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A Make-Model-Year Case Involving Unusual Primer Chemistry and Good Resources

ABSTRACT: The case example presented will describe how the FBI Laboratory was able to develop investigative lead information in a hit-and-run fatality using resources such as the Paint Data Query (PDQ) database, automotive paint supplier contacts and refinish color pages, and the internet. This case highlights the utility of a database such as PDQ in providing spectral data of known paint layers that can be directly compared to the layers analyzed in a paint chip recovered from a crime scene. Conversely, this case also depicts the limitations inherent in a database compiled from the relatively limited pool of vehicles sampled primarily from salvage yards by participating partner laboratory systems. Such a database can only be as broad as the population available for sampling, and gaps in representation are to be expected. Nonetheless, compelling investigative lead information was reported to the contributor using the described resources, most of which are readily available or can be developed by every laboratory system conducting these types of automotive paint examinations.

KEYWORDS: Paint, Make-Model-Year Determination; Automotive Databases, FTIR, Benzoguanamine, PDQ

INTRODUCTION

In June 2009, the FBI Laboratory's Chemistry Unit received a request for make-model-year (MMY) investigative lead information in a hit-and-run fatality involving a motorcycle and what was described by the contributing agency as a "blue car, possibly a sedan." Eyewitness accounts provided with the request for examination named the suspect vehicle as "a dark blue vehicle, possibly a station wagon" and as a "dark blue Volvo." Dark blue streaks were readily observed on the submitted metal fender from the motorcycle.

MICROSCOPIC EXAMINATIONS

Microscopic examination of the damaged area of the motorcycle fender yielded numerous paint chips containing partial layer structures. Some of the chips had two-layers: clearcoat over a blue metallic basecoat. Some of the chips were fragmented such

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that a portion of the chip was clearcoat only and another portion of the same chip contained only the blue metallic basecoat. However, one of the recovered paint chips consisted of four original equipment manufacturer (OEM) layers. On this chip, the clearcoat and each of the two primers were of the same relative thickness, and the blue metallic basecoat was approximately half this thickness. Colorimetric analyses were conducted on the basecoat and primers using a Chroma Meter CR-241 reflected light colorimeter (Konica Minolta Sensing Americas, Inc, Ramsey, NJ) calibrated for a 0.3 mm measurement area and set to report out the resulting colorimetric data as Munsell values. The basecoat measured at 4PB 3/1, while the primer surfacer, adjacent to both the basecoat and electrocoat (e-coat), was a dark gray color, equivalent to N 3 on the Munsell Neutral Scale. The electrocoated primer (e-coat) was a lighter gray, equivalent to N 5.

FTIR ANALYSES

Fourier transform infrared spectroscopic (FTIR) analysis was performed on each of the four layers present on the paint chip using a Nicolet 670 Nexus FTIR E.S.P. spectrometer with a MCT/A detector (4000-650 cm^{-1}) scanning at a resolution of 4 cm^{-1} (Thermo Nicolet, Madison, WI). The analysis was conducted using a microscope accessory in which a micro compression cell with two diamond windows (Thermo Scientific, Waltham, MA) was used to compress the individual layers. One of the diamond windows was then used as a sample holder for analysis. One hundred twenty-eight scans were run on both the sample and background of each layer. Interpretation of the FTIR data for three of the layers was straightforward. The clearcoat was observed to contain an acrylic binder (peaks at 1728, 1473, 1367, and 1151 cm^{-1}) with styrene modification (peaks at 760 and 702 cm^{-1}) and melamine as the cross-linker (peaks at 1557 and 816 cm^{-1}). The blue metallic basecoat binder was composed of polyester, also known as an isophthalic alkyd (peaks at 1731, 1473, 1372, 1239, 1076, and 731 cm^{-1}), and melamine (1553 and 813 cm^{-1}). The e-coat was a typical formulation of epoxy (major peaks at 1607, 1509, and 830 cm^{-1}) with some polyurethane modification (noted by a broadening of the carbonyl peak at 1731 cm^{-1}), kaolin (major peaks at 3696, 3621, 1036, 1012, and 915 cm^{-1}), and titanium dioxide (evident by a broad peak beginning at 800 cm^{-1} to the detector cut-off at 650 cm^{-1}). However, the primer surfacer layer (Figure 1) proved to be the most critical layer to define the chemistry of this paint system.

