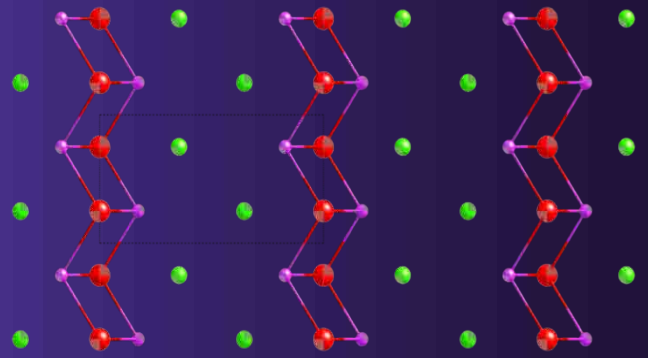
Identification of Bismuth Oxychloride, a Pearlescent Pigment, in Automotive Paint Using Infrared Spectroscopy and Elemental Analysis

Edward M. Suzuki
Washington State Crime Laboratory
Washington State Patrol
Seattle, Washington

Bismuth Oxychloride (BiOCl) Structure



$Bi^{+}(OCl)^{-}$ or $Bi^{+3}\ O^{-2}\ Cl^{-1}$?

Has a covalent bond

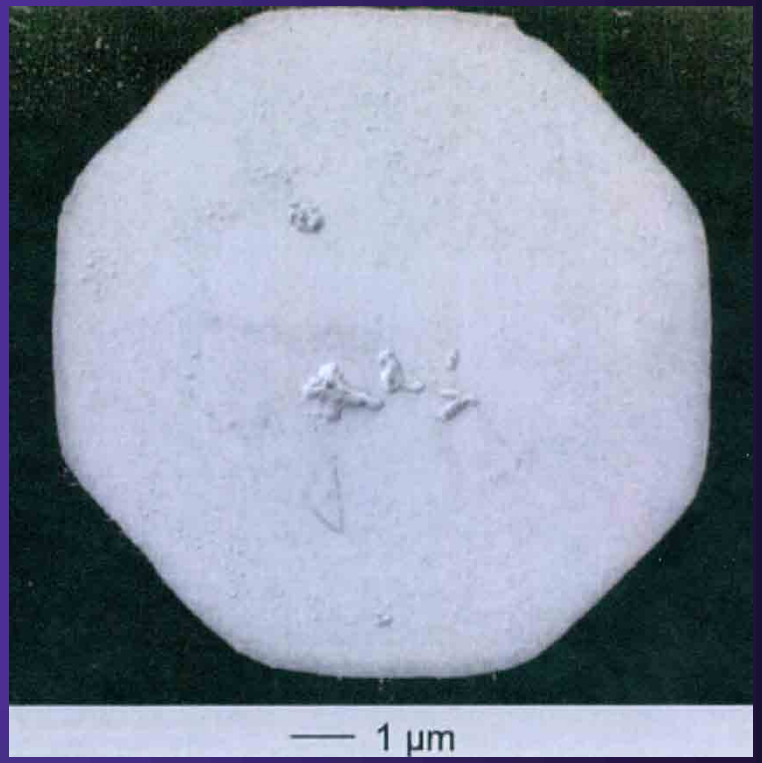
Has only ionic bonds (like NaCl)

Infrared Absorptions:

The former should have an O—Cl stretch, the latter, only far-infrared absorptions

Bismuth Oxychloride Properties

- Flat octagonal and square crystals.
- Smoother microscopic surface compared to mica coated with TiO_2 .
- Reflect twice as much light as mica pigments and reflectivity approaches that of aluminum.



SEM Micrograph of a crystal of bismuth oxychloride. From G. Pfaff, *Special Effect Pigments*, 2008.

Bismuth Oxychloride Uses

- The first synthetic pearl pigment developed 50 years ago.
- Used for several decades in various beauty care products:
  - (1) Eye shadow
  - (2) Makeup powder
  - (3) Lipstick
  - (4) Fingernail polish

Bismuth Oxychloride: More Uses

- Printing inks
- Plastics
- Paints and Coatings:
  - (1) Furniture
  - (2) Metals
  - (3) Buttons
  - (4) Graphic art items
  - (5) Electronic items
  - (6) Jewelry (including imitation pearls)

Merck Ad

Bismuth Oxychloride in Automotive Paint

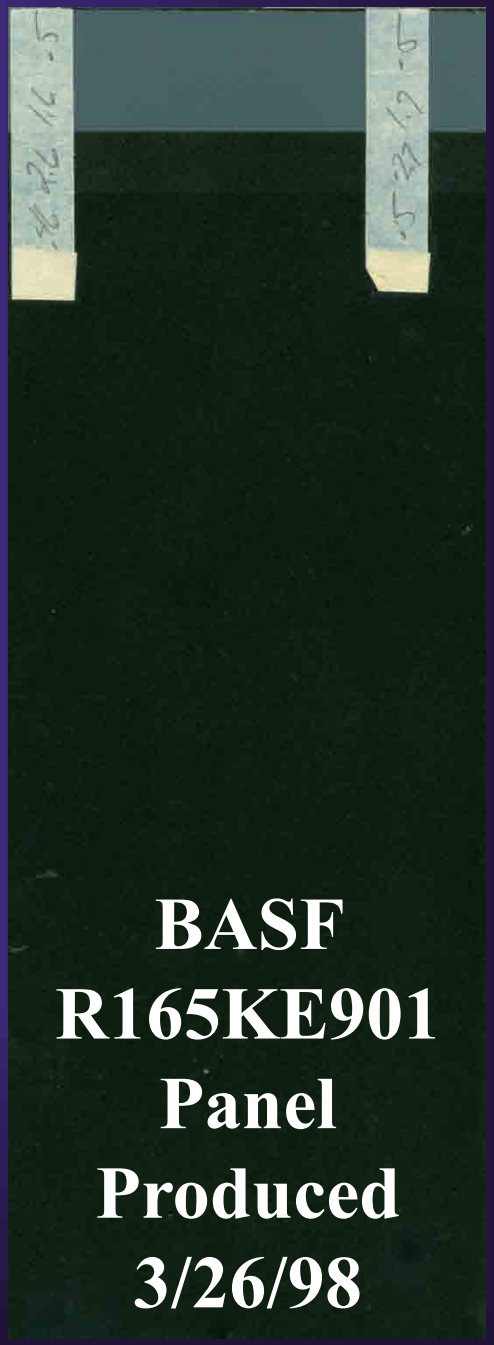
- Originally not suitable for extended outdoor use.
- BiOCl darkened on exposure to light—Bi^{+3} photo-reduced to Bi metal.
- More light-durable form patented in 1992.

Bismuth Oxychloride in Automotive Paint

- New formulation included a coating of cerium hydroxide, which oxidizes Bi back to Bi^{+3}.
- Used by PPG and BASF to produce one black metallic finish for the Chrysler Corporation, Color Code AY112-VAW (VAW)
Trade Name: ***Deep Slate Pearl Coat***.
- First used on some Chrysler 1998 models.

Chrysler Color VAW

(AY112-VAW)



BASF R165KE901 Panel Produced 3/26/98

Infrared spectra of:

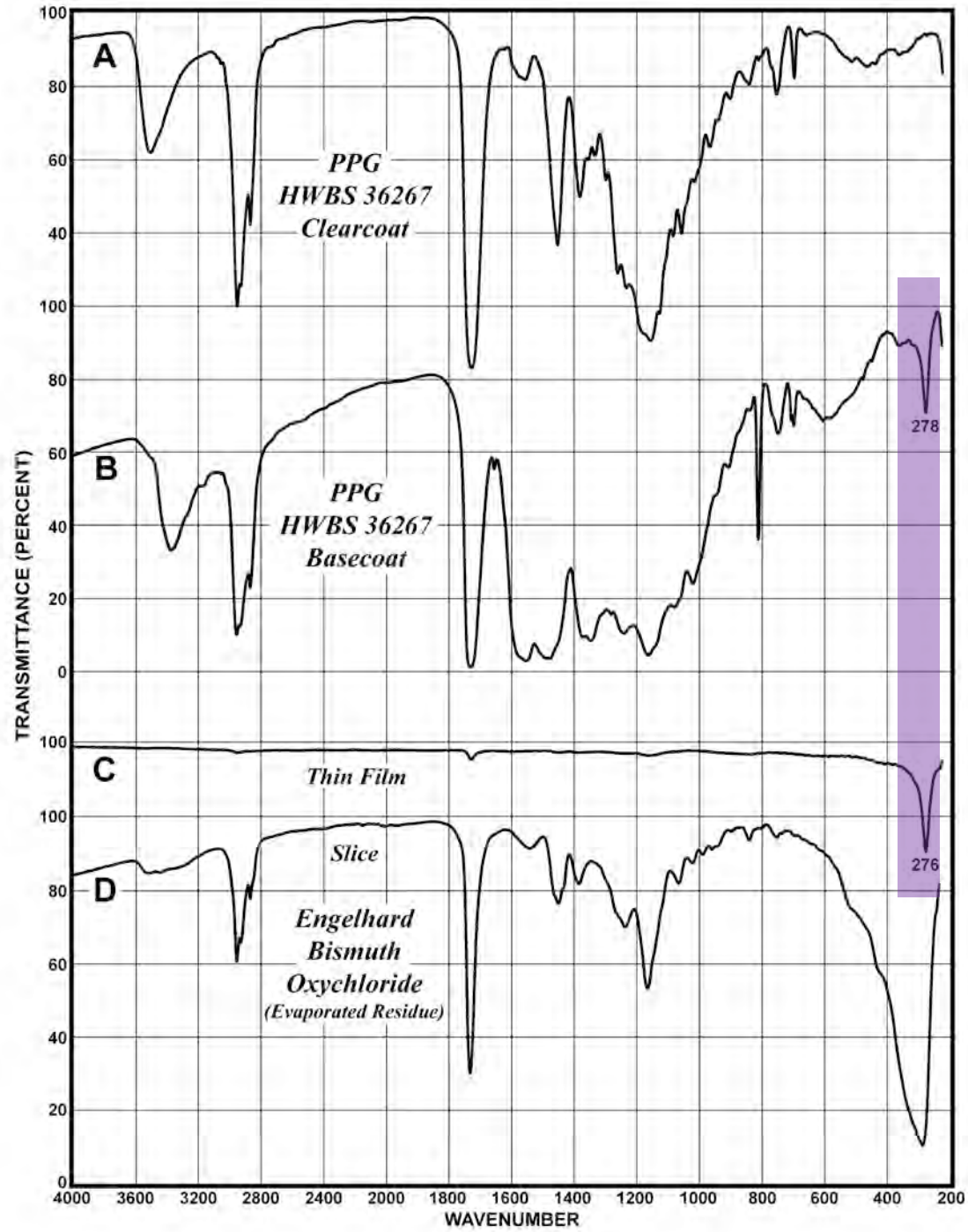
PPG HWBS 36267

Panel produced January 1998
Was used at Bramalea Plant (Canada) for Chrysler *Concordes* and *Intrepids*, and

