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## The Evidential Value of Automobile Paint Chips

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Automotive paint technology has been in a state of constant change over the past 15 years. Along with this change in technology has come a new challenge for the criminalist. With the courts relying more on physical evidence, a thorough and accurate explanation of the value of class evidence is necessary. It is the forensic scientist's responsibility not only to report his laboratory findings, but also to assess the probative meaning of those results.

Instrumentation in the field of analytical chemistry has seen new developments paralleling the new technology in the paint industry. New techniques have afforded greater differentiation capabilities as well as simplified analytical procedures. Several studies of these instrumental methods have appeared in the literature over the past few years. A majority of these incorporates the analysis of nonrandom samples to evaluate the differentiation capability of a particular type of instrumentation [1-4]. Manura and Saferstein [5] conducted examinations of random automotive paint samples to evaluate the capabilities of the laser microprobe emission spectrograph.

Recently, Gothard [6] published the results of a comprehensive study of the differentiation of 500 automobile paints collected at random in New South Wales, Australia. This survey provided details on the distribution of the specimens throughout a complete analytical scheme similar to that which would be used in examining paint chips submitted to the laboratory as evidence: microscopic tests, solvent tests, instrumental binder analysis, and instrumental element analysis. When a limited sample does not permit complete examination, information of this type is invaluable.

It is obvious that paint types will differ in distribution from one geographic area to another. The warmer climates may have different popular colors than cooler climates and metropolitan/suburban areas may have a different distribution of makes and models than rural areas. The population distribution will most certainly change from one country to another, and for this reason, additional studies similar to that of Gothard are required to permit proper assessment of the evidential value of automobile paint chips.

### Sample Collection

During the month of July, 1977, 200 paint chip specimens were obtained from automobiles chosen at random in three salvage yards in the Philadelphia, Pennsylvania area. Two of these yards stocked vehicles for the purpose of salvaging used parts, while the third was a salvage auction yard which held damaged vehicles pending the decision of the insurance company as to the disposition of the vehicle. Approximately half of the samples were obtained at the latter. Vehicles ten years or more in age were avoided because the possible preponderance of older vehicles would not be representative of the automobile population on the road. In all other respects, sampling was random.

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The specimens were removed from the damaged area of the vehicles much as would be done in the collection of standard and questioned samples in an actual case. A sharp metal spatula was used to chip intact fragments of paint from the vehicles. They were collected in a white paper envelope, which was then sealed and labeled as to the make, year, and model of the source when the information was available. Occasionally, chips with only partial layer structure were recovered. Since this is the way the finish would be expected to fragment in an accident, the samples were considered acceptable.

### **Examination Procedure**

Initially, the 200 samples were sorted into groups according to topcoat color (Table 1). The following procedure was then applied to each group.

A 45-deg angular cross section was made on each specimen in the color group and the layer structure was briefly noted along with the topcoat color, shade (light, medium, or dark), and finish (metallic or nonmetallic). When spot putty or body filler was encountered, it was recorded as a paint layer.

Subgroups were then formed according to the noted similarity of topcoat colors. Each subgroup was examined and compared microscopically to determine which specimens had topcoats consistent with one another. These paint chips were then subjected to a detailed comparison of layer structure accomplished by scraping down through layers and microscopically comparing each questioned group side by side. Samples having the same order of layers but not the same number of layers were considered similar, since partial fragmentation of layers is possible.

The paint chips remaining undiscriminated were subjected to microscopic solvent tests using chloroform, acetone, concentrated sulfuric acid, and diphenylamine test solution. Solubility, texture change, and color change upon agitation were noted and compared for each.

Those fragments still consistent with one another following the microscopic and solvent examinations were analyzed by pyrolysis-gas chromatography (topcoat only). If differentiation was not achieved, the samples were then compared by diamond-cell infrared spectrophotometry (topcoat and individual primer coats), energy dispersive X-ray spectrometry, emission spectroscopy, and neutron activation analysis.

