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Technical Note

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Color Analysis of Apparently Achromatic Automotive Paints by Visible Microspectrophotometry

ABSTRACT: Chromatic secondary pigments are utilized in achromatic automotive paints to create unique paint systems. These pigments may not be observable in reflected light; however, utilizing visible microspectrophotometry (MSP) discriminating data may be gathered. This study analyzed 160 apparently achromatic automotive paints via this technique for spectral evidence of secondary pigmentation. These results were compared with visual observations made via polarizing light microscopy. Positive spectral results were attained in approximately 25% of the black and gray/silver topcoat sample sets, whereas the white topcoat and gray undercoat set yielded no probative spectral data. The black sample set did yield several samples that produced spectral evidence of pigmentation when no visual chromatic data was observed. The results of this study suggest that paint analysis schemes should incorporate visible MSP for apparently achromatic black and gray/silver paint samples.

KEYWORDS: forensic science, visible microspectrophotometry, automotive paint, achromatic

Color analysis is a valuable aspect of any paint comparison performed in a forensic setting. ASTM International (ASTM) and the Scientific Working Group on Materials Analysis (SWGMAT) recognize the importance of this element and outline guidelines for consistent definition and comparison of color. Different techniques have been developed to provide information on color including visible microspectrophotometry (MSP) that allows discrimination of samples by their interaction with light in the visible region of the electromagnetic spectrum. Both ASTM and SWGMAT have recommended absorption spectrophotometry as a discriminating technique for paint color (1,2). As light strikes a paint coating, some wavelengths will be absorbed based on the chemical composition of the paint, and all others will be reflected resulting in the observable color of the paint. A paint that appears blue is reflecting the wavelengths of visible light in the blue region and absorbing the wavelengths of the complementary colors, which comprise the remainder of the color spectrum. Variables involved with observation by the human eye include the physical state of the observer, lighting, and microscope optics. One of the primary goals of the ASTM and SWGMAT guidelines is to promote consistent analysis, and removing the subjective analysis of color is a step toward achieving this goal.

MSP eliminates the majority of these variables and produces a calibrated, objective measurement of the sample's interaction with light. MSP has been proven to be more sensitive than the human eye to differences in color (3). Early MSP was based upon reflectance, which measured the amount of white light a sample would reflect while later developments allowed for transmission spectroscopy, which is preferred over reflectance because of the absence of noise and artifacts (4). The transmitted light is dispersed by wavelength and graphically represented as a spectrum.

Both black and white are considered achromatic because of their interactions with visible light, as are neutral grays, which are without hue. The color perceived as white is a result of the reflection of all wavelengths of visible light. On the contrary, black objects absorb all wavelengths, and the resulting lack of reflected light is perceived as the color black. Achromatic materials are considered to absorb light in the visible region flatly as they either reflect or absorb all wavelengths approximately equally. Due to this aspect, achromatic forensic samples are not typically analyzed via visible MSP.

Automotive paint is a nonhomogenous suspension of a binder and pigments whose purpose is twofold—appearance and corrosion prevention. The pigments used can be divided into four groups—white, color, inert, and functional (5). Also called extenders, inert and functional pigments serve as fillers and may impart some beneficial attribute to the coating such as corrosion inhibition whereas white and color pigments account for the physical appearance of the layer. Rutile titanium dioxide is the predominant pigment used in white colored layers and as a shading agent in conjunction with other pigments. This pigment has a relatively high refractive index of 2.76 whereas most binders have a refractive index around 1.5, a difference of 1.26. As light travels from one material to another of a different refractive index, scattering occurs, which is important for hiding in paints. Scattering is the internal reflection of light in an object and increases as the difference in refractive indices increases. Hiding prevents the darker undercoat or raw substrate layers from being observable in the finished product. Effective hiding is integral to quality paint appearance and industry demands for superior paint systems have supported the use of titanium dioxide for this beneficial attribute.

