Garnik P. Voskertchian,[1] *Ph.D.*

Quantitative Analysis of Organic Pigments in Forensic Paint Examination

ABSTRACT: A method is used to determine the qualitative and quantitative composition of small paint samples (7–15 micrograms) containing different phthalocyanine (copper and metal-free) pigments and their mixture using visible spectrophotometry.

In some cases during forensic examination of paints, there is a need for the identification of organic pigments. FT-IR spectroscopy in most of the cases cannot be used for the identification of many organic pigments in paint chips for several reasons: the low concentration of organic pigments (0.2 to 1.5 w.w.%) the relatively low sensitivity of IR spectroscopy and spectral interferences of different nonpigment components (vehicles, binders, dryers and oils) with similar characteristic bands of organic pigments. Colorimetric measurements of small paint fragments are useful for color comparison but not for specific pigment identification especially in' the case of pigment mixtures. Technical problems related to the extraction of organic pigments from paints, which are practically insoluble in organic solvents significantly limit the application of traditional analytical methods to this problem.

The identification of phthalocyanine pigments on different substrates using spectrophotometric analysis has been described [*1*]. In most of the articles related to forensic paint examination this approach is not used. This is because the standard scheme of forensic paint analysis includes several instrumental methods (IR, pyrolysis gas chromatography, electron microprobe, X-ray analysis, emission spectroscopy), determines the generic type of paint binder and elemental composition as well as the crystal composition of inorganic compounds. Microspectrophotometry of paint fragments is carried out principally for comparison of pigments without their identification and usually can discriminate different types of pigments. Identification is limited because reflectance spectra lack detailed information and tristimulus values determined by colorimetric measurements are also limited. Unfortunately the information obtained by using reflectance and tristimulus methods is insufficient for forensic examination of paint fragments. We have established that there is distinct variation of pigment(s) concentration among different batches of visually similar automotive

paints produced by the same manufacturer. Examination of paint fragment color usually is conducted by mere qualitative comparison with a lack of quantitative analysis of the paint's color producing ingredients (pigments).

Phthalocyanine pigments are one of the most commonly used pigments in the textile, paint, rubber, and printing industries. They are complex compounds with organic ligands such as benzotetraazoporphine with or without metal ions (for instance, copper, cobalt, nickel, etc.). Visible light spectroscopy is one of the best methods for identification of phthalocyanine pigments in paint fragments due to their large absorptivity in both the visible and near-infrared regions of the spectrum (500 to 900 nm).

The purpose of the work is to advocate a relatively simple method for the analysis of different phthalocyanine pigments in paint chips. Visible spectrophotometry was capable of discriminating paint fragments of similar color but which contained different pigment compounds. Qualitative and quantitative determination of different pigments provides additional information for individualization of paint fragments in forensic analysis.

Experimental

The majority of samples were Russian-made automotive finishes. The automobile paints had different colors, pigment composition and ingredients. Samples were obtained from both manufacturers and car factories. A collection of phthalocyanine pigments which were used for compounding the paints was received from the manufacturer. Automobile paint samples were the following colors and types: Blue ML-1110 (I), Green ML-1110 (II), Dark Green ML-1110 (III), Light Navy ML-1229 (IV), Light Gray ML-1289 (V). All samples contained the individual phthalocyanine pigments—Blue 5 (CI 74160) (VI), Green 7 (CI 74260) (VII) or their mixture, Green (metal-free) (VIII). The size of a minute fragment of paint was measured by microscope, then weighed on an electronic autotobalance AD-2 (Perkin-Elmer). The fragment was placed into a glass vial with 0.8 mL of concentrated sulfuric acid (90%, analytical grade) for few hours. The paint chip completely dissolved in 2 to 4 hours. The visible spectra of dissolved samples of constant volume (0.6 mL) were recorded on double beam spectrophotometer (Cary-17D, Varian, USA), equipped with 2 mm wide microcells of 10 mm path length (Varian).

The metallized and metal-free phthalocyanines were not decomposed during dissolution of the paints in sulfuric acid as were the resinous vehicles and oils. Electronic spectra of paints in acid solution were recorded between 600-1000 nm region. The UV-region was avoided because of the intense bands due to polymer decomposition products.

823

TABLE 1—*Spectral characteristics of paint fragments and pigments, dissolved in sulfuric acid.*

Paint brand	Pigment composition, %	Absorption band peaks and shoulders (sh), nm
Blue ML-1110	Blue 5 (3.4%) + Green 7 (1.63%)	255, 304, 379(sh), 440, 702, 751(sh), 791, 862
Green ML-1110	Green 7 (3.16%) + Blue 5 (1.73%)	306, 378(sh), 702(sh), 791, 862
Dark Green ML-1110	Green 7 (1.73%)	307, 378(sh), 555, 645, 730(sh), 769(sh), 816, 862
Light Navy ML-1229	Green 7 (0.63%)	307, 378(sh), 526(sh), 730(sh), 769(sh), 813, 862
Light Gray ML-1229	Blue 5 (0.08%)	307, 373(sh), 435(sh), 702, 752(sh), 791
Pigment Blue 5		304, 440, 555(sh), 645, 702, 751(sh), 791
Pigment Green 7		322, 514, 588(sh), 738, 781(sh), 830, 875
Pigment Green (metal-free)		311(sh), 736, 779, 825, 870

Results

A total of five different brands of paints were identified by spectrophotometry. A summary of the results of the analysis is given in Table 1 and Figs. 1, 2.