Windsor Plant (Canada) for *Chrysler Minivans*

Engelhard Mearlite Radiant Pearl SUQ

Bismuth Oxychloride formulation used in automotive finishes



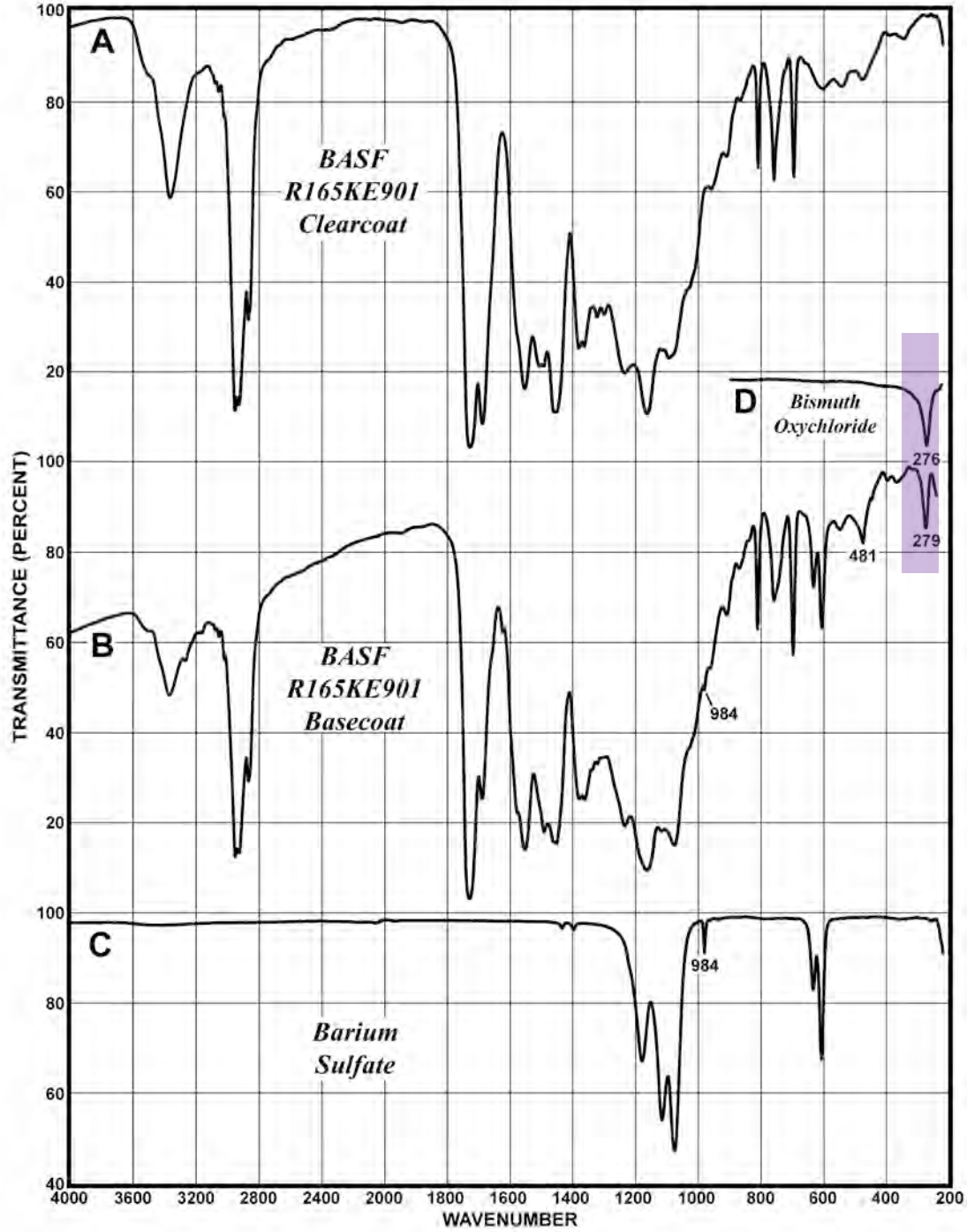
Infrared spectra of:

BASF R165KE901

Panel produced March 1998
For metal substrates
Used at the Chrysler Jefferson North Assembly Plant (which was producing *Jeep Grand Cherokees*)

Barium Sulfate

- ❑ Viscosity control agent (to prevent sagging)
- ❑ Improves bc/cc adhesion
- ❑ Lowers cost



Infrared spectra of:

BASF E175AM113

Panel produced July 1999

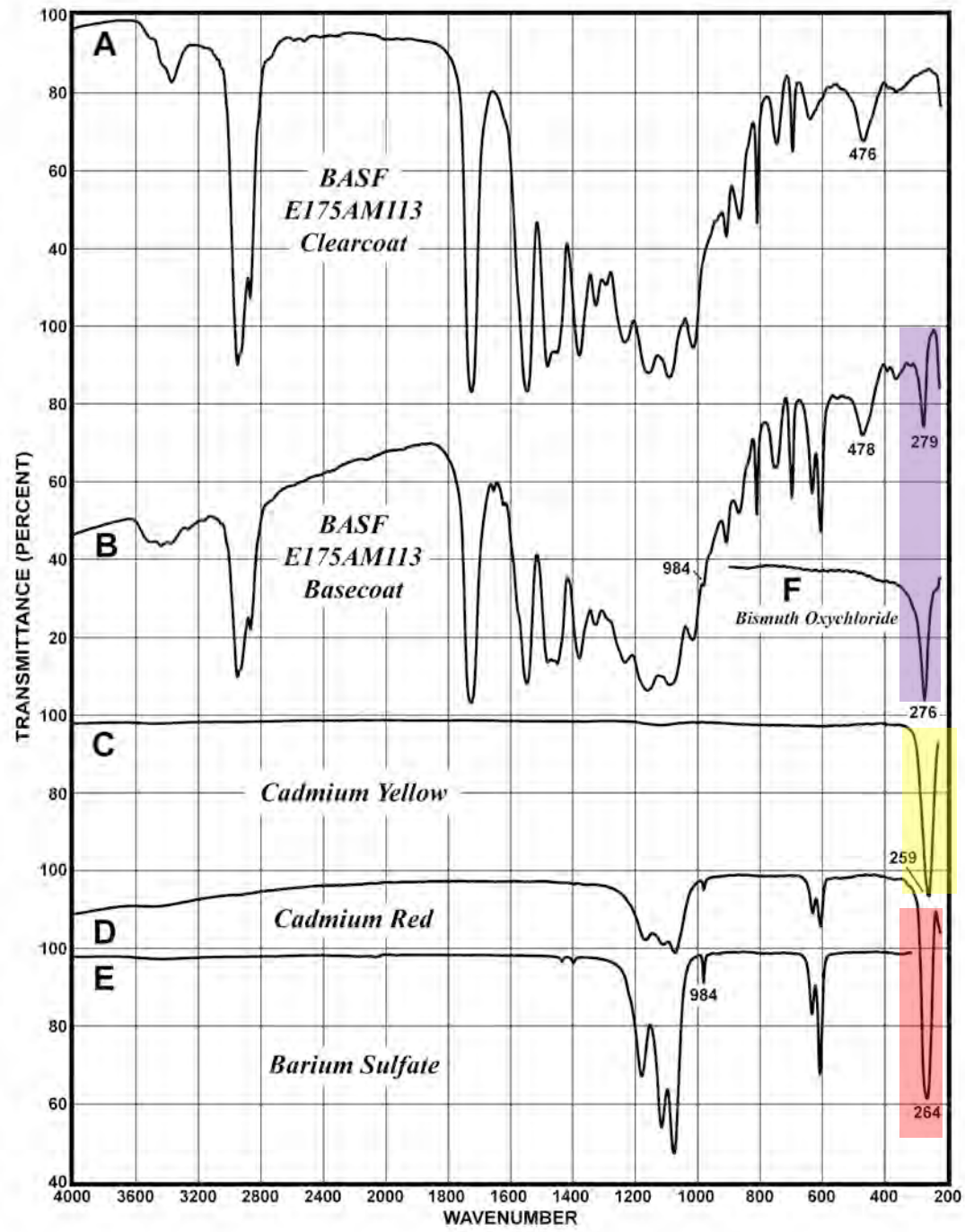
For plastic substrates

Only Other Known Pigments Having Similar Absorptions

Cadmium Yellow (CdS)

Cadmium Red ($CdS{\cdot}CdSe/BaSO_4$)

Last used in 1950s for automotive finishes



Infrared spectra of:

