristic of these particular topcoats. Although 1989 was the last year covered in this study, DuPont continued to produce this type of nonmetallic topcoat through the 1995 model year.<sup>6</sup>

#### Ferrocyanide Pigment Absorptions

Iron Salts of the ferrocyanide anion,  $[\text{Fe}(\text{CN})_6]^{-4}$ , are used for a number of blue paint pigments, including some used in automobile

<sup>4</sup>Now part of the DuPont Company, Automotive Paint Division, personal communication, May 1991.

<sup>5</sup>The DuPont Company, Automotive Paint Division, personal communication, August 1993.

<sup>6</sup>DuPont Automotive Products, personal communication, June 1995. These single layer finishes are not common since most topcoats are now basecoat/clearcoat finishes, and the high-solids enamels may now be used mostly for white colors.



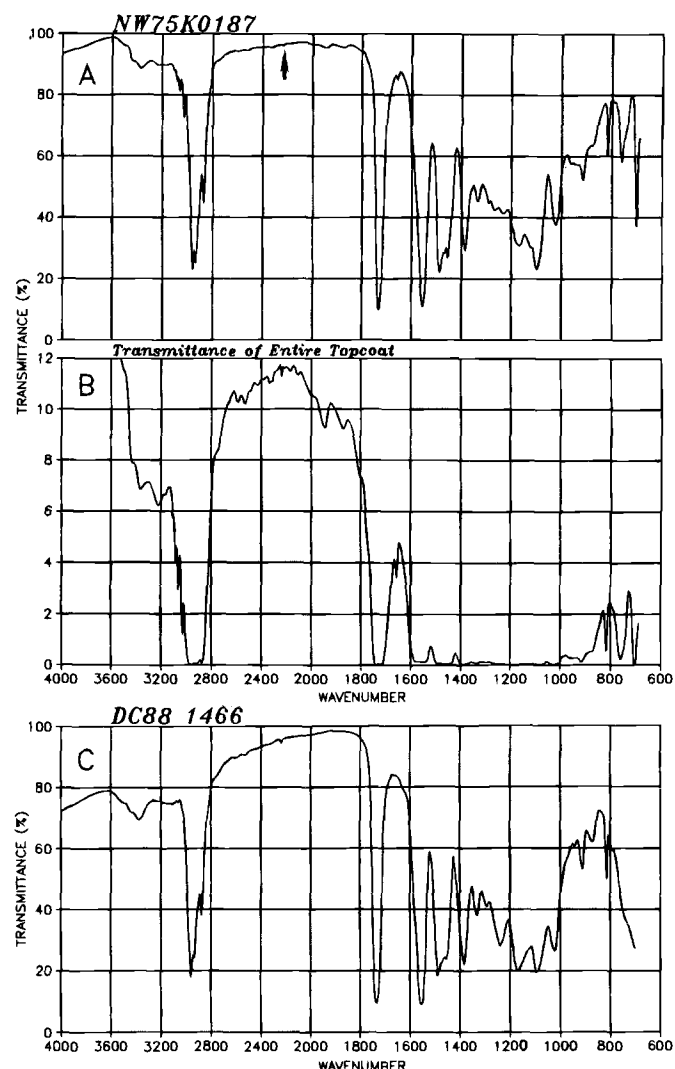


FIG. 2—Infrared microscope spectra of two topcoats sampled without substrates: (a) NW75K0187, spectrum of a thin slice; the position of the very weak nitrile absorption is indicated by an arrow; (b) NW75K0187, spectrum of the entire topcoat layer; and (c) DC88 1466.

topcoats. The ferrocyanide pigments include varieties known as Iron Blue, Prussian Blue, and so forth, and they differ primarily in the specific composition of the cations used and the method of preparation (49,54,55). The cations may include—in addition to iron—potassium, sodium, and ammonium, and combinations thereof. Ferrocyanide may also be found in some green paints since Prussian Blue is an ingredient of Chrome Green.

The spectra of the ferrocyanide pigments are dominated by the cyano stretching fundamental, which occurs near  $2090\text{ cm}^{-1}$ . This can be seen from the spectrum (Fig. 4a) of Prussian Blue (Aldrich Chemical Co.; Aldrich lists this pigment as ferric ferrocyanide,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ). Although both acrylonitrile and ferrocyanide absorptions involve  $\text{C}\equiv\text{N}$  stretching modes, they are easily distinguished since the former occurs at a higher frequency; ferrocyanide peaks are also broader than acrylonitrile peaks.

Table 5 lists the U.S. original nonmetallic topcoats (1974–1989) which have ferrocyanide absorptions in their spectra. All are blue paints (as defined by their generic color codes) and all have acrylic melamine enamel binders. The intensities of the ferrocyanide cyano peaks were found to vary over a very wide range for nonmetallic finishes, but generally they tended to be quite strong. For most of the topcoats of Table 5, in fact, the cyano stretching peak is the

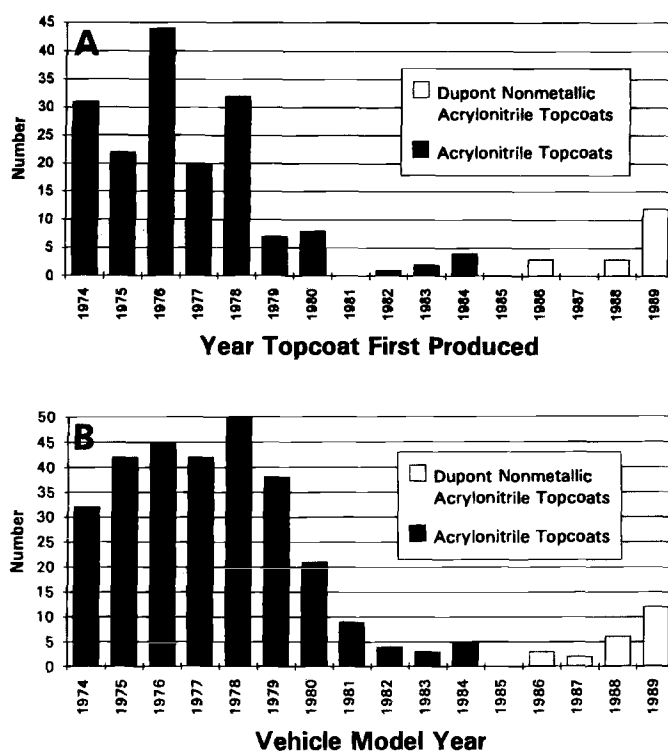


FIG. 3—Histograms depicting the chronological distribution of U.S. automobile original topcoats (1974–1989) that have acrylonitrile absorptions in their infrared spectra: (a) distribution of acrylonitrile topcoats according to the year in which they were first manufactured or introduced into the Reference Collection; and (b) distribution according to the model years that a particular topcoat was used. The DuPont nonmetallic enamels (1986–1989) having very weak nitrile peaks are shown in clear bars.