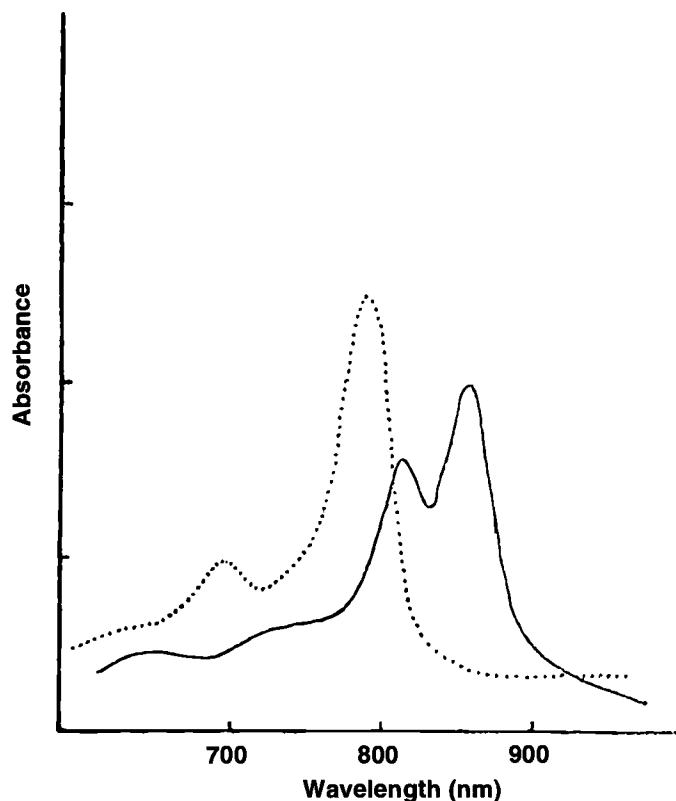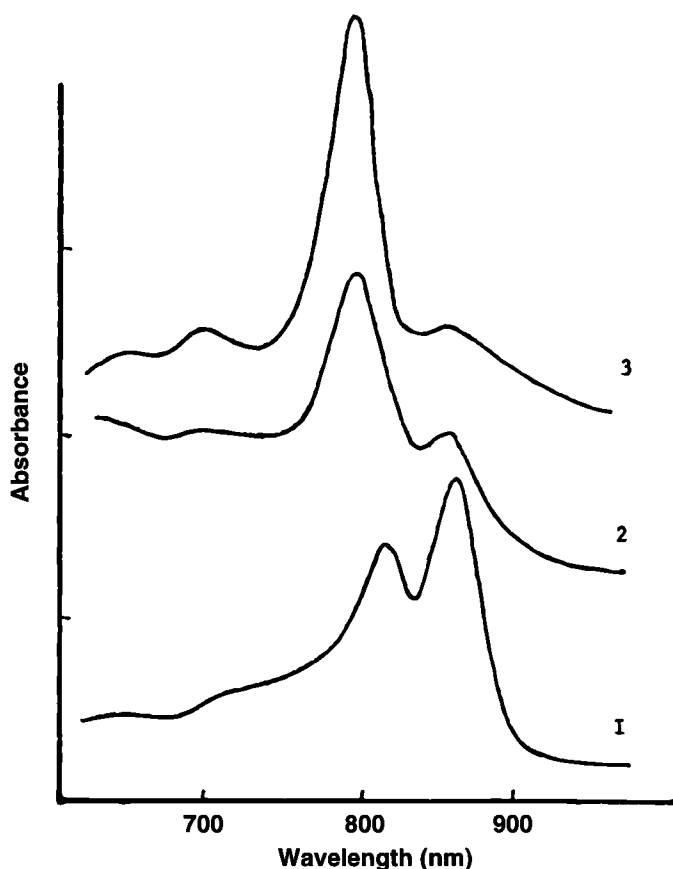Samples of paint chips contain individual pigments as well as

FIG. 2—*Absorption spectra of paint fragments with different ratio of pigments blue 5 and green 7: green ML-1110 (1), blue ML-1110 (2) and light blue ML-1110 (3).*