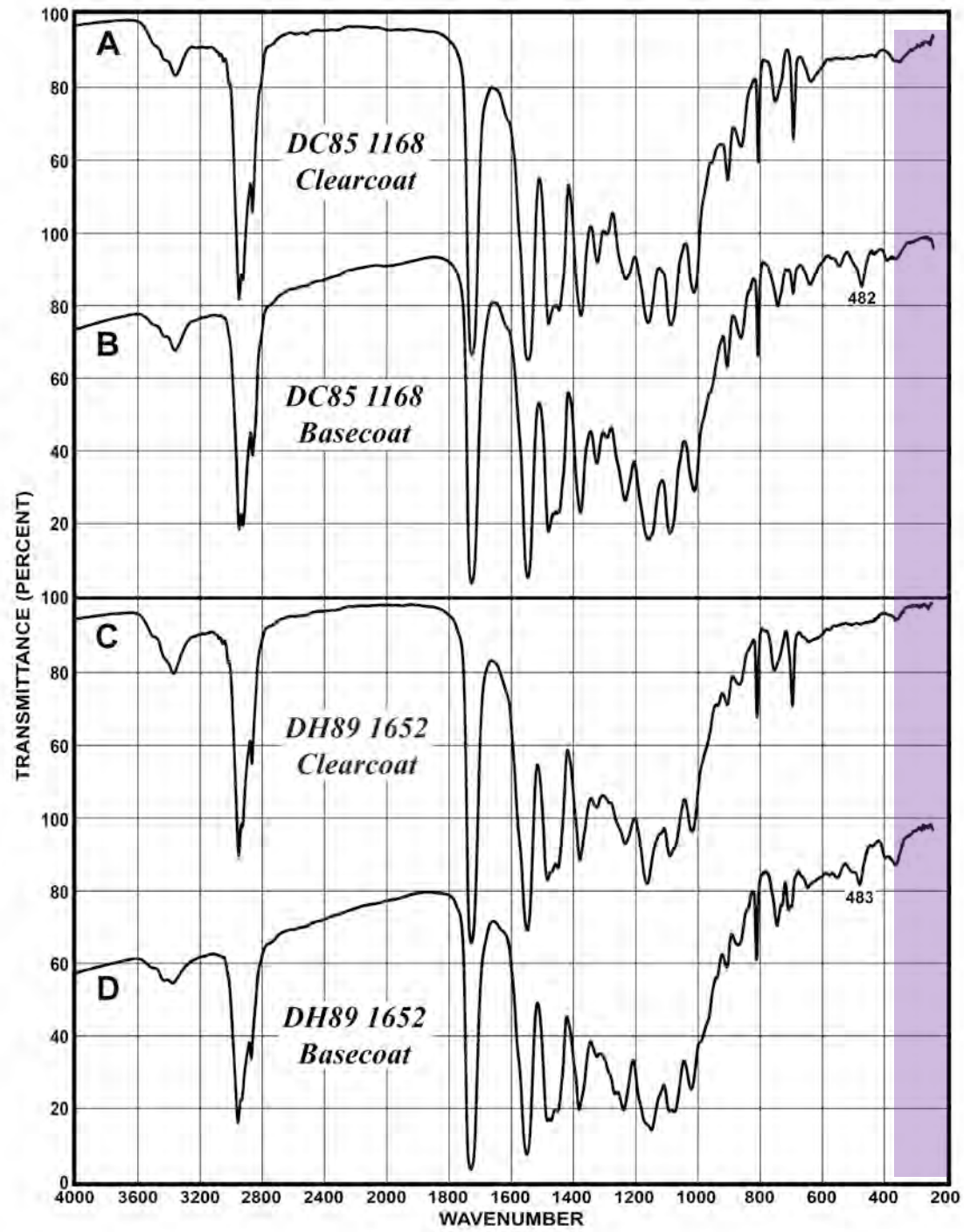
Two CTS Panels Having Colors Closest to VAW*

DC85 1168

DH89 1652

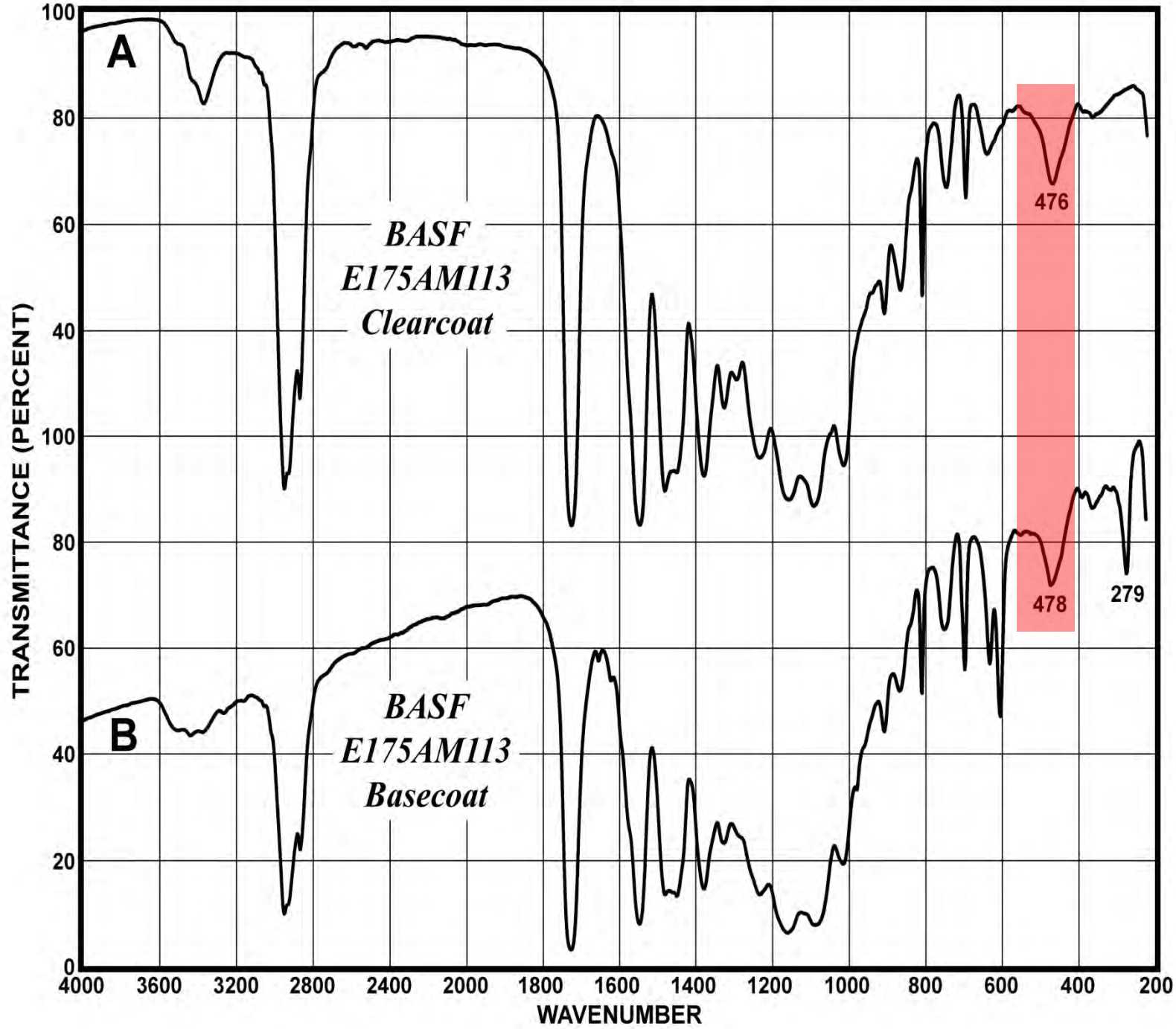
Both are black metallic basecoat/clearcoat finishes

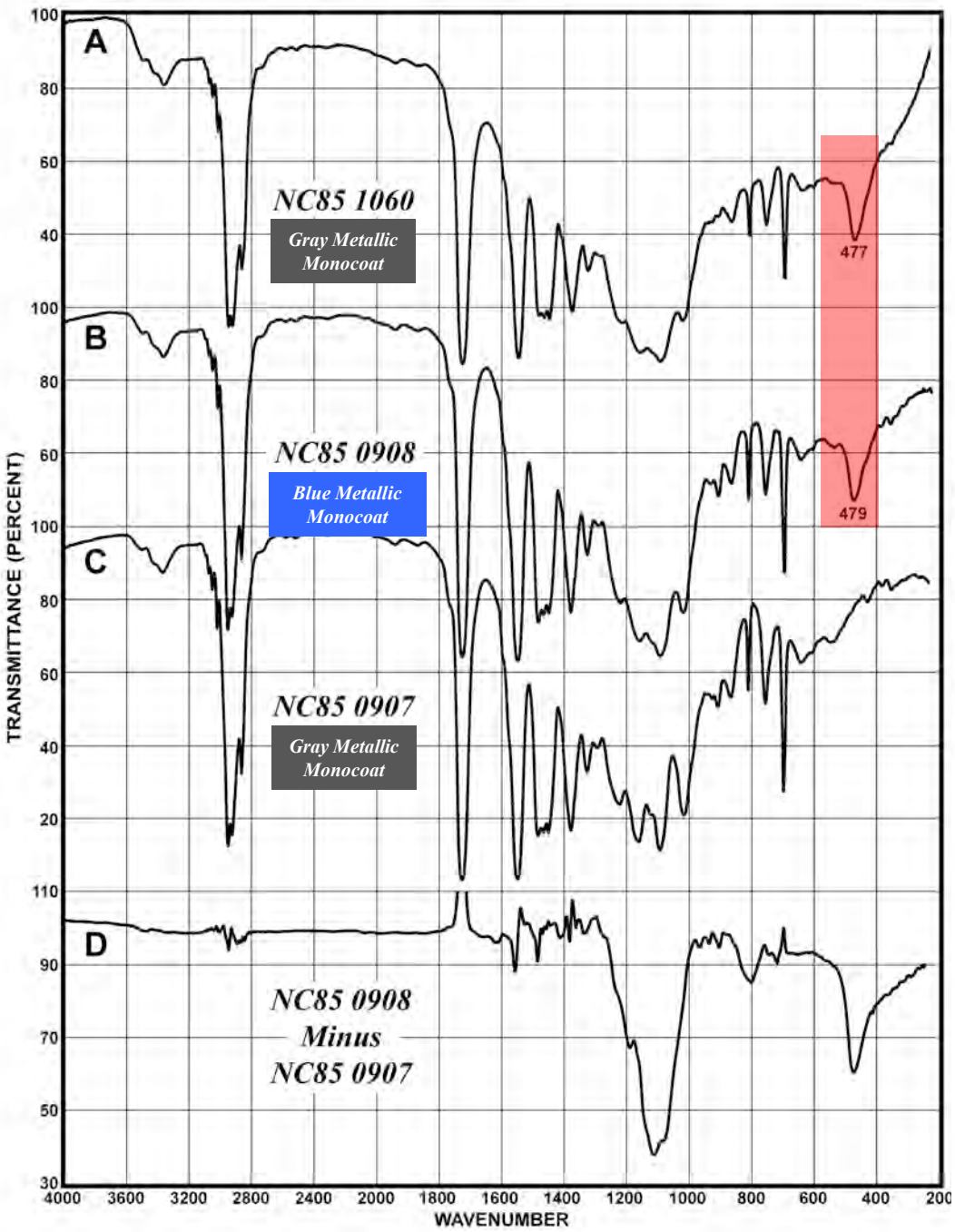
*Collaborative Testing Services *Reference Collection of Automotive Paints* (1974-1989)