strongest absorption in the spectrum, as may be seen from the spectrum of one of these, FN84 0525 (Fig. 4b). For these particular topcoats, the absorption intensities of Table 5 are indicated as “very strong,” and all are very dark blue in color. The spectrum of a nonmetallic topcoat (NC84 0830) having a medium intensity cyano peak is depicted in Fig. 4c; for these, as well as for topcoats having stronger cyano absorptions, some of the other weaker pigment absorptions may also be observed in the topcoat spectra (compare Figs. 4a, 4b and 4c). Note, however, that the trio of ferrocyanide absorptions below  $700\text{ cm}^{-1}$  cannot be observed if an infrared microscope equipped with a narrow-band MCT detector is used, since the three occur below the low frequency limit of this detector.

One nonmetallic topcoat, KN82L0830 (Fig. 4d), has a weak cyano peak, but it may still be quite conspicuous since absorptions are not common in this spectral region. Two Ford nonmetallic NAD topcoats, FN77L0309 (Fig. 5b) and FN84 0475 (Fig. 5d), have very weak cyano peaks with intensities comparable to the adjacent styrene overtone/combination bands. These particular cyano peaks could be easily overlooked, but they are real features; they are not observed in the spectra of two topcoats which have identical colors to these,<sup>7</sup> NC77L0309 and FN78L0475 (Figs. 5a and 5c, respectively), nor in spectra of any other blue nonmetallic topcoats other than those listed in Table 5. Interestingly, both FN77L0309 and FN84 0475 also contain acrylonitrile, and it is

<sup>7</sup>Elemental analyses were performed on FN77L0309, FN84 0475, NC77L0309, and FN78L0475 using X-ray fluorescence (XRF) spectrometry. The instrument and methods used for this are described elsewhere (45). Using a germanium secondary target as the excitation source, titanium

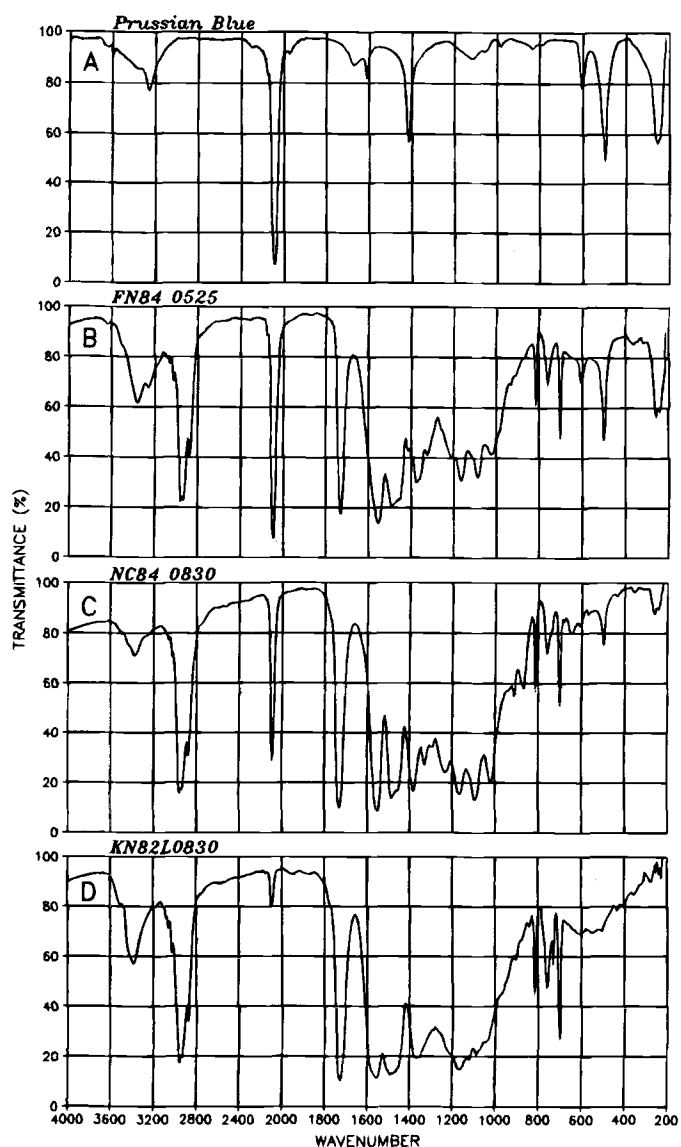


FIG. 4—Low pressure DAC spectra obtained using the CsI/DTGS system: (a) Prussian Blue plus excess CsI pressed between both anvils; (b) FN84 0525 pressed onto a single anvil; (c) NC84 0830 pressed onto a single anvil; and (d) KN82L0830 pressed onto a single anvil. A total of 1000 scans were averaged for each sample.

possible that the stronger (and more conspicuous) nitrile absorptions may prompt the analyst to examine this spectral region more carefully, and perhaps be more likely to detect the very weak cyano absorptions.

Of the 400 nonmetallic colors, 47 are classified as blue and nine more, added after 1982, also fall within the blue classification

was the main element detected for all four topcoats, along with small amounts of iron and copper; aluminum, silicon and sulfur were also detected for FN77L0309 and NC77L0309, and small amounts of zinc were detected for FN77L0309 and FN78L0475. The levels of iron appear to be higher for FN77L0309 compared to NC77L0309, and for FN84 0475 compared to FN78L0475; the iron of NC77L0309 and FN78L0475 may be due to contaminants (45). The copper most likely reflects use of the blue pigment Copper Phthalocyanine Blue. Elemental analyses of these four topcoats were also conducted using energy dispersive X-ray analysis on a scanning electron microscope (a Leica S430 microscope was used with an Oxford Isis® X-ray analysis unit). Using an electron excitation voltage of 20 KV, aluminum, silicon, sulfur and titanium (along with oxygen) were detected as with XRF, but iron, copper, and zinc were not.

TABLE 5—U.S. automobile original nonmetallic topcoats (1974–1989) that have a ferrocyanide cyano stretching absorption in their infrared spectra.