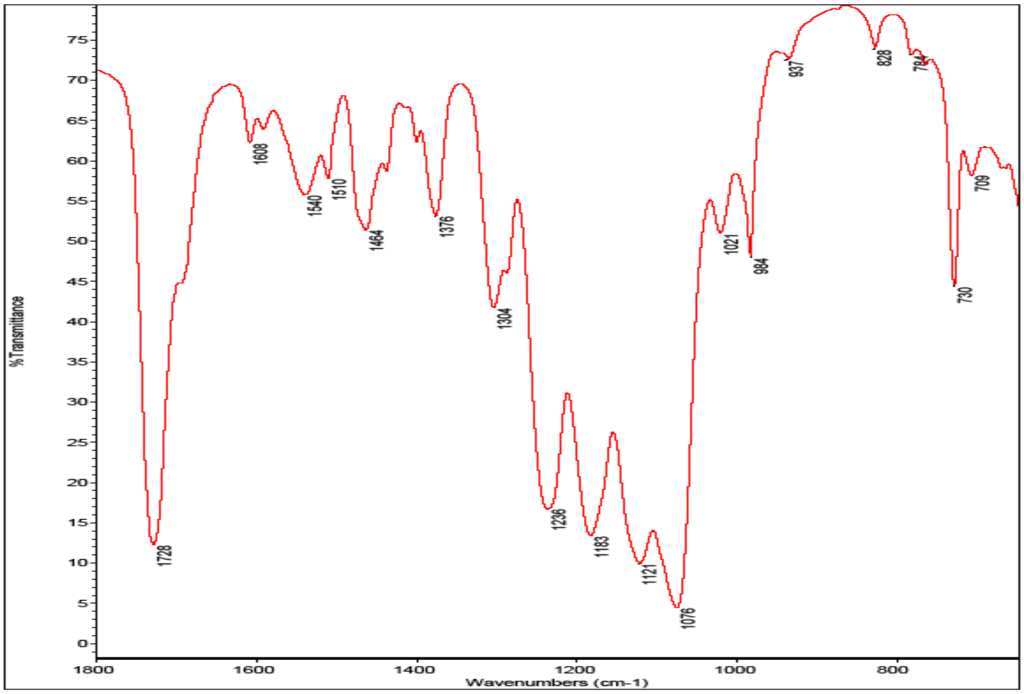

Figure 1. FTIR spectrum of the primer surfacer layer obtained from the case sample.

The binder for this primer layer was also an iso-alkyd/polyester, which contained some epoxy and polyurethane modification. Barium sulfate was readily observed as a pigment in this layer, along with possible contribution from titanium dioxide. Peaks were also noted at 1540 cm^{-1} and 828 cm^{-1}. The latter peak was attributed to the epoxy group that was also evident at 1608 cm^{-1} and 1510 cm^{-1}. However, the peak at 1540 cm^{-1} was distinctly present between the epoxy peaks and appeared to be shifted too far from the 1550 cm^{-1} region to be attributed to the in-plane deformation stretching of melamine's triazine ring. There was also a peak at 709 cm^{-1}, which was not accounted for by the other functional groups observed in the formulation. Based on these peak designations, the cross-linker was designated as benzoguanamine [1].

Benzoguanamine is structurally similar to melamine, with the major difference that it contains only two functional reaction sites as opposed to melamine's three reactive sites (Figure 2). This difference makes melamine a better cross-linker and more weather resistant. The absence of a third reaction site on benzoguanamine, however, enables it to be more flexible and provide better bond (adhesive) strength than melamine resins. For these reasons, benzoguanamine usage in automotive coatings is restricted to primer layers [2].

Melamine Benzoguanamine

Figure 2. Structures for melamine and benzoguanamine, respectively.