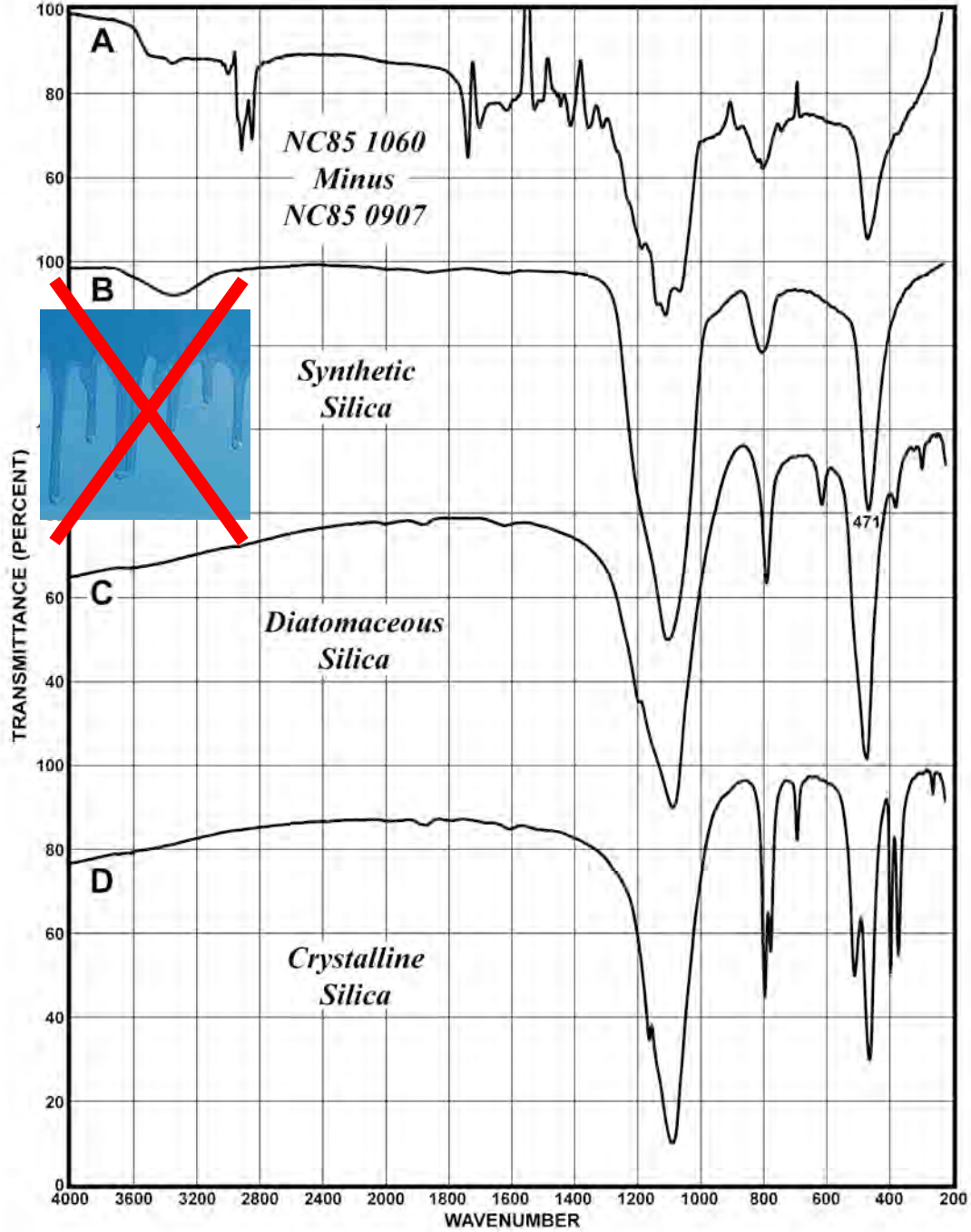


What Else is Absorbing Down There?

An Absorption at 476 cm^{-1} Seen in Spectra of Some Clearcoats, Basecoats, and Metallic Monocoats