The pigments used to create black automotive coatings are the products of partial combustion of petroleum products or natural

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gas called carbon blacks. The exact process and raw materials used in production determine the chemical nature of the pigment; however, they are essentially elemental carbon. Different groups of these carbon-black pigments exist with different particle sizes and jetness—measure of blackness. Channel, furnace, and lamp blacks are examples of carbon-black pigments with increasing particle size and decreasing jetness, respectively (5).

Although titanium dioxide is the preferred white pigment, it does absorb in the violet region of white light, which results in a white paint that may display a yellowish tint because of the violet wavelengths that are not reflected. To counter this, manufacturers may add a secondary pigment that will not absorb where titanium dioxide does such as Carbazole violet or even black pigments (5). This type of pigment modification is an example of secondary pigments being used to improve the final achromatic color of the coating. There is also demand on the automotive industry to develop paint systems, which are unique and appealing yet still maintain high quality. The use of secondary pigments to impart a chromatic effect in an achromatic color system would be an example of this, and the benefit in this instance would be a subtle chromatic addition to the achromatic shade.

Automotive paint manufacturers also often add secondary pigments in paint formulations to produce unique vehicle coatings. As the final paint coating appears achromatic, it contains pigments that are chromatic and could yield spectral data. This study examined a set of apparently achromatic automotive paints via MSP. The goals of this project were to determine if it is possible to obtain informative spectral data from apparently achromatic paints in the visible region and if the spectra could be of value in forensic comparisons.

Methods

One hundred and twenty samples were obtained from damaged vehicle panels at salvage yards and local body shops. Forty samples each were obtained from vehicles with white, gray/silver, and black topcoats. An additional 40 samples of gray undercoat were obtained from the original vehicular samples resulting in a total sample set of 160. The vehicle data was recorded to track the origin of the samples.

Samples were prepared by manually removing a thin peel of the desired layer and mounting on a microscope slide. This peel was thinned by rolling (Excel razor), immersed in 1.520 Cargille refractive index oil, and a coverslip was applied. A second rolling over the coverslip was performed immediately before instrumental analysis. This preparation is consistent with techniques reported in published literature (6).

Examination via polarizing light microscopy (PLM) ensured proper preparation and absence of contamination by adjacent layers. Presence of metallic flake or visible pigments was also recorded.

Visible microspectrophotometric analysis was performed in transmission mode on an SEE 2100 instrument (Middleborough, MA) with a 12 × 12 μm effective aperture size at × 15 and equipped with Grams 32 software. NIST (National Institute of Standards and Technology) traceable standards were used to calibrate the instrument. Dark and reference scans were performed before analysis of each sample. Samples were analyzed in five locations, and each location analysis result was an average of ten scans.

Results and Discussion

The majority of the samples resulted in a featureless curve in the visible range. This is characteristic of the flat absorption expected with achromatic samples. A portion of samples showed a spectrum with some increase in absorption within the same region. This was typically seen between 550 and 700 nm and varied in intensity. Any absorption that was visually distinguishable from the flat absorption samples was included in the positive spectral results (Fig. 1, Table 1).

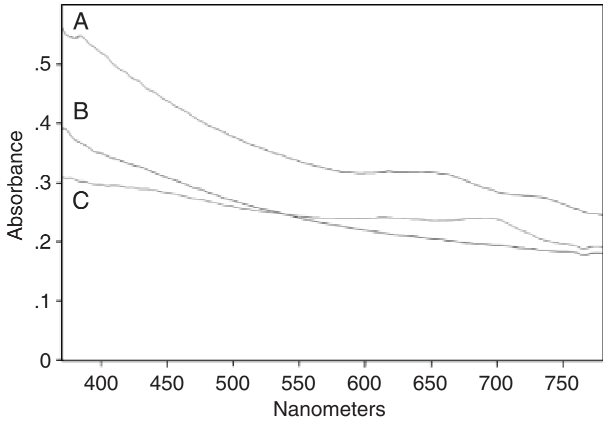

FIG. 1—*Spectra of three black vehicular samples. One displays expected flat absorption, two exhibit absorbances in visible region (A, 1993 BMW 318i; B, 1997 Buick Park Avenue; C, 2002 Chevy S10).*