FIG. 1—*Absorption spectra of paints navy ML-1229 with pigment green 7 (-----) and light gray ML-1229 with pigment blue 5 (.....) in sulfuric acid.*

mixtures in different proportions. As a result the absorption spectra in NIR of some paints contain characteristic absorption bands of individual phthalocyanine pigments—Blue 5 and Green 7 (Fig. 1). Absorption spectra of paint samples Blue ML-1110(I) and Green ML-1110(II) consist of superposition of spectra of pigments Blue 5 and Green 7, their ratio in paints are 2.1:1 and 14:1, respectively (Fig. 2). Pigment Blue 5 shows an intensive band at 791 nm and weak peak at 702 nm, while Green 7 shows intense bands at both 817 and 862 nm. When paint fragments consist of mixture of two phthalocyanine pigments there are intensive bands at 702, 791, 817 and 862 nm. The intensity ratio of these bands is proportional to the concentration of the Green and Blue pigments in the paint chip. It was shown that when a multilayered paint fragment was dissolved in sulfuric acid, decomposition products of primer, clear coat did not affect the absorption bands in NIR region. In paint chips with less saturated colors due to the pigments such as Light Blue and Light Navy which have low concentrations of pigments (less than 0.1%) and a high concentration of titanium dioxide a shift of the zero line of the visible spectrum was observed. This can be compensated for by the addition of some quantity of titanium dioxide to the comparison cuvette.

Presented below are the results of the examination of fragments of five brands of paint which have linear dimensions less than 0.5 sq.mm. As seen in Table 2 there is as expected a linear dependence of paint fragment weight to absorbance of the pigments. This relationship can be used for comparative semiquantitive examination of paints. It should be noted, that spectrophotometric methods for paint analysis can also be used for differentiation of paints,

TABLE 2—*Results of qualitative analysis of paint fragments.*

Paint brand	Pigment(s) composition, (%)	Weight of fragment, microgram	Optical density at wavelengths, nm			
			702	791	817	862
Blue ML-1110	Blue 5 (3,47) + Green 7 (1,63)	9	0,017	0,051	...	0,013
		21	0,039	0,108	...	0,028
Green ML-1110	Green 7 (3,16) + Blue 5 (0,22)	7	...	0,028	...	0,028
		19	...	0,082	...	0,063
Dark Green ML-1110	Green 7 (1,73)	8	...	...	0,01	0,018
		12	...	...	0,02	0,032
Light Navy ML-1129	Green 7 (0,63)	14	...	...	0,01	0,02
		22	...	...	0,02	0,035
Light Gray ML-1289	Blue 5 (0,08)	42	0,002	0,06	...	...
		78	0,004	0,12	...	...

which consist of other types of blue pigments like Indantrone Blue or Ultramarine Blue. Absorption spectra of these paint pigments have no characteristic bands in spectral range 600 to 900 nm. Absorption band peaks of decomposition products of the pigment Indantrone Blue in sulfuric acid lie at 312 and 370 nm. Iron Blue, which totally decomposes, exhibited one peak at 290 nm. This information can be used for differentiation of paint chips that have similar colors but contain different pigments.

Discussion

In "hit and run" cases it may be necessary to examine paint fragment by means of the semi-quantitative analysis of organic pigments. The spatial distribution of pigment in the top-coat of different parts of the car is not homogeneous, and this must be taken into account. From the damaged parts of suspected car, it is necessary to take several samples [6–8] which must have similar linear dimensions and weights. The samples from the suspect car

and paint fragments from victim's garment are dissolved in sulfuric acid and the absorbance of the most intense peaks are measured. For example, for Blue ML-1110 the absorbance value at 791 nm is measured while for paints with mixture of pigments the absorbance at 791 and 862 nm are measured. These values are normalized on the weights of the samples and can be used for comparative analysis of pigment concentration in paint fragments. The extinction coefficient (absorptivity) of pigment Blue 5 is 5.5 × 10^5 [2], so it can be used to define the absolute concentration of pigment in the paint chip.

The results reported in this paper show that spectrophotometry offers a high degree of identification for phthalocyanine pigments in paint fragments. Our approach is technically simple and requires only standard spectrophotometer with microcells. It is a destructive technique, as is pyrolysis gas chromatography for polymers and vehicles, but not for phthalocyanine pigments. In our practice we use it for identification and quantitative comparison of phthalocyanine pigments in paint chips and single fibers after FT-IR microscopy, electron microprobe analysis of the fragments. The procedure can be used to discriminate different compositions of pigment mixtures in paint fragments and fibers and provide semiquantitative information which is difficult to obtain using the other more commonly employed instrumental methods.

References

[1] Thomson, J., "Identification of Organic Pigments on Substrate Other Than Textile Fibers," In *The Analytical Chemistry of Synthetic Dyes*, K. Venkatrama, John Wiley & Sons, N.Y., 1977.
[2] Berezin, B. D., Dokl. Akad. Nauk SSSR, v. 150, 1039, 1963.

Address requests for reprints or additional information to
Dr. Garnik P. Voskertchian
Lab for Instrumental Method
All Russia Institute for Forensic Sciences (VNIISE)
Khokholovsky PER. 13 B.2
Moscow, Russia 109028