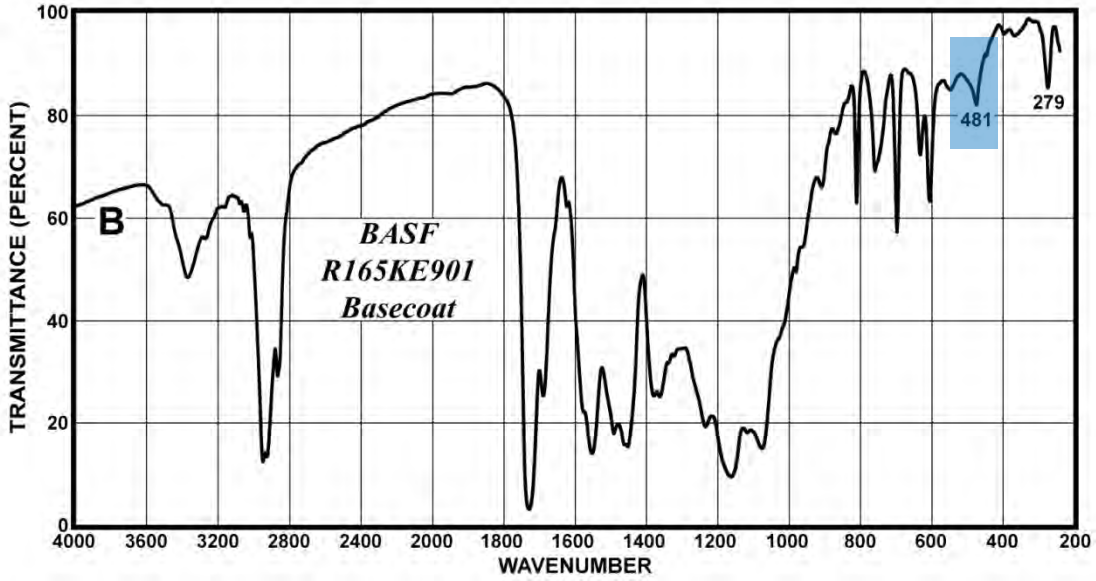


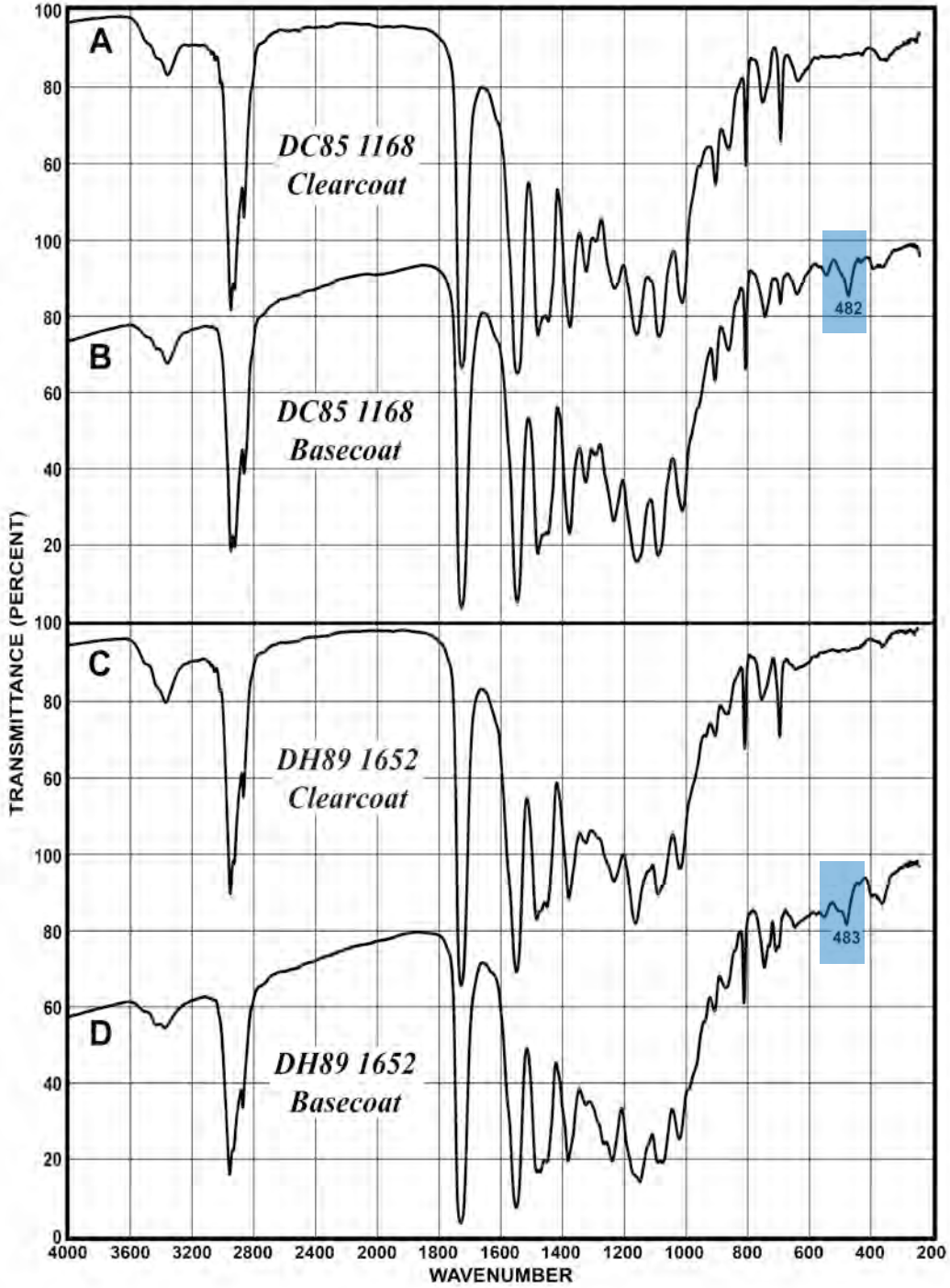

A
NC85 1060
Gray Metallic
Monocoat
477
B
NC85 0908
Blue Metallic
Monocoat
479
C
NC85 0907
Gray Metallic
Monocoat
D
NC85 0908
Minus
NC85 0907
TRANSMITTANCE (PERCENT)
WAVENUMBER

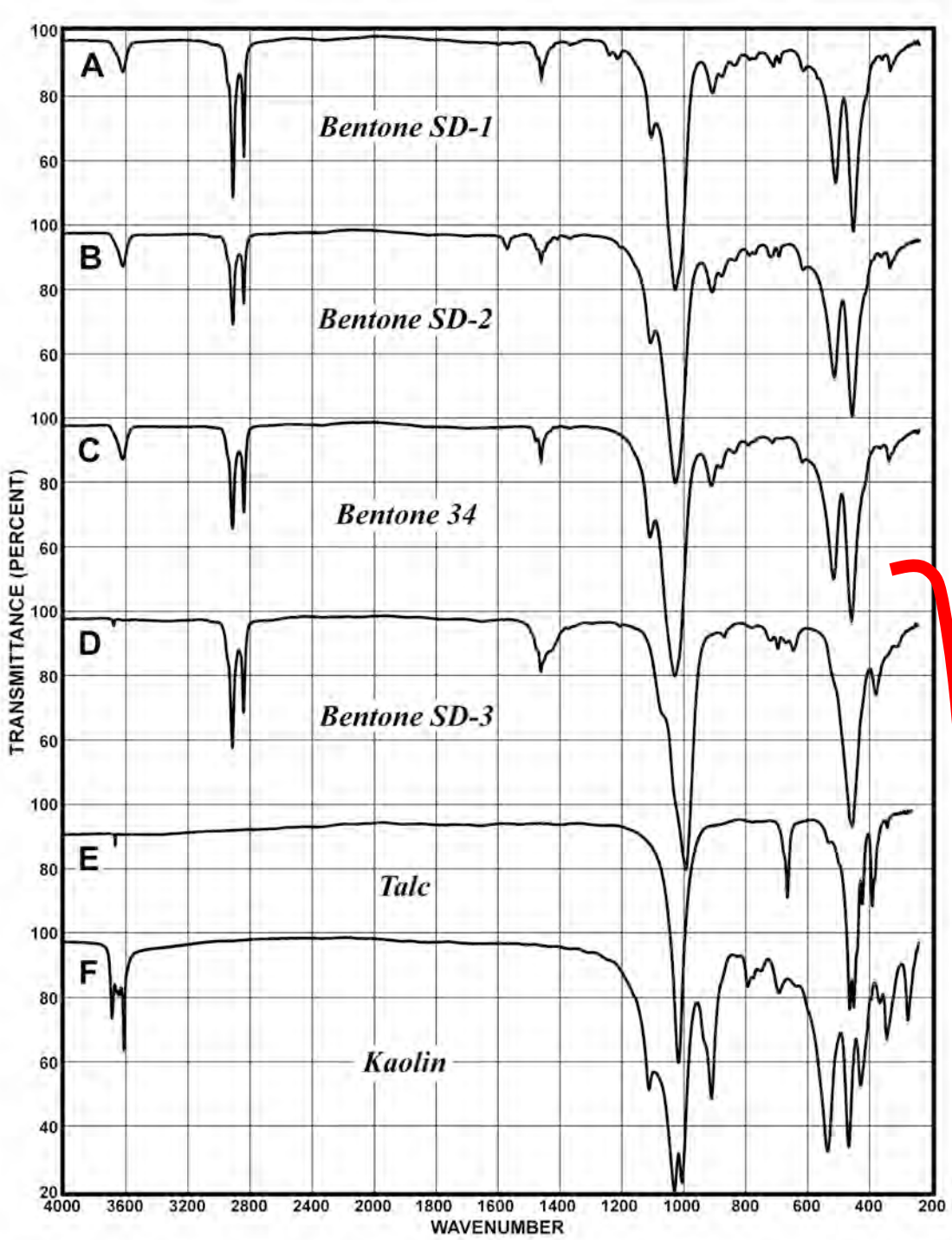

A
NC85 1060
Minus
NC85 0907
B
Synthetic
Silica
471
C
Diatomaceous
Silica
D
Crystalline
Silica
TRANSMITTANCE (PERCENT)
WAVENUMBER

What Else is Absorbing Down There?