### *Microscopic Examination*

Comparisons were made under varied lighting conditions using a Bausch and Lomb stereozoom microscope (magnification,  $\times 10$  to  $\times 20$ ). All chips were examined for color, tint, texture, metallic dispersion, layer order and thickness, inclusions between layers, and sanding striations on the primer layers resulting from refinishing procedures.

### *Solvent Tests*

Solvent tests were performed by adding one or two drops of reagent to small particles of each layer and microscopically observing the reaction of the test solution with the layer. The diphenylamine solution gives a bright dark-blue color with nitrocellulose-modified binders. The reagent consists of 0.15 g diphenylamine, 10 ml concentrated sulfuric acid, and 5 ml glacial acetic acid.

### *Pyrolysis-Gas Chromatography*

Pyrolysis-gas chromatography (PGC) was performed on the topcoats employing a Chemical Data Systems (CDS) Pyroprobe equipped with a platinum filament coil and

TABLE 1—*Distribution of samples by topcoat color and type of finish.*

Color Group	Metallic Samples		Nonmetallic Samples		Combined	
	<i>n</i>	% of Total	<i>n</i>	% of Total	<i>n</i>	% of Total
Brown/gold/tan	34	17.0	14	7.0	48	24.0
Green	34	17.0	6	3.0	40	20.0
Blue	25	12.5	13	6.5	38	19.0
Red/maroon/pink	10	5.0	21	10.5	31	15.5
White	0	0	12	6.0	12	6.0
Yellow	0	0	11	5.5	11	5.5
Gray/silver	10	5.0	0	0	10	5.0
Orange	2	1.0	4	2.0	6	3.0
Black	0	0	3	1.5	3	1.5
Purple	0	0	1	0.5	1	0.5
Totals	115	57.5	85	42.5	200	100

quartz tube [7]. Approximately 100  $\mu\text{g}$  of paint was placed in the quartz tube and pyrolyzed at 800°C for 10 s with a heating rate of approximately 75°C/ms.

Separation of the resulting pyrolysates was accomplished with a Perkin-Elmer Series 900 gas chromatograph equipped with flame ionization detectors. The carrier gas (helium) flow rate was set at 40 ml/min with the injection port held at 250°C and the detector manifold at 300°C. A 1.2-m (4-ft), 3.2-mm ( $1/8$ -in.) outside diameter steel column packed with 80-100 mesh Porapak Q was installed in the chromatograph, which was programmed from 90 to 240°C at 8°C/min with a 1-min initial hold and a 20-min hold at the final temperature.

#### *Diamond-Cell Infrared Spectrophotometry*

A 2- $\mu\text{g}$  sample (approximate) was taken from the layer and placed in the diamond cell. The cell was placed in the cell holder, which was mounted in a 4 $\times$  beam condenser positioned in the sample beam of a Perkin-Elmer Model 621 infrared spectrophotometer. The infrared spectrum of the sample was recorded from 2000 to 200  $\text{cm}^{-1}$ .

#### *Emission Spectroscopy*

In the analysis by emission spectroscopy (ES), paint chips with layers intact weighing 0.5 mg were analyzed with a Baird-Atomic 3-m spectrograph. Samples were burned to completion in graphite cup electrodes at 20 A in the d-c arc mode. Kodak No. SA-1 spectrographic plates were used to record the emission spectra from 221.5 to 359.0 nm. Spectra were compared by using a Baird-Atomic RC-3 densitometer.

#### *Scanning Electron Microscopy/Energy-Dispersive X-Ray Analysis*

Energy-dispersive X-ray analysis (EDX) was conducted with a Hitachi HHR-2S scanning electron microscope (SEM) equipped with a KeveX 500.0-nm X-ray analyzer. Single paint chips were mounted perpendicularly on an aluminum stub with double-sided tape and vacuum-coated with gold/palladium. An electron beam accelerating potential of 20 kV was used in the reduced raster mode at  $\times 1000$  with a 45-deg specimen tilt. X-rays were collected from 1 to 10 keV and the elemental profiles of each layer were compared by peak heights.