PAINT DATA QUERY

Once the FTIR data had been interpreted, spectral searches using Paint Data Query (PDQ) libraries were conducted. The PDQ database itself is compiled and maintained by the Royal Canadian Mounted Police (RCMP) and contains about a 70/30 ratio of street samples to factory panels obtained from participating laboratories primarily located throughout North America. Version 4.05.0 of PDQ was utilized for this case. Approximately 500 new samples are added to the database each year. The current version (4.07.0 released in October, 2010) contains 17,592 samples, comprised of 66,332 paint layers, and 76 spectral libraries. Its purpose is to develop make-model-year lead information in hit-and-run investigations using the chemical composition of the paint layers that comprise an OEM automotive paint system [3]. Traditionally, the primer (surfacer) layer is considered to be the most discriminating layer within an OEM automotive paint because it tends to be specific to individual assembly plants. Therefore, this layer was used to conduct initial spectral searches in this case.

Using both the correlation and first derivative Euclidean search algorithms and requesting the top 200 hits for each, four manufacturers were initially identified as possible candidates for the striking vehicle. This assessment was based on direct spectral comparison of each of these 400 hits versus the primer spectrum collected on the case sample. The four manufacturers were as follows: Audi (one hit); BMW (eight hits comprised of vehicles from two different European assembly plants over the course of five model years); Volkswagen (11 hits all from the same assembly plant in Mexico with a four year range for the model year); and Volvo (seven hits from the same European assembly plant with a four year model year range). Therefore, based on the information available from PDQ for this one layer, the vehicle likely originated from a European manufacturer.

A comparable spectral search was then conducted on the clearcoat layer. Of the top 200 hits using one of the named algorithms, only three manufacturers were identified: Saab (one hit), Volkswagen (three plants, two in Mexico and one in Europe, consisting of four hits in two different model years), and Volvo (29 hits spanning three European plants and a twelve year model year range).

Cross-referencing the spectral searches for the primer and clearcoat layers revealed that only Volvo had specific samples represented on both lists. All of these samples were from vehicles assembled at the Ghent plant in Belgium. The model year (MY) range spanned MY'92-95. The models were two Volvo 740s (both from MY'92), and three Volvo 850s, one each from MY'93, MY'94, and MY'95. The library spectra of the electrocoat for these five samples were also comparable to the case sample.

PDQ was then used to conduct a Layer System Query (LSQ) in which components identified by the FTIR spectral interpretation discussed earlier were entered for each layer. With this search, the user can identify all PDQ library entries for layer systems that contain the same components as what has been entered for the case sample. Therefore, in order to maximize the potential of finding a good chemical fit for each layer, users are encouraged to be conservative in the codes assigned for each paint layer in the system. Conversely, the PDQ Maintenance Team utilizes a very broad approach to codes entered into the database for each layer in order to prevent false exclusions in user searches. In other words, even trace levels of a constituent might be entered into the database for a given layer so that this sample would not be overlooked in a user search.

With this process in mind, no cross-linker code was entered for the primer surfacer layer containing benzoguanamine. This approach yielded 143 hits representing 22 makes and models from 43 assembly plants. Direct spectral comparisons of the primer layer for these hits to the case sample was only conducted on hits not previously compared in the spectral searches. Three makes and assembly plants were considered viable options based on these searches: BMW (Dingolfing, Germany), Land Rover (Solihull, UK), and Volvo (Ghent, Belgium). However, this BMW plant was previously eliminated based on the clearcoat, and Land Rover was eliminated based on discussions with an industry contact there; only the Volvo hit remained viable.

The spectral discrepancies that resulted in the elimination of a majority of the hits in this search were largely attributable to the observable peak differences between melamine at 1550 cm^{-1} and 815 cm^{-1} and the peaks noted in the case sample's primer layer. Yet, the overlay of samples from Volvo's Ghent plant to the case sample was compelling for the primer as well as for the clearcoat and e-coat layers. Therefore, a spectral search of the clearcoat was conducted restricting the hits to only Volvos produced at the Ghent plant. This was achieved by setting criteria that the name had to contain VLV (Volvo), GHE (Ghent), and OT2 (assuming this would be a clearcoat layer in each hit returned with these search parameters). The search generated twenty-six hits. Four of the hits were on plastic substrates, which do not require an e-coat layer since they contain no metal and therefore are not susceptible to corrosion. Therefore, the spectral library only contained twenty-two entries for clearcoat comparison to the case sample data. Based on comparison of the clearcoat spectra to the case sample, the model year range was determined to be MY'88-'98. Beyond this range, the chemical formulations were vastly different from the case sample.