Topcoat	Abs. Int.*	Binder Type†	Color‡	Vehicle Type§ and Year	No. of Paints
FN77L0309	vw	AME	Blue	FORD IME 77,78	2YA
FC77L0310	vs	AME	Blue	LIME 77,78	2N
NN77L0310	vs	AME	Blue	LIME 77	2N
FN78L0356	vs	AME	Blue	LIME 78	2NAB
FN78L0401	vs	AME	Blue	FORD LIME 78	3NA
NN78L0401	s	AME	Blue	FORD LIME 78	3N
FN84 0475	vw	AME	Blue	FORD 84	8YA
PN79L0525	vs	AME	Blue	CRPL DODG 79–81	6NM
NN80L0525	vs	AME	Blue	CRPL DODG 79–82	6NM
KN81L0525	vs	AME	Blue	CRPL DODG 81–83	6NM
KN84 0525	vs	AME	Blue	CRPL DODG 84	6NM
PN84 0525	vs	AME	Blue	CRPL DODG 84	6NM
BN81L0724	vs	AME	Blue	AMER JEEP 81	2N
PN81L0724	vs	AME	Blue	AMER JEEP 81	2N
AC82L0824	m	AME	Blue	GNMO 82	12YM
NC82L0824	m	AME	Blue	GNMO 82–84	12YM
AC84 0824	m	AME	Blue	GNMO 83,84	12YM
NC85 0824	m	AME	Blue	GNMO 85	12YM
KN82L0830	w	AME	Blue	AMER JEEP 82	6YB
NC84 0830	m	AME	Blue	AMER JEEP 84	6YB

\*Absorption intensity of the ferrocyanide cyano stretching peak; vw = very weak, w = weak, m = medium, s = strong, vs = very strong (these are the strongest peaks in the spectrum).

†AME = acrylic melamine enamel.

‡As in Table 3.

§The abbreviations are as in Table 3.

||The number of different paints used for this color is given; if there is more than one, the possibility of distinguishing between the various vehicles using this color based on the presence of a cyano peak is indicated: Y means that the presence of a cyano peak can serve, by itself, to eliminate some vehicles as possible sources; N means that this is not possible based on this criterion alone. An A indicates that the spectrum of this topcoat also has a nitrile stretching absorption; a B indicates that at least one of the topcoats of this color consists of a basecoat/clearcoat finish; and an M indicates that at least one other topcoat of this color is not in the Reference Collection.

¶This panel is labeled FN77L0310 but it is listed in the 1989 Reference Collection Technical Data booklet (43) under color 0310 as FC77.

based on comparisons to earlier panels. There are 168 topcoats comprising these 56 blue colors and ferrocyanide absorptions occur in spectra of 20 of them (12%). These 20 topcoats represent nine of the 56 blue colors (16%). All nine of these colors have multiple sources of paint and for six of them, two or more of the topcoats contain ferrocyanide. The presence or absence of a ferrocyanide absorption, by itself, is thus less useful for discriminating between vehicles of the same color (Table 5) than was the case with acrylonitrile peaks. Although the relative intensities of the ferrocyanide peaks for the identical color topcoats are usually comparable, this may not always be the case—compare, for example, Figs. 4c and 4d, and Figs. 6b and 6c. Also, while topcoats having spectra with very strong cyano absorptions are invariably dark blue, topcoats with weaker cyano absorptions can also be dark blue since other pigments may be used together with ferrocyanide (see Footnote 7).

In contrast to the nonmetallic topcoats, which have a wide range of cyano peak intensities, the ten metallic topcoats which were found to contain ferrocyanide all have very weak cyano peaks (Figs. 7a, 7b, and 7c, and Table 6). The weaker ones are barely noticeable (Fig. 7a), and probably would not be detected unless actively sought. Although very weak, these peaks can still serve in certain cases to help discriminate between similar paints; compare, for example, Figs. 7c and 7d, which depict spectra of two

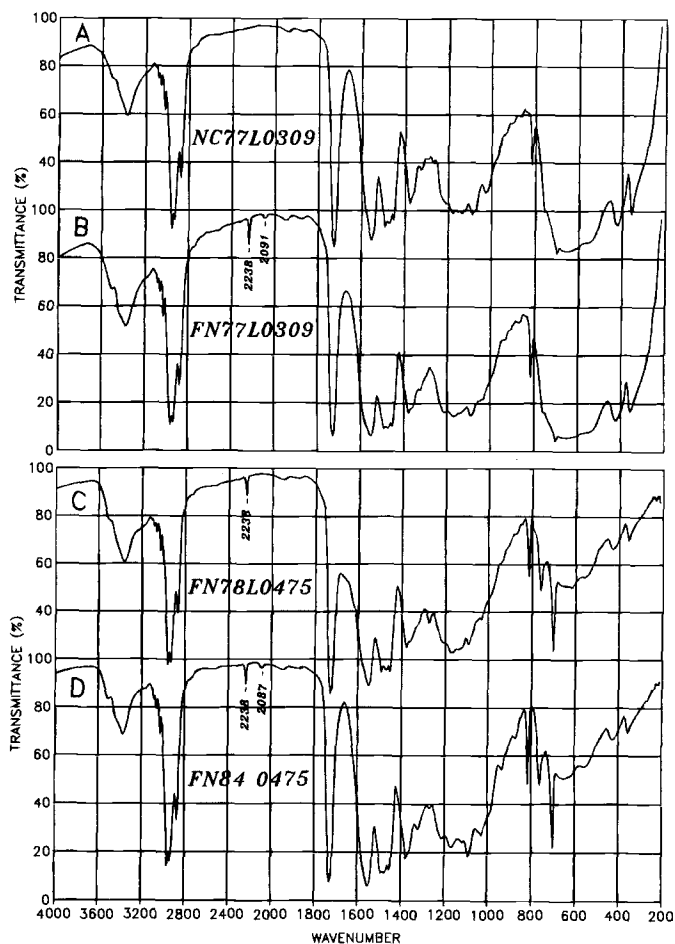


FIG. 5—Spectra of four nonmetallic topcoats sampled without substrates using the CsI/DTGS system: (a) NC77L0309; (b) FN77L0309; (c) FN78L0475; and (d) FN84 0475. A total of 1000 scans were averaged for each topcoat.

PPG Industries blue metallic enamels having the same color. With metallic finishes, ferrocyanide also occurs in a few acrylic lacquers (Table 6 and Fig. 7b), and one of the ferrocyanide metallic topcoats is classified as green (the rest are all blue).