*Neutron Activation Analysis*

For neutron activation analysis (NAA), paint chips with layers intact weighing 50  $\mu\text{g}$  were irradiated at the National Bureau of Standards reactor. An irradiation period of 1 min at a thermal neutron flux of  $4.85 \times 10^{13}$  n/cm<sup>2</sup>·s at 9.9 MW was used. After a decay of 3 min, short-lived radioisotopes were determined by using a 60-cm<sup>3</sup> Ge(Li) detector coupled to a 4096 channel pulse height analyzer.

**Results and Discussion**

The samples were cataloged according to year and manufacturer in order to evaluate the validity of the sampling procedure (Tables 2 and 3).

The majority of the vehicles falls in the 1970 to 1974 years of production. This was expected, considering newer automobiles are less frequently declared "total losses" by insurance companies. Although the average year is slightly older than that which might be seen on the road at the present date, the collection is still representative of the types of finishes found on cars in that age group. Differentiation capability is even greater with the newer finishes because of the recent application of advanced paint technology, such as water-based acrylic enamels, nonaqueous dispersion lacquers, high solids coatings, clear topcoat system on metallics, a wider variety of bright-color metallics, two-tone finish systems, and frequent alteration in monomers and plasticizers used in binder formulation.

The randomness of the survey is corroborated by the distribution according to manufacturer, which is in agreement with that reported by the U.S. Motor Vehicle Manufacturers' Association (Tables 3 and 4). The possible preponderance of vehicles more prone to accidents was considered; however, this factor would also be evident in the type of vehicle commonly encountered in case work.

Initial differentiation by topcoat color and finish gives an indication of the frequency of occurrence of various paints (Table 1). As can be seen, a pair of matching purple topcoats would hold more evidential weight than a pair of matching green topcoats, since the frequency of occurrence for the purple paint is much less than that of the green paint. This type of information is quite useful in evaluating a case where only a topcoat is present and some idea of the prevalence of that particular color is required, as in an abrasion-type transfer.

Further examination by microscopic comparison of topcoat tint and layer structure

TABLE 2—*Distribution of samples by year of make of vehicle.*

Year	Vehicles, <i>n</i>	% of Total
1977	2	1.0
1976	6	3.0
1975	16	8.0
1974	28	14.0
1973	25	12.5
1972	24	12.0
1971	24	12.0
1970	36	18.0
1969	15	7.5
1968	2	1.0
1967	2	1.0
1966	1	0.5
1965	1	0.5
Miscellaneous (year unknown)	18	9.0
Total	200	100

TABLE 3—Distribution of samples by vehicle make.

Make	Vehicles, <i>n</i>	% of Vehicles
Domestic manufacture (80.0%)		
General Motors	86	43.0
Ford	48	24.0
Chrysler	17	8.5
AMC	9	4.5
Foreign manufacture (20.0%)		
Volkswagen	10	5.0
Audi	2	1.0
Porsche	1	0.5
Toyota	7	3.5
Fiat	3	1.5
British Leyland	3	1.5
Mazda	2	1.0
Honda	2	1.0
Opel (Buick)	4	2.0
Datsun	2	1.0
Saab	1	0.5
Renault	1	0.5
BMW	1	0.5
Subaru	1	0.5
Total	200	100

TABLE 4—Distribution of domestic automobile production and foreign automobile imports as reported by the U.S. Motor Vehicle Manufacturers' Association<sup>a</sup> (reported as percentage of total vehicles manufactured).

Make	1974	1975	1976	Range
Foreign	19.3	16.6	17.9	17 to 19
Domestic	80.7	83.4	82.1	81 to 83
General Motors	39.5	45.7	47.2	40 to 47
Ford	24.3	22.5	19.9	20 to 24
Chrysler	13.0	11.2	12.9	11 to 13
AMC	3.9	4.0	2.1	2 to 4

<sup>a</sup>Motor Vehicle Facts and Figures 1977, Motor Vehicle Manufacturers' Association of U.S., Inc., Detroit, Mich.

permitted differentiation of 174 of the 200 samples (87.0%). Application of solvent tests to the 26 undifferentiated paint chips left only 12 (six pairs) that required instrumental analysis for possible differentiation. Thus, 94% of the samples were differentiated by microscopic examination and solvent tests.