A Sharp Absorption at 481 cm^{-1} Seen in Spectra of Some Metallic Basecoats

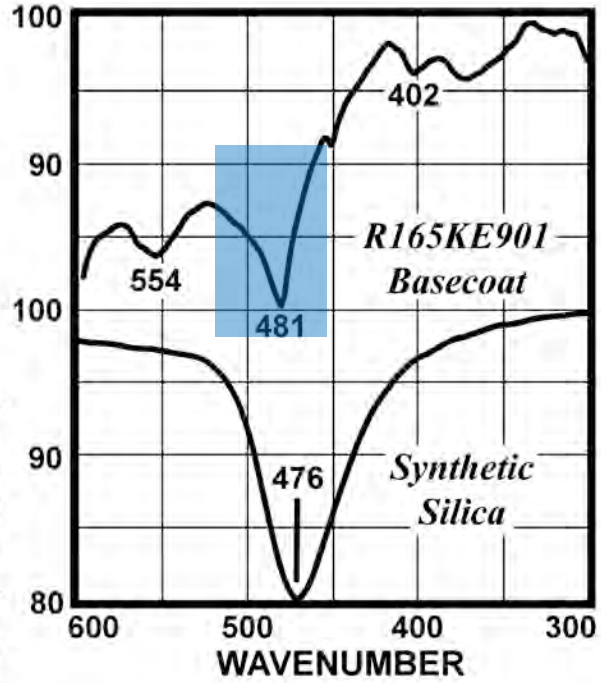


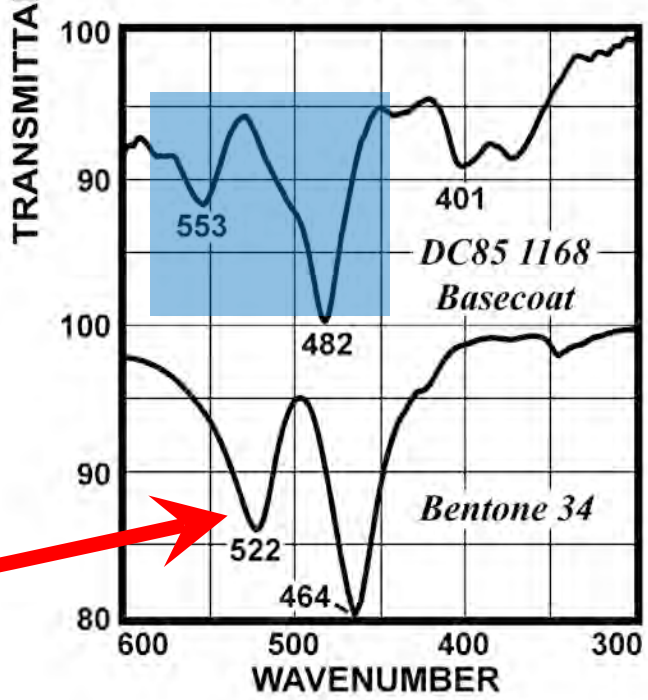


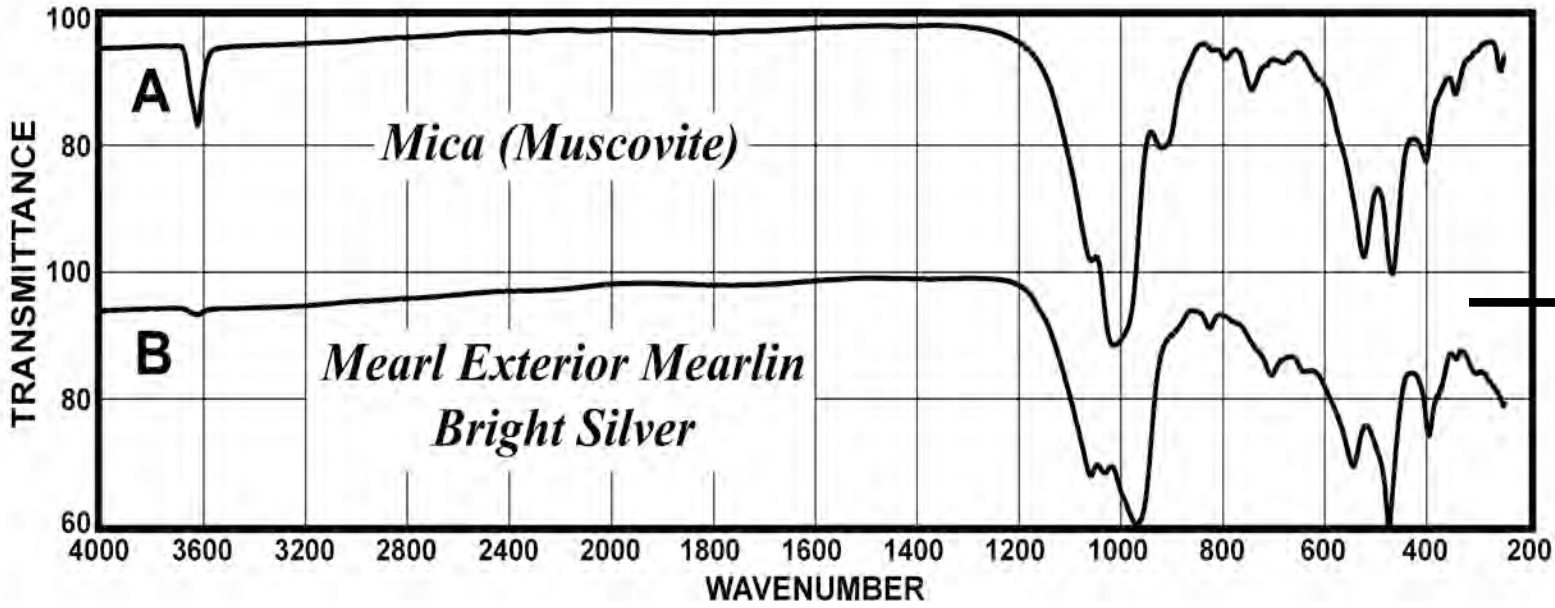


It's not synthetic silica

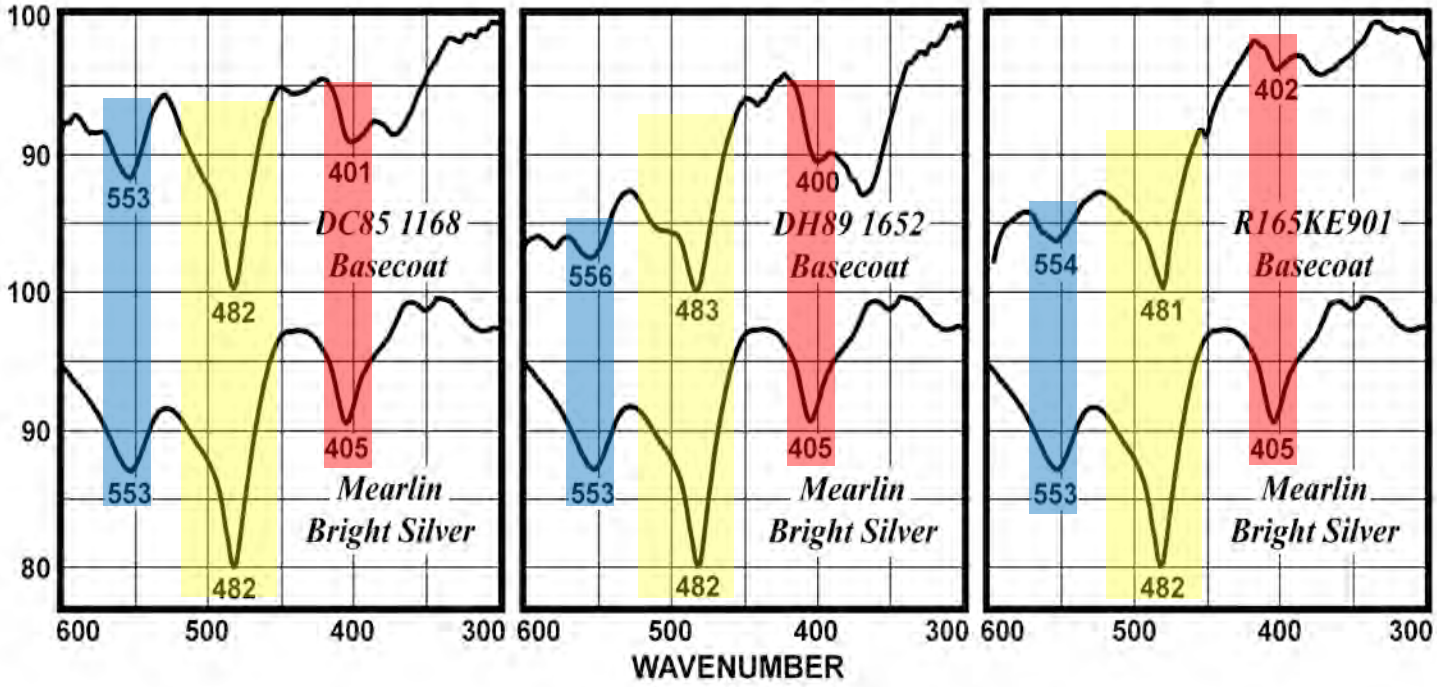
Bentones are anti-settling agents used with metallics