#### Acrylonitrile and Ferrocyanide Absorptions

In addition to FN77L0309 and FN84 0475, which have very weak cyano peaks (Fig. 5), two other Ford nonmetallic NAD enamels were also found to have both acrylonitrile and ferrocyanide absorptions in their spectra. These topcoats, FN78L0356 and FN78L0401, have similar dark blue colors and very strong cyano spectral absorptions (Figs. 6a and 6b, respectively). The two spectra exhibit some differences in binder absorptions in the 1500–900  $\text{cm}^{-1}$  region, however, where acrylic monomer differences are sometimes manifested (21). Also shown (Fig. 6c) is the spectrum of NN78L0401, an Inmont NAD enamel which has the same color as FN78L0401, but this spectrum lacks the nitrile peak and the cyano peak is not as strong (relative to binder absorptions) as it is for FN78L0401. Because of the presence of both nitrile and (very strong) cyano absorptions, FN78L0356 and FN78L0401 should be particularly easy to identify.

#### Detection of Nitrile and Cyano Absorptions Using Diamond Anvil Cells

As noted earlier, no information can be obtained for the 2400 to 1900  $\text{cm}^{-1}$  spectral region using a high pressure DAC on a

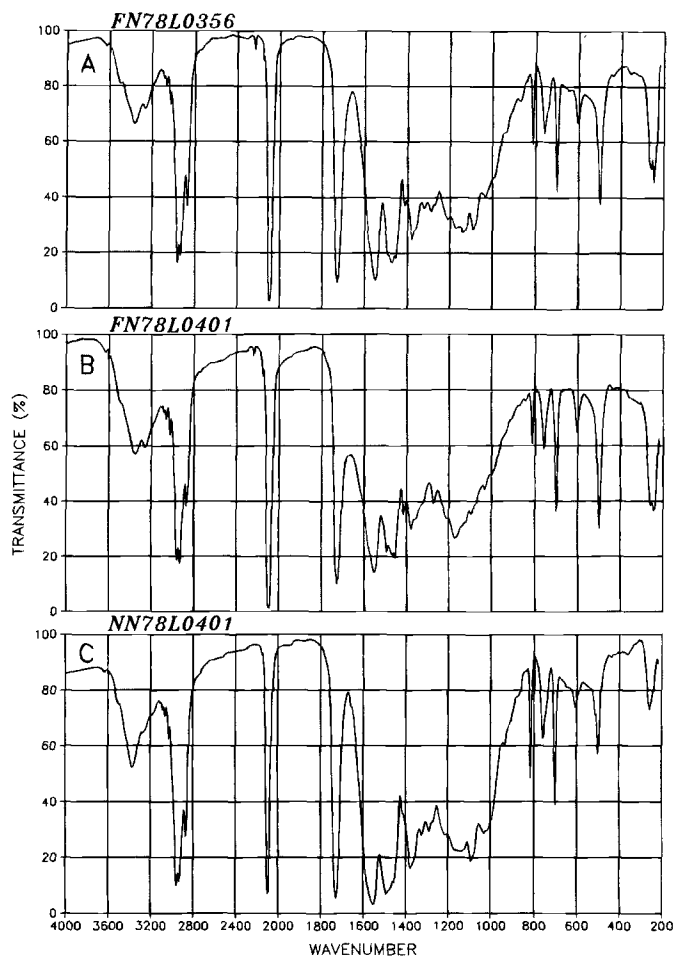


FIG. 6—Spectra of three dark blue nonmetallic topcoats having similar or identical colors sampled without substrates using the CsI/DTGS system: (a) FN78L0356; (b) FN78L0401; and (c) NN78L0401. A total of 1000 scans were averaged for each topcoat.

dispersive instrument, and nitrile and cyano peaks cannot be observed. With an FT-IR instrument and accessories, a variety of DAC sampling modes is possible and these were examined to determine their suitability for detecting nitrile and cyano peaks. Because of the diamond absorptions, the main factor affecting this is the thickness of the anvil window. The transmissions (obtained using the infrared microscope) of a single anvil of the low pressure DAC, both anvils of the low pressure DAC, and both anvils of the high pressure DAC are shown in Figs. 8d, 8e, and 8f, respectively. The positions of the nitrile and cyano peaks in relation to the diamond absorptions may also be seen from this depiction, where portions of the spectra of acrylonitrile (Fig. 8b) and ferrocyanide (Fig. 8c) topcoats are shown. Both of these  $\text{C}\equiv\text{N}$  stretching modes absorb where the strongest diamond features occur.

Although the high pressure DAC is not completely opaque in this region (Fig. 8f), the noise levels that appear in ratioed FT-IR spectra usually preclude an identification of nitrile peaks. Figure 8j shows a portion of the high pressure DAC spectrum of BN75L0164 obtained using a broad-band MCT detector. The nitrile peak of BN75L0164—shown in Fig. 8b for an infrared microscope sampling without a substrate—is buried in the noise of this spectrum, which resulted from averaging 100 scans. When 1000 scans are averaged for this same sample, the nitrile absorption becomes somewhat more apparent (Fig. 8a), but it is still difficult to identify.

While the same problem occurs for cyano peaks, it may be possible in some cases to observe the more intense ferrocyanide absorptions using a high pressure DAC/FT-IR system (Fig. 8k).

Increased noise levels for the diamond absorbing region also occur using the low pressure DAC, but nitrile peaks can be more easily discerned from the noise. Figures 8i, 8h, and 8g, depict portions of the low pressure DAC spectra of BN75L0164 obtained using, respectively, both anvils with the beam condenser, a single anvil with the beam condenser, and a single anvil with the infrared microscope. A 100 micrometer by 100 micrometer area was sampled for the latter, and 100 scans were collected for all three spectra. The diamond region noise levels may be seen to decrease progressively for these three samplings; with the beam condenser