In the black sample set, 11 of the 40 did yield spectral information. Four of the 11 samples demonstrated a slight absorbance at 700 nm. Six of the 11 had absorbances from 575 to 700 nm. One sample displayed a very strong absorbance at 620 nm with a shoulder at 580 nm and a second absorbance at 700 nm. Review of microscopy notes revealed that this sample had a blue binder and was taken from a vehicle that appeared black or dark blue–black. Chromatic pigments would then be present and strong absorbances would be expected. The six samples with absorbances at 575 to 700 nm were noted to have chromatic pigment particles visible in PLM analysis. All three were distinguishable from one another. The four samples with slight absorbances near 700 nm did not show any chromatic pigment particles during initial examination via PLM.

In the gray/silver sample set, 10 of 40 yielded some spectral variation. Two of the 10 gave weak absorbances at 525 and 575 nm. These samples were not distinguishable based on visible spectra. Eight of 10 resulted in stronger and more distinct absorbances throughout the entire visible region. The binder in this larger set was found via PLM to contain secondary chromatic pigments. Similar to the single black sample with strong absorbances, this

TABLE 1–*Results of polarizing light microscopy (PLM) and microspectrophotometry (MSP) analysis of apparently achromatic paint.*

Sample Set	Samples Yielding MSP Spectra	Associated Wavelengths (nm)	Chromatic Features Noted During PLM Examination
Black	4	700	None
	6	575–600	Chromatic pigment particles
	1	620, 580, 700	Blue binder
	Total: 11		
Gray/silver	2	525, 575	Chromatic pigment particles
	8	Throughout visible region	Chromatic binder
	Total: 10		
White	0	N/A	N/A
Gray undercoat	0	N/A	N/A

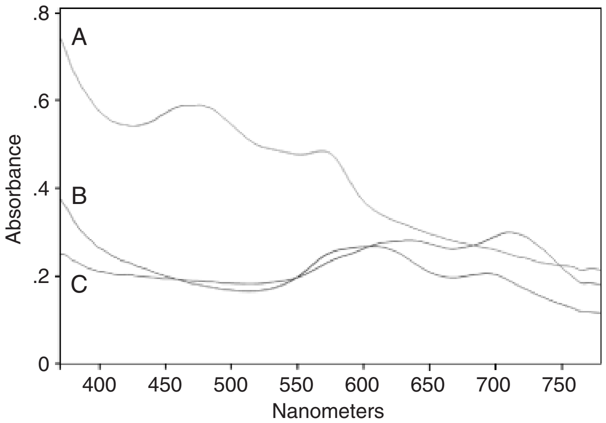

FIG. 2—*Spectra of apparently achromatic samples with colored films that show strong absorbances at different wavelengths within the visible region (A, 1994 Buick LeSabre with red tinted binder; B, 1990 Mercury Grand Marquis with blue binder; C, 1999 Mercury Sable with green tinted binder).*

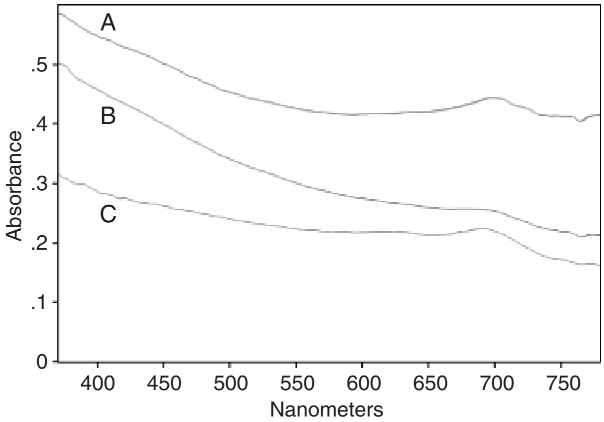

FIG. 4—*Spectra of three black vehicular samples with no visible chromatic pigmentation via PLM (A, 1997 Ford Taurus; B, 1997 Ford Taurus; C, 1996 Ford Explorer).*

type of response in MSP would be expected with a colored substance. In the initial PLM exam of the set of two samples, chromatic pigment particles were identified.