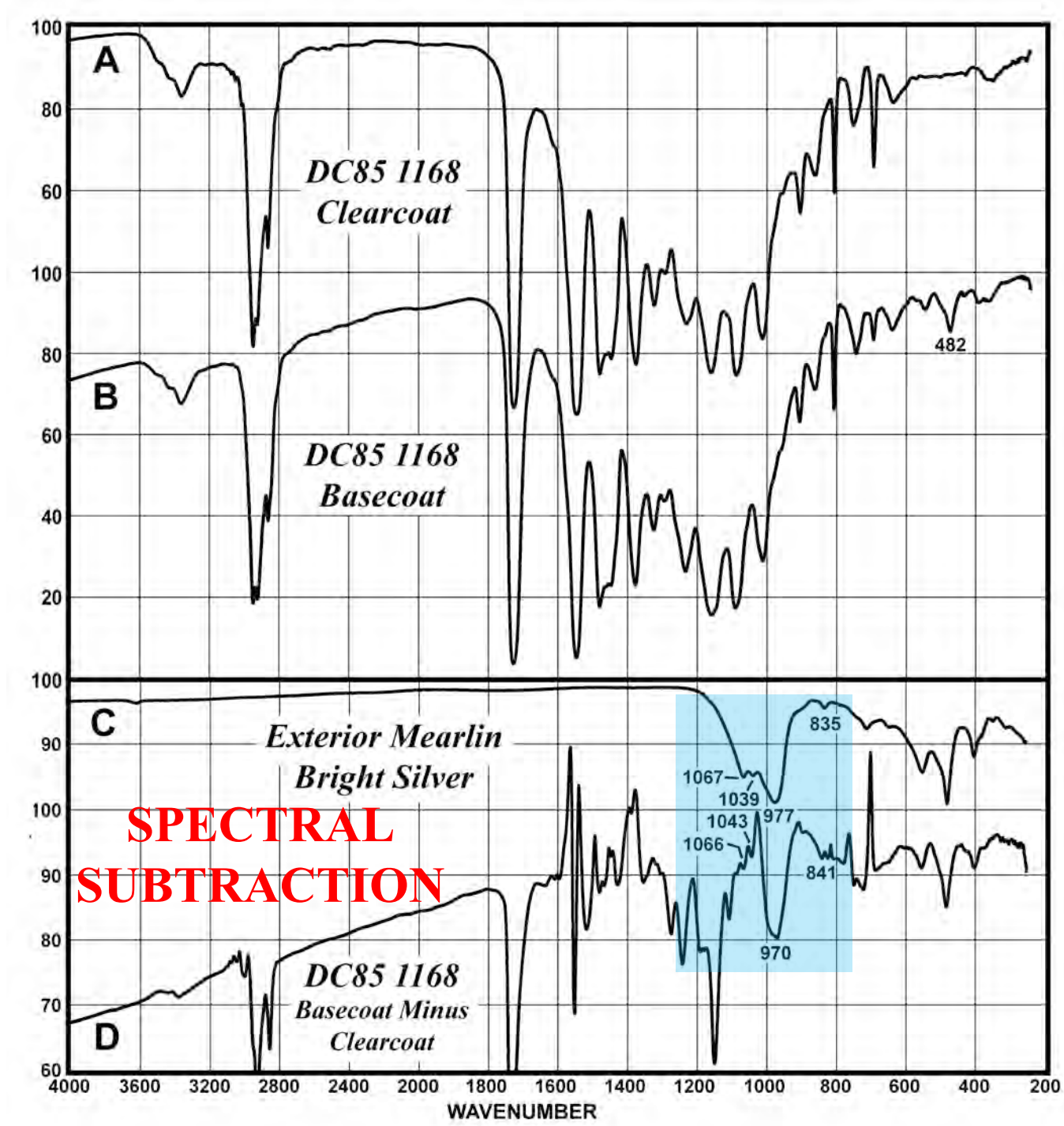


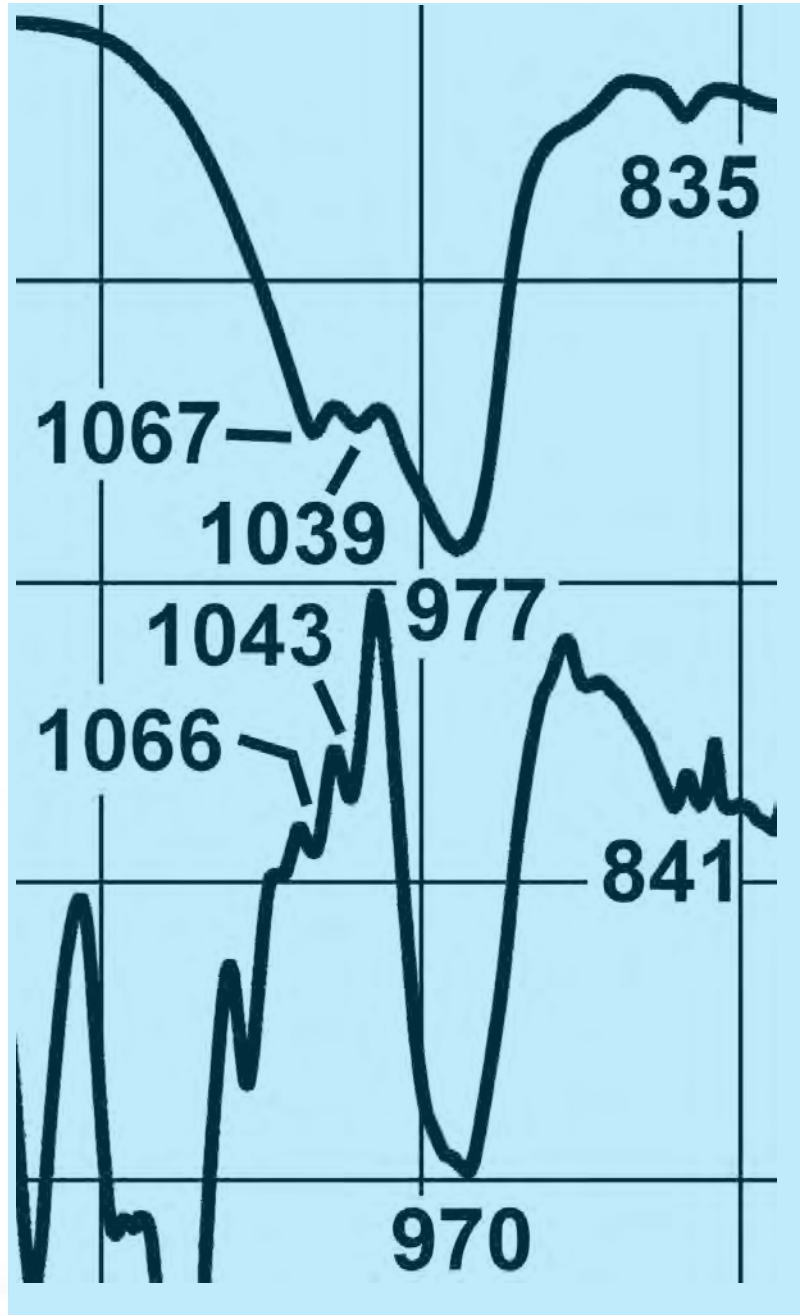




The sharp peaks are from the "metal" flakes



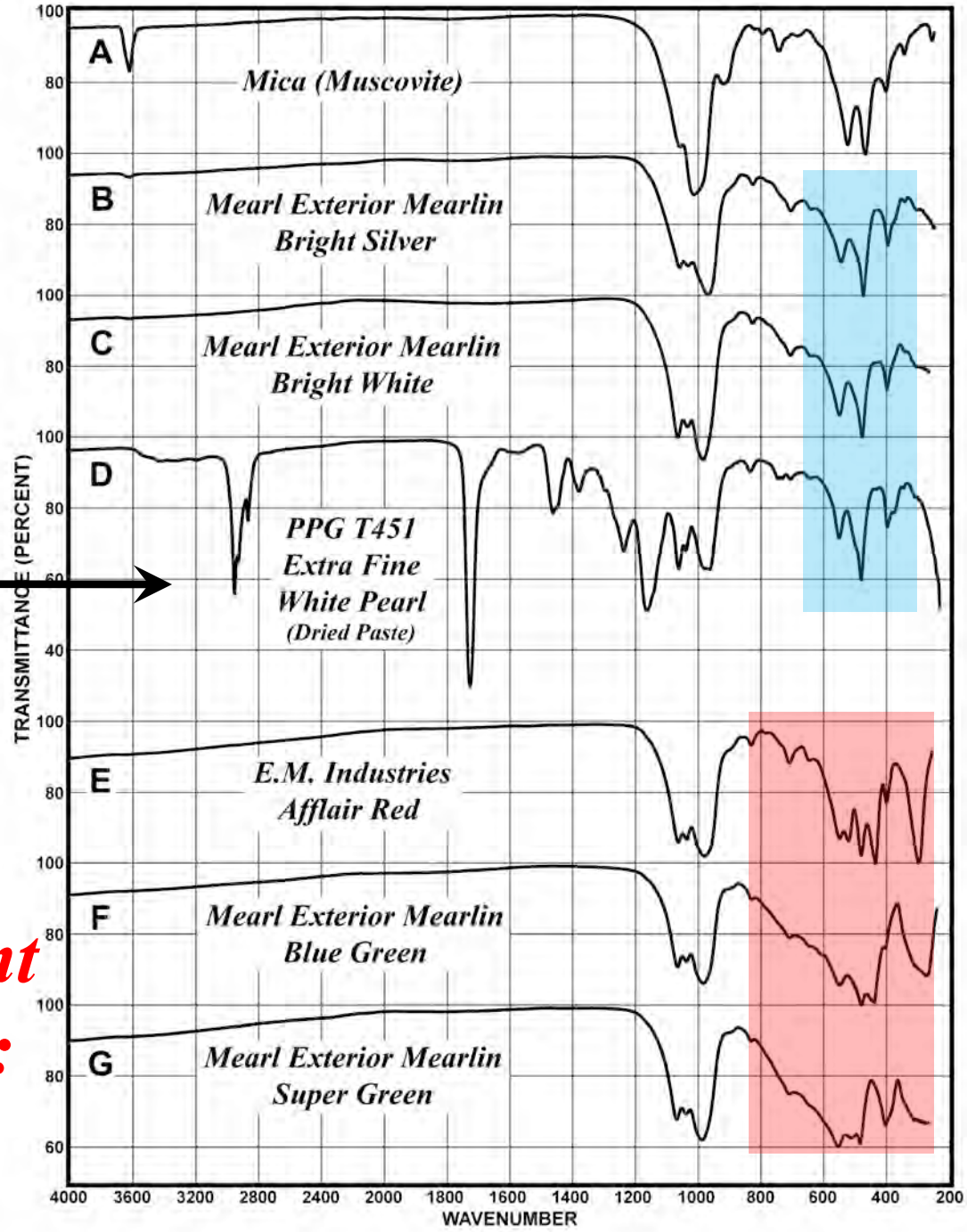

A
DC85 1168
Clearcoat
482
B
DC85 1168
Basecoat
C
Exterior Mearlin
Bright Silver
SPECTRAL
SUBTRACTION
835
1067
1039
1043
977
1066
841
970
D
DC85 1168
Basecoat Minus
Clearcoat
100
80
60
40
20
90
70
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER


835
1067
1039
977
1043
1066
841
970

Silver/White Mica Pearlescent Pigments: B,C,D

Pigment used to formulate color VAW in a PPG automotive refinish

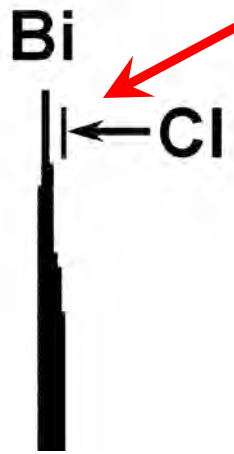
Colored Mica Pearlescent Pigments: E,F,G