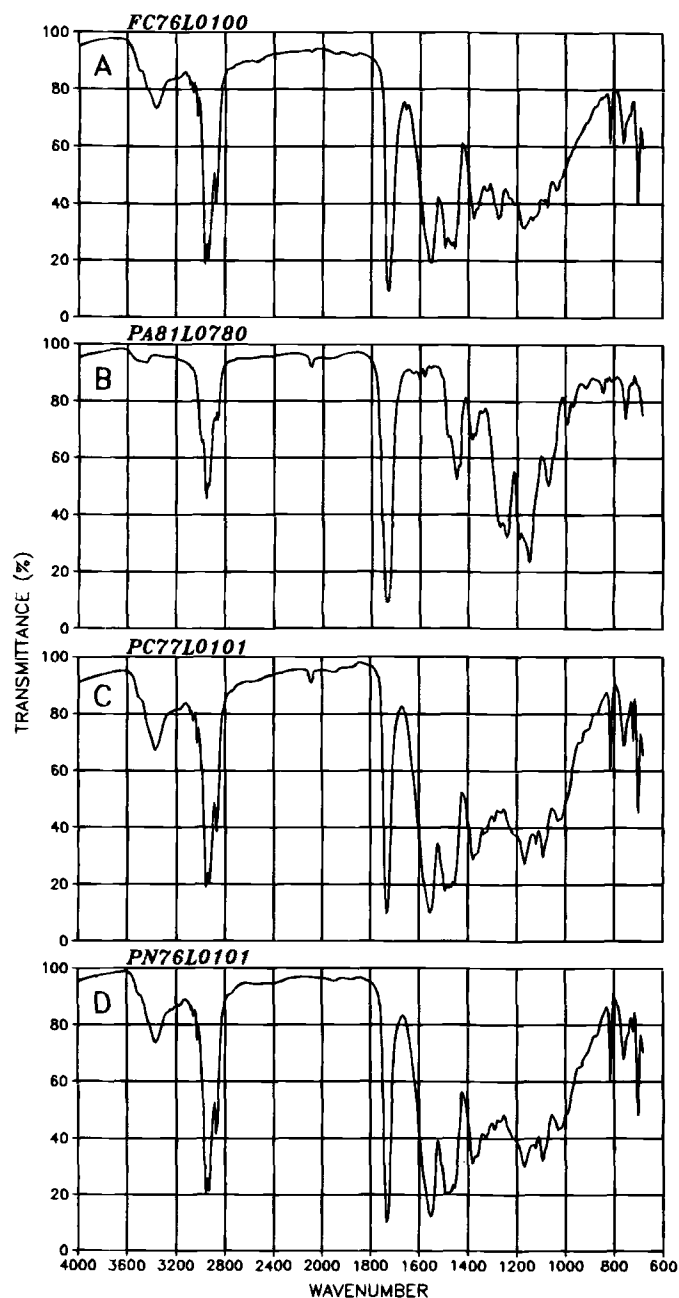


FIG. 7—Infrared microscope spectra of four metallic topcoats sampled without substrates: (a) FC76L0100; (b) PA81L0780; (c) PC77L0101; and (d) PN76L0101.

TABLE 6—U.S. automobile original metallic topcoats (1974–1989) which have a ferrocyanide cyano stretching absorption in their infrared spectra.

Topcoat	Abs. Int.*	Binder Type†	Color‡	Vehicle Type§ and Year	No. of Paints
FC76L0100	vvw	AME	Blue	FORD LIME 76	4Y
PC77L0101	vw	AME	Blue	FORD 77–79 LIME 77,78	6Y
DB76L0264	vw	AL	Blue	BUIC CHEV OLDS PONT 76	6N
DB77K0340	vw	AL	Green	BUIC CHEV OLDS PONT 77	5N
FN79L0579	vvw	AME	Blue	FORD 79–81	5NM
FN83 0637	vw	AME	Blue	FORD LIME 83	9YM
PA81L0780	vw	AL	Blue	CHEV PONT 81	1
NN82L0925	vvw	AME	Blue	CRPL DODG 82	1
PC84 0988	vvw	AME	(Blue)	BUIC CADI CHEV OLDS PONT 84	7?IM
NC84 1092	vvw	AME	(Blue)	GNMO 84,85	3Y

\*Absorption intensity of the ferrocyanide cyano stretching peak; vwv = very very weak, vw = very weak.

†The abbreviations are as follows: AME = acrylic melamine enamel, AL = acrylic lacquer.

‡As in Table 3.

§The abbreviations are as in Table 3.

||As in Table 5.

¶Whether the ferrocyanide absorption can be used to eliminate from consideration some vehicles having this color cannot be determined since NC83 0988 is not in the Collection.

system, use of a single anvil (Fig. 8h) produced an improvement over use of both anvils. For single anvil sampling, the decreased noise resulting from use of the microscope compared to the beam condenser is due primarily to the increased sensitivity of the narrow-band MCT detector, since a smaller area was actually sampled with the microscope.

The ability to identify nitrile or cyano peaks using a low pressure DAC thus depends on a number of factors. Using a beam condenser, these include the intensity of the nitrile or cyano peak, whether one or both anvils are used, the type of detector employed, the efficiency of the beam condenser system, and the number of scans collected. With the infrared microscope, the aperture size is also a factor. In general, nitrile peaks having a “normal” intensity and cyano peaks of most nonmetallic topcoats should not be difficult to detect. The very weak nitrile or cyano peaks, however, may be lost in the noise, and an infrared microscope/single anvil method, or use of a salt substrate or no substrate, is better suited for detecting these particular peaks.

In addition to producing increased relative noise in this spectral region, DAC spectra may also have what appear to be weak residual diamond absorptions. These may not always be apparent because of the noise (see, for example, Fig. 8i), but they are usually seen more clearly when sufficiently long acquisition times are used. Figure 9b shows a portion of the infrared microscope spectrum of FN76L0101 pressed onto a single anvil of the DAC. The apparent diamond peaks may be seen between 2200 and 1900  $\text{cm}^{-1}$ ; they do not occur in the spectrum of this topcoat sampled without a substrate (Fig. 9a). These peaks are stronger when both anvils are used, as may be seen from the spectrum of KN76A0163 (Fig. 9c—note that this topcoat does not contain acrylonitrile). Expanded views of the spectra of KN76A0163 sampled with a single anvil