A Fill-in-the-Blank (FITB) search in PDQ was then conducted to search all Volvos produced at the Ghent plant. This search yielded a total of 33 hits, five of which were on plastic substrates and six of which were monocoats (a formulation that does not require a clearcoat). The twenty-two samples with clearcoats were those whose spectra had already been compared.

<u>CONFIRMING THE "BEST FIT" PDQ ENTRIES</u>

The FBI Laboratory maintains a duplicate collection of all PDQ samples submitted to the RCMP from US laboratory participants. These samples are available to paint examiners for direct comparison to casework to confirm hits obtained via spectral library searches or PDQ code searches. If the sample(s) of interest were submitted by a Canadian partner lab, a portion of that sample could be obtained from the PDQ Maintenance Team for these direct comparison assessments. Any PDQ partner laboratory can also request that a portion of PDQ samples of interest be forwarded to them from either the RCMP or FBI as needed to further a MMY examination.

As discussed earlier, each of the five PDQ samples previously identified as viable comparison options to the sample recovered from the motorcycle fender spanned MY'92 through '95. Four of the five were submitted by US laboratories. The Volvo 850 from MY'93 was submitted by a Canadian partner lab. The four samples submitted by US labs were obtained from the FBI's PDQ collection and directly compared to the case sample. The basecoat color of each of these samples differed from the case sample. Therefore, this layer was not compared further. Also, three out of four of the US submissions were distinguishable from the case sample based on microscopic and colorimetric comparison of the primers. The fourth sample (a MY'95 Volvo 850) was visually consistent with the primers used in the case sample. Therefore, FTIR analysis was conducted on the clearcoat and both primer layers to allow direct spectral comparisons to be made (Figures 3 through 5).

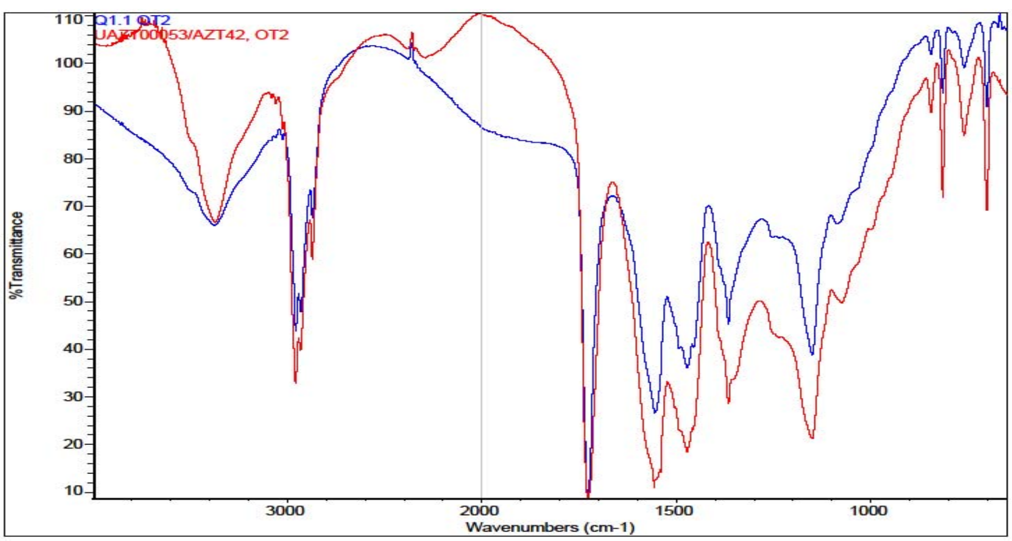

Figure 3. Comparison of the clearcoat layer from the case sample versus a PDQ sample.