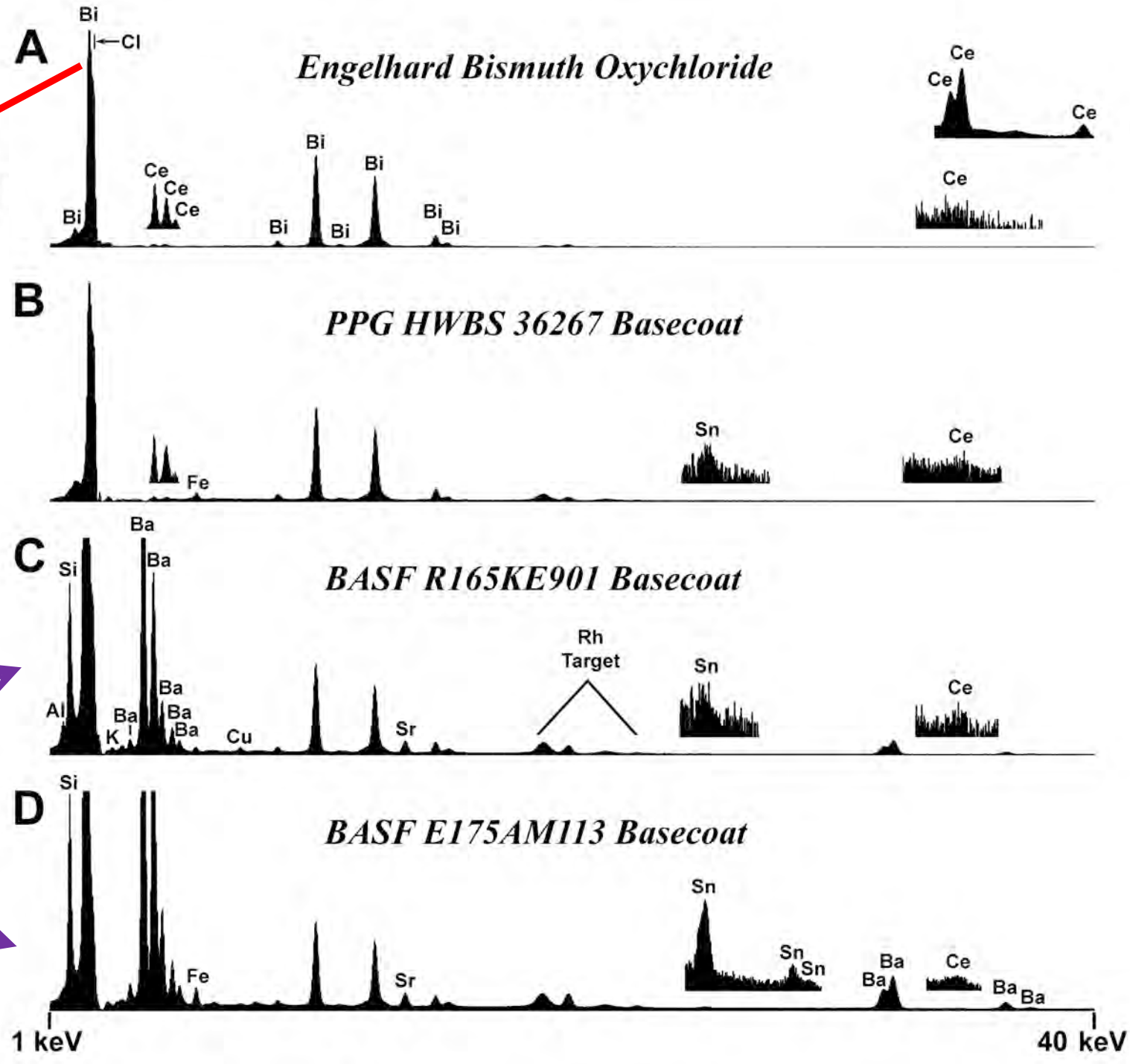
XRF Spectra

Rh target
55 kV, 70 µA
1 mm beam

BiOCl
+
$Ce(OH)_4$



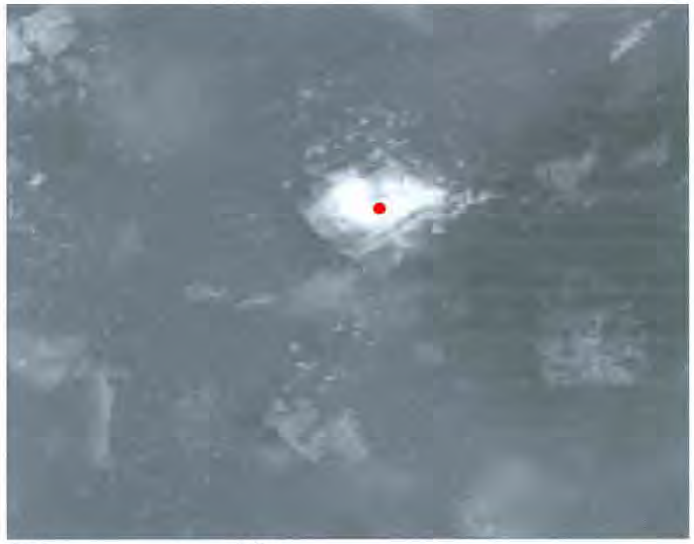
The two VAW basecoats with $BaSO_4$



SEM/EDS Data

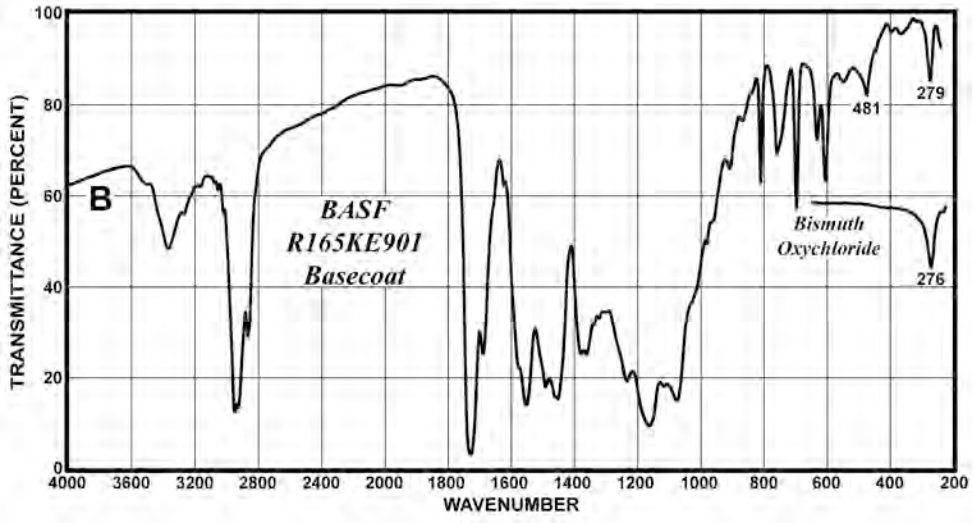
25kV, 35º, 9 mm

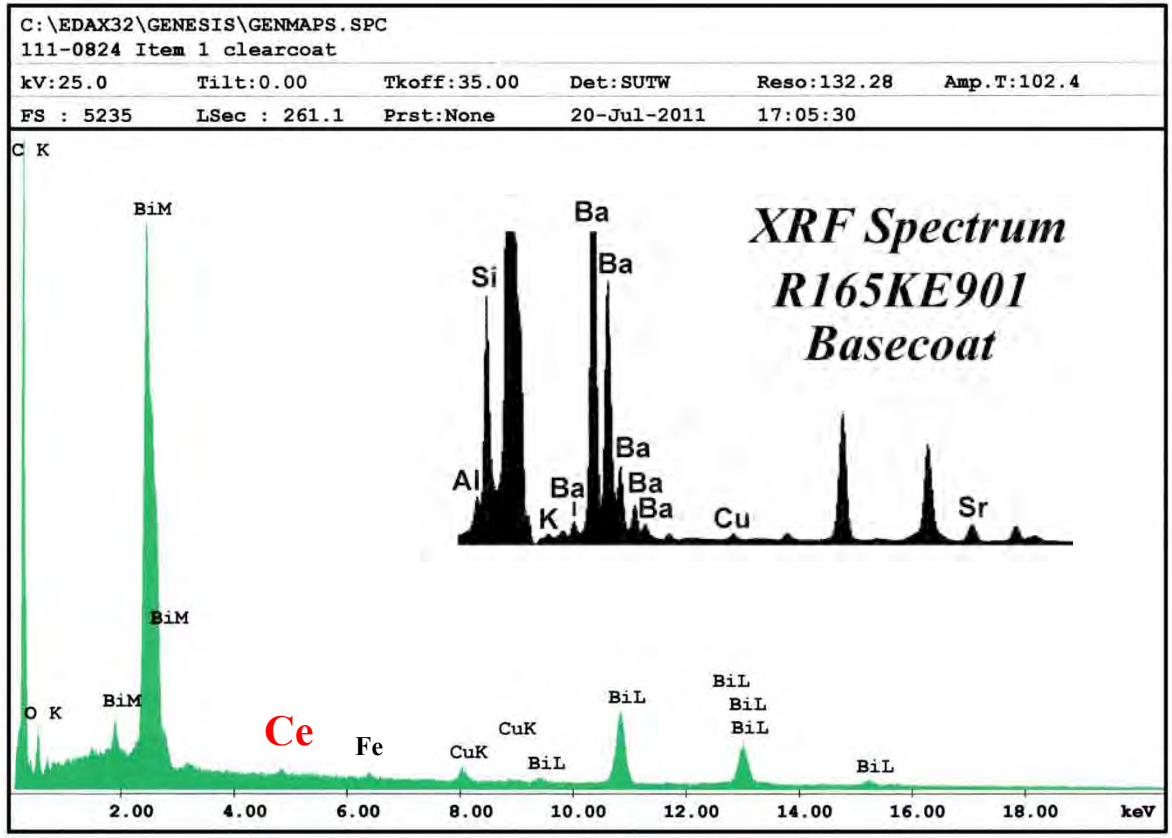
EDS spot analysis of a flake in R165KE901, the basecoat containing bismuth oxychloride, mica pearlescent flakes, and barium sulfate



Matrix:	512x400
Data Type:	BSE (ADC)
Magnification:	1000x
Image Size:	0.1240x0.1070mm
kV:	25.0
Tilt:	0

←Backscattered Electron Image





Chrysler Color VAW was only used for three model years (1998-2000)

Bismuth oxychloride automotive use was discontinued because:

- Darkening issues were never completely resolved.
- Bismuth oxychloride crystals tended to fragment from the sheer forces generated in the automobile plant paint recirculation system.

Chrysler Color VAW was used on:

- 1998-2000 Concordes
- 1999 Stratuses, Cirruses, and Jeep Grand Cherokees
- 1999-2000 Intrepids
- 2000 Grand Caravans, Town and Countries, and Voyagers.

Note: This list is not necessarily exclusive and color VAW was also produced without bismuth oxychloride.

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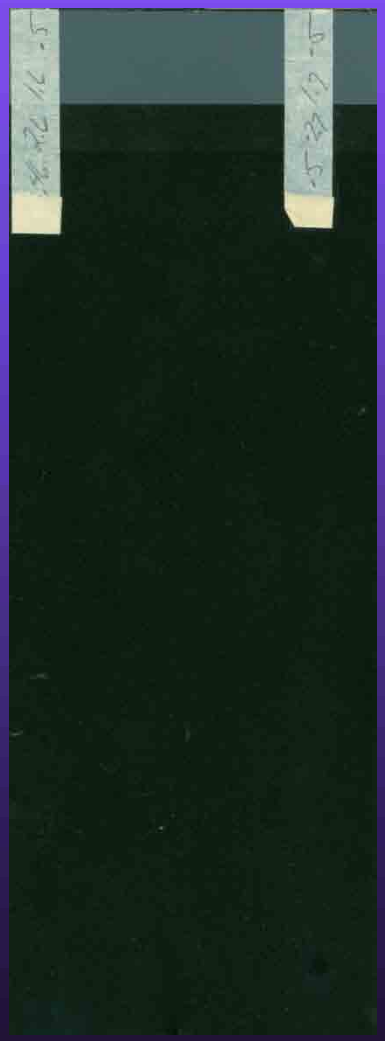

There are 60 samples of BASF R165KE901 and information about this finish system.

PLEASE HELP YOURSELF

Thanks To:

1. **Scott Ryland** (Florida Department of Law Enforcement, Orlando Forensic Laboratory) for his many helpful discussions.

2. **Dr. Diana Wright** (FBI Laboratory) for sending us some samples from the FBI Laboratory National Automotive Paint File.

3. **Bailey** (Right) for her invaluable assistance.