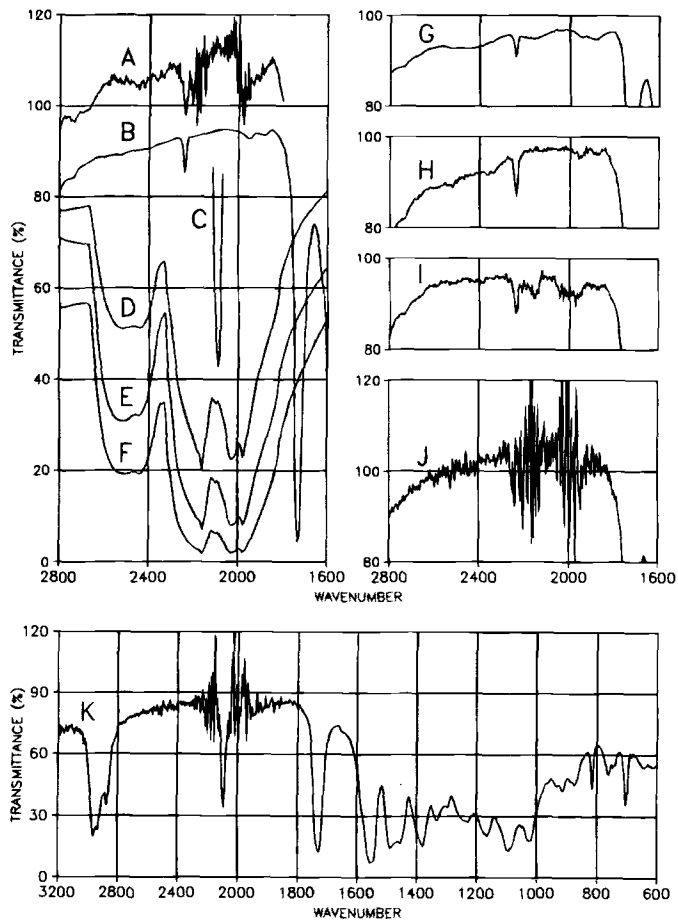


FIG. 8—(a) High pressure DAC spectrum of BN75L0164; (b) infrared microscope spectrum of BN75L0164 sampled without a substrate; (c) the cyano absorption of NC84 0830; (d) transmittance spectrum of a single anvil of the low pressure DAC; (e) transmittance spectrum of both anvils of the low pressure DAC; (f) transmittance spectrum of both anvils of the high pressure DAC; the three anvil spectra were obtained using the infrared microscope; (g) infrared microscope spectrum of BN75L0164 pressed onto a single anvil of the low pressure DAC; (h) spectrum of BN75L0164 pressed onto a single anvil of the low pressure DAC and sampled using the beam condenser Cs/DTGS system; (i) same slice as used for (h) sampled between both anvils of the low pressure DAC; (j) same sample as (a) collected for a shorter time period; (k) high pressure DAC spectrum of NC85 0824. For all of the above samples except for (a), 100 scans were collected; for (a) 1000 scans were collected.

and both anvils of the DAC are shown in Figs. 9e and 9f, respectively. The absorptions of diamond are depicted above in Fig. 9d. Clearly, these features are related to diamond absorptions.

For Fig. 9b these features have intensities comparable to the weak nitrile peak of the topcoat, but their intensities may vary and in some cases, negative peaks may even occur. These features are not observed when topcoat slices are sampled with an air gap between the slice and the anvil surface. This strongly suggests that they arise from differences in reflectivities between the air-diamond and sample-diamond interfaces. This effect is more pronounced with diamond windows because of the high index of refraction of diamond, as well as its strong absorptions. The presence of a sample—especially a relatively refractive one such as certain types of paint—causes a decrease in the index of refraction difference at the interface (or interfaces if both anvils are used) compared to that which occurred without a sample when the reference spectrum was acquired. Consequently, reflection losses from

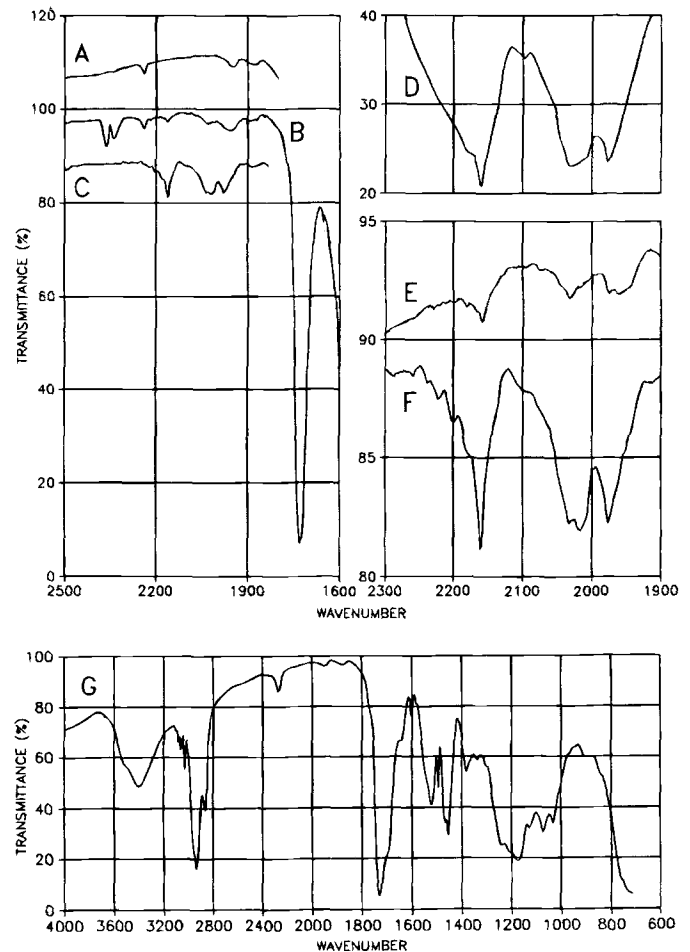


FIG. 9—(a) Infrared microscope spectrum of FN76L0101 sampled without a substrate; (b) infrared microscope spectrum of FN76L0101 pressed onto a single anvil of the low pressure DAC; the flow of the purge gas was decreased for this sample relative to that used for the reference scan; (c) DAC/beam condenser spectrum of KN76A0163 between both anvils of the low pressure DAC, 2000 scans; (d) spectrum of a single anvil of the low pressure DAC; (e) an expanded view of the DAC/beam condenser spectrum of KN76A0163 sampled using a single anvil; (f) expanded view of (c); and (g) infrared microscope spectrum of a nonmetallic refinish topcoat (Sickens Urethane) sampled without a substrate.

the interface(s) were greater when the reference spectrum was acquired, and this difference is responsible for the baselines of some DAC spectra being above 100 percent transmittance (42). For the diamond absorbing region—where the apparent residual peaks occur—the reflection losses from the empty cell are even greater since strong absorption enhances specular reflection (46). This specular reflection may be reduced somewhat when a sample is present, however, and in ratioed spectra, this results in what appear to be weak diamond absorptions. Other factors, such as the specific geometry of the optical system, may affect this difference and this is probably the reason why inverse peaks may sometimes occur.