Within the white sample set, no informative spectra were obtained. All samples resulted in a very noisy, flat absorption. This is likely because of the prominent white pigment, rutile titanium dioxide. Its high refractive index and effective light scattering attributes prevent light from being transmitted and spectra being obtained. Similarly, the gray undercoat set also gave noisy, uninformative spectra. As undercoat layers are not typically seen in the final automotive finish, there is little need for these layers to be pigmented with a secondary pigment.

When the data gained during MSP analysis is compared with the observations made via PLM, three sources of color in the achromatic samples can be identified. In the case of the samples where a colored film or binder was identified, this is clearly the chromatic element. Whether the coloration is a result of a dye element or finely dispersed pigment particles, the effect is visible in reflected light. The MSP spectra were reproducible and were valuable in distinguishing between samples whose binders appeared similarly colored via PLM (Fig. 2). The second source of color is the pigment particles visible via PLM analysis. These samples had a clear binder and individual chromatic pigments interspersed with the achromatic pigments. Concentration of the particles varied between samples as did the colors observed. Some samples only displayed one color of pigment whereas others displayed up to five. The spectra of these samples had greater noise and displayed weaker absorbances than that of the colored film set; however, they did not vary based on analysis location within a sample. This indicates that while the heterogeneity of the sample is visible in PLM, the spectral analysis via MSP was fairly consistent within the aperture size utilized.

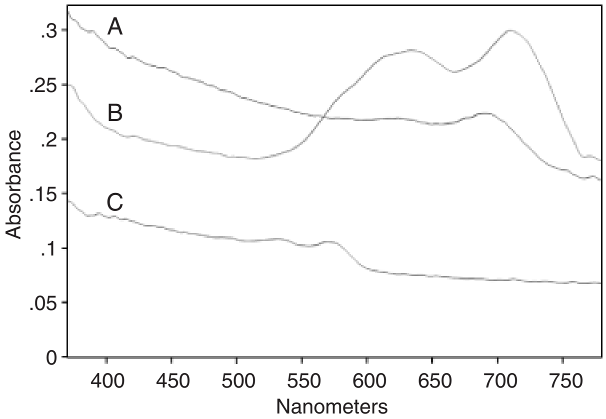

FIG. 3—*Absorbances in the visible spectrum may be the result of colored binders or pigments that may or may not be visible in reflected light (A, 1996 Ford Explorer where no pigments were visible via PLM; B, 1999 Mercury Sable with tinted binder; C, 1996 Oldsmobile Cutlass where pigments were visible via PLM).*

The final group of samples that yielded positive spectral information was not identified as having chromatic pigment particles during the initial microscopic examination. The group had very consistent spectra in MSP with slight absorbances at 700 nm. Sample reproducibility within this group was also good (Figs. 3 and 4).

As with any nonhomogenous sample, the control of preparation and sampling is extremely important to ensure quality analysis. Sample considerations include obtaining consistent thickness and parallel planes during sample preparation. Microscopic comparisons must be made under identical conditions, e.g., same instrument and analyst, etc. Sample thinning was performed to obtain the shortest possible path length for improved MSP resolution. The analysis locations were also chosen to improve resolution. The thinnest areas of the mounted sample were scanned regardless of pigment presence or density. The only other consideration made during sampling was the avoidance of metallic flakes that efficiently reflect light to produce their effects and would interfere with obtaining spectra.

Conclusions

This study of achromatic paints shows that black and gray samples may give spectral information in the visible region. Although this data that may or may not be gained via PLM, MSP can provide additional discrimination information. This is due to the presence of secondary chromatic pigments added to the achromatic paint formula, which may result in a colored binder, visible agglomerations of pigments, or may not be observable in reflected light. White and gray undercoat samples did not give valuable information with this procedure. When MSP is regularly included in an automotive paint analysis scheme it should be included in schemes involving black and gray/silver topcoats.

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