As noted by Gothard [6], "The layer sequence of paint flakes is the most significant point of comparison, particularly because of the variety of ways in which cars may be refinished." In addition, many foreign and domestic automobile manufacturers use various different types of primer systems, which provide additional parameters for the differentiation of similarly colored topcoats [8].

The layer distribution of the samples is shown in Table 5. Only 6% of the specimens had more than five layers. Following differentiation by microscopic examination of the topcoat color and layer structure, only 1.5% of the paint chips had more than three layers (Table 6). None of the samples requiring instrumental analysis for possible differentiation had more than three layers. Thus, the probability of two paint chips ori-

TABLE 5—*Layer distribution of total sample population.*

Layers, <i>n</i>	Samples, <i>n</i>	% of Total Samples
1	0	0
2	49	24.5
3	96	48.0
4	29	14.5
5	14	7.0
6	9	4.5
7	1	0.5
8	1	0.5
9	1	0.5
Total	200	100

TABLE 6—*Layer distribution of samples not differentiated by microscopic comparison of topcoat color and layer structure.*

Layers, <i>n</i>	Samples, <i>n</i>	% of Total Samples
1	0	0
2	5	2.5
3	18	9.0
4	1	0.5
5	1	0.5
6	1	0.5
Total	26	13.0

ginating from different sources is extremely remote when they have numerous layers (six or more) consistent in color, tint, type of finish, layer sequence, layer colors and textures, approximate layer thickness, and reaction to acetone, sulfuric acid, and diphenylamine test solution. This observation is in agreement with that reported by Klug et al [9] and indicated in Gothard's study [6].

Five of the six pairs of paint chips remaining undifferentiated by microscopic examination and solvent tests originated from vehicles having the same make and approximate year of manufacture (maximum of one year difference). The one pair of samples not having the same manufacturer consisted of two layers having characteristics typical of a repaint finish. Because of the limited quantity of this sample, not all of the instrumental techniques could be used. The two specimens were differentiated by SEM/EDX and ES.

Binder analysis of the topcoats with PGC served to differentiate three of the five pairs. One had only slight variations in the ratios of pyrolysis products. This pair and the remaining two pairs of samples having indistinguishable topcoat binder formulations were subjected to further examination of each layer by diamond-cell infrared spectrophotometry [10-12]. Confirmation of differentiation was achieved for the one pair and the other two pairs remained indistinguishable. Thus, 97.0% of the samples were discriminated without the aid of elemental examination.

The two remaining pairs of paint chips were then compared by elemental analysis using ES, SEM/EDX, and NAA. In general, the samples were distinguished on the basis of differing elemental profiles. Analysis by SEM/EDX and NAA revealed different ratios of the same elements; however, ES indicated, in addition, the presence of different trace element content.

### Summary

A survey of 200 random automobile paint chips with a standard forensic laboratory examination procedure (microscopic examination, solvent reactivity tests, instrumental analysis of organic constituents, and instrumental analysis of inorganic constituents) served to differentiate all samples. Specimen characteristics were tabulated throughout the examination to evaluate their frequency of occurrence in samples similar to those encountered in case work.

Ninety-four percent of the samples were differentiated by microscopic examination and solvent reactivity tests. Of the remaining 6% that were undifferentiated, none of the paint chips had more than three layers. This observation leads to the conclusion that the probability of two paint chips originating from different sources is extremely remote when they have numerous layers (six or more) consistent in color, tint, type of finish, layer thickness, and reaction to acetone, sulfuric acid, and diphenylamine test solution.

Ninety-seven percent of the samples were differentiated without the use of elemental analysis. For maximum differentiation capability, at least one instrumental analysis technique for organic components and one for elemental components should be incorporated into the analytical scheme when sample size permits.

A review of the literature reveals the lack of frequency of occurrence studies for automobile paint evidence. Additional studies, similar to the one presented here, are being initiated to further assess the statistical value of this type of class evidence.

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