Analysts using infrared instruments which are not purged (or purged with gas which is not CO<sub>2</sub>-free) may observe a doublet in their spectra centered near 2350 cm<sup>-1</sup> (Fig. 9b) due to uncompensated CO<sub>2</sub> vapor (this doublet may also appear as an inverse peak). Sharp absorptions of water vapor may also occur in the low frequency end of the 2400–1900 cm<sup>-1</sup> region (Fig. 9b) for unpurged sampling. Neither of these vapor bands interfere with the detection

TABLE 7—U.S. automobile original topcoats of twelve colors for which there are no samples in the Reference Collection of Automotive paints.

Topcoat	Description*	Reference Collection Panels Having Similar Colors†	Binder‡/Pigments§
DN79 0536	Gray Met	CN76B0227	AME
FN79 0555	Blue Met	NC86 1282 B/C, NC88 1574 B/C	AME
FN79 0570	Brown Met	FN84 1053¶	AME/FO w
PN79 0570	Brown Met	DB85 1186¶	AME/FO w
DA79 0594	Brown Met	PH87 1404 B/C	AL
FX80 0769	Brown Met B/C	FN78F0420 B/C, PC86 1303 B/C	CC: AME BC: AME/HF w
NC82 0892	Blue Met B/C	PC84 1047 B/C	CC: AME BC: AME
NC82 0899	Red NM	NA81E0787, DC82E0912, NH88 1547	AME/OR m
ND83 0962	Gray Met B/C	FD84 1059 B/C	CC: AME BC: AME
NN83 0975	Red NM B/C	74E0046, NN79E0561, FN80E0636, DA80E0705 CN81E0774, PB89 1669, PC84 1084 B/C	CC: AME BC: AME/MO s RU w
NN83 0976	Yellow NM B/C	CN80H0664 B/C, FN82H0865	CC: AME BC: AME/RU vs
PB82 1015	Brown Met	KC82F0832, DB82F0874, PN85 1114	AL
DB84 1083	Brown Met	DB83 1027	AL/OR w

\*Since these particular topcoats were not assigned to a general color category, the colors listed are those of panels added to the Reference Collection before 1983 which have colors closest to them. The abbreviations used are: Met = metallic finish, NM = nonmetallic finish, B/C = basecoat/clearcoat finish.

†The topcoats were compared to Reference Collection color comparison samples in the three ring binders and not to any of the chemical supplement panels. They were not compared to any of the samples from the 1991 Supplement, which are not actual topcoats. Panels having a basecoat/clearcoat finishes are indicated with a "B/C" suffix.

‡Binder and pigment data are given for both the clearcoat (CC) and basecoat (BC) layers of panels having basecoat/clearcoat finishes. The abbreviations for binder types are: AME = acrylic melamine enamel, and AL = acrylic lacquer. The spectra of all of the clearcoats contained absorptions of styrene, whereas the basecoats all had only very weak or no styrene absorptions in their spectra.

§The abbreviations for pigments are: FO = ferric oxide, HF = hydrous ferric oxide, MO = Molybdate Orange, RU = rutile (titanium dioxide), and OR = an unidentified organic pigment. The inorganic pigments are described in (45). The pigment absorption intensity (or the intensity of the strongest absorption of each pigment if there is more than one) is listed after each pigment using the following abbreviations: vs = very strong (these absorptions are the strongest in the spectrum), s = strong, m = medium, and w = weak. Pigments are not listed if none were detected in the spectra.

¶Although FN79 0570 and PN79 0570 nominally have the same color, there are slight differences between them. Many of the Reference Collection chemical supplement panels having the same color exhibit similar variations in color.

of nitrile or cyano absorptions, but they should be recognized as such and not be confused with sample absorptions.

#### Polyurethane Isocyanate Absorptions

In addition to acrylonitrile and ferrocyanide  $C\equiv N$  stretching absorptions, another fundamental transition that may be useful in the analysis of automobile topcoats also occurs in this spectral region. Spectra of polyurethanes, which are finding increasing use in automobile topcoats, may have absorptions of residual unreacted isocyanate. Isocyanates are one of the starting components used for polyurethanes and they produce characteristic antisymmetric  $N=C=O$  stretching absorptions near  $2270\text{ cm}^{-1}$ . None of the U.S. automobile original topcoats of this study, however, were found to have isocyanate spectral absorptions.

Polyurethanes are also used in repaints consisting of both single layer and basecoat/clearcoat finishes. Figure 9g depicts the spectrum of a single layer nonmetallic refinish ("Sickens Urethane"), and the isocyanate peak can be seen as a weak broad absorption. The intensity of this isocyanate absorption was found to vary over a fairly wide range (more so than the nitrile peak but less than the ferrocyanide peak) based on a very limited survey of the spectra of some repaints. Because the amount of isocyanate depends on the degree to which the starting material is consumed and this may be influenced by a number of factors, there is the potential for this absorption to exhibit some degree of individuality. For this same reason, however, it is possible that the intensity of this

absorption may have a noticeable variation *within* a sample, as was found to be the case for certain types of polyurethane foams (56). Further studies are needed to determine whether this is the case, but like acrylonitrile and ferrocyanide  $C\equiv N$  stretching absorptions, the isocyanate  $N=C=O$  absorption may potentially be useful for both differentiation and identification of certain topcoats.

#### Topcoats of Colors Not Represented in the Reference Collection of Automotive Paints

As mentioned earlier, there are 17 colors, consisting of 19 topcoats, for which there are no panels in the Reference Collection of Automotive Paints. Samples of 13 of these topcoats (12 colors) were obtained from the FBI Laboratory; information about them is given in Table 7.

The Reference Collection *Technical Data* booklet lists two topcoats for color 0769, NN82 0769 and CN81 0769, neither of which is in the Collection. According to these codes, they were produced by Inmont and Celanese, respectively. The FBI Laboratory collection had only one panel for this color and the panel label, dated 2/25/80, indicated that it was made by Ford; this topcoat will be referred to as FX80 0769. The one topcoat listed for color 1015, NW83 1015, an aqueous dispersion enamel produced by Inmont according to this code, also is not in the Reference Collection. The FBI Laboratory had only one sample for this color and according to the information on the panel label, it is an acrylic dispersion lacquer produced by PPG with

a 1982 date; this topcoat will be referred to as PB82 1015. The other 11 topcoats from the FBI Laboratory are consistent with their codes listed in the *Technical Data* booklet.

Five of the 13 topcoats have basecoat/clearcoat finishes; none of the eight which have single layer finishes were found to contain either acrylonitrile or ferrocyanide. The panels from the FBI Laboratory were compared with the color comparison samples in the Reference Collection three-ring binders, and the Collection panels which had colors most similar to each are listed in Table 7. In most cases, the colors were distinct from those of the color comparison samples, but NN83 0976 (with a red nonmetallic basecoat/clearcoat finish) was quite similar to several (most of which were single layer topcoats). Binder and pigment data, obtained from infrared spectra taken between 4000 and 220  $\text{cm}^{-1}$ , are also listed in Table 7.

Panels for five of the colors which are not represented in the Reference Collection were not in the FBI Laboratory collection. The five topcoats of these colors, together with their sales color names, are: DA79 0595, nonmetallic, yellow beige; NC81 0805, metallic, dark bronze; NC81 0806, metallic, dark blue; NC81 0809, nonmetallic, frost beige; and NN83 0974, metallic, dove grey.

#### Inorganic Pigments in Acrylonitrile Topcoats

The presence of both a nitrile stretching absorption and ferrocyanide pigment absorptions served to make a few spectra quite distinct. The spectra of many other acrylonitrile topcoats—especially those with nonmetallic finishes—also contain inorganic pigment absorptions, and these may also be useful for differentiation and identification. Figure 10 illustrates how the combination of nitrile and pigment absorptions can be used to help distinguish between three red nonmetallic enamels having similar or identical colors. FN85 1138 (Fig. 10a) contains ferric oxide, which has three broad absorptions below 700  $\text{cm}^{-1}$ , and an organic pigment that produces the weak sharp peaks. Spectra of two enamels of color 0400, which is similar to color 1138, are also depicted. NN78E0400 (Fig. 10b) and FN78E0400 (Fig. 10c) both contain Molybdate Orange, which produces the broad absorptions near 860  $\text{cm}^{-1}$  (labeled in the figures); NN78E0400 may also contain a small amount of ferric oxide, and FN78E0400 appears to contain a small amount of rutile. A more definitive difference, however, is the acrylonitrile peak of FN78E0400.

The identification of some inorganic pigments used in Reference Collection topcoats is described in paper II of this series (45). For certain inorganic pigments, the absorptions occur primarily in the far-infrared region. Each of the acrylonitrile topcoats was therefore sampled from 4000 to 220  $\text{cm}^{-1}$  and the inorganic pigments which were identified are listed in the last columns of Tables 3 and 4.

#### Summary

A survey of the infrared spectra of all available U.S. automobile original single layer topcoats (1974–1989) for the presence of acrylonitrile and ferrocyanide  $\text{C}\equiv\text{N}$  stretching absorptions has been conducted. Acrylonitrile absorptions, which occur as sharp, weak to very weak peaks between 2240 and 2238  $\text{cm}^{-1}$ , were observed in the spectra of 105 of the 1330 nonmetallic topcoats (8%), and 84 of the 1669 metallic ones (5%). They occur for acrylic melamine enamel topcoats of all colors, and except for three of 18 DuPont nonmetallic enamels having very weak nitrile peaks, the acrylonitrile topcoats were used exclusively on non-GM vehicles (mostly Fords) from the 1970s and early 1980s.

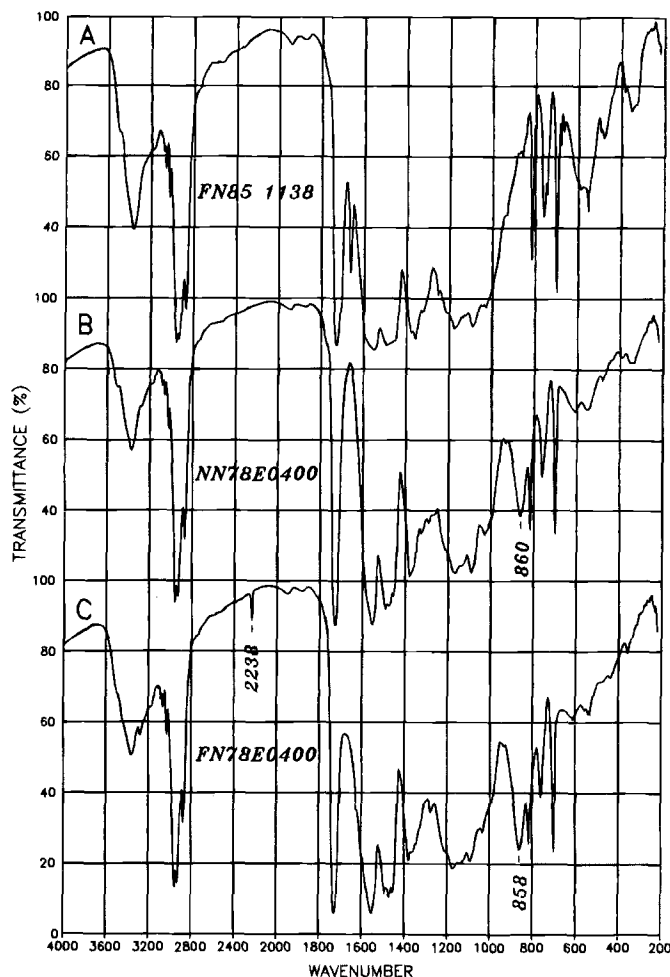


FIG. 10—Spectra of three red nonmetallic topcoats having similar or identical colors sampled without substrates using the CsI/DTGS system: (a) FN85 1138; (b) NN78E0400; and (c) FN78E0400. A total of 1000 scans were averaged for each topcoat.

The intensities of the ferrocyanide absorptions, which occur as medium broad peaks near 2090  $\text{cm}^{-1}$ , vary from very strong to very weak in the spectra of nonmetallic topcoats. These absorptions were observed for 20 of the 168 Reference Collection blue nonmetallic topcoats (12%), and all 20 have acrylic melamine enamel binders. The ferrocyanide absorptions are all very weak in the spectra of the ten metallic topcoats in which they occur. Four blue nonmetallic topcoats have absorptions of both acrylonitrile and ferrocyanide in their spectra, although the latter peaks are quite weak for two of them. The spectra of many other acrylonitrile topcoats also have observable inorganic pigment absorptions, which in some cases likewise serve to make them quite distinct.

Acrylonitrile and ferrocyanide absorptions for most topcoats can be detected using low pressure diamond anvil cells with FT-IR instruments, but the weakest such absorptions may not be distinguishable from the increased noise in this region, and they are best observed using a single diamond anvil with the infrared microscope or with other non-diamond substrates. Polyurethane isocyanate absorptions were not detected for any of the topcoats of this study. This survey has focused on U.S. original finishes used on vehicles during a 16 year time period, and repaints and imported automobile original topcoats were not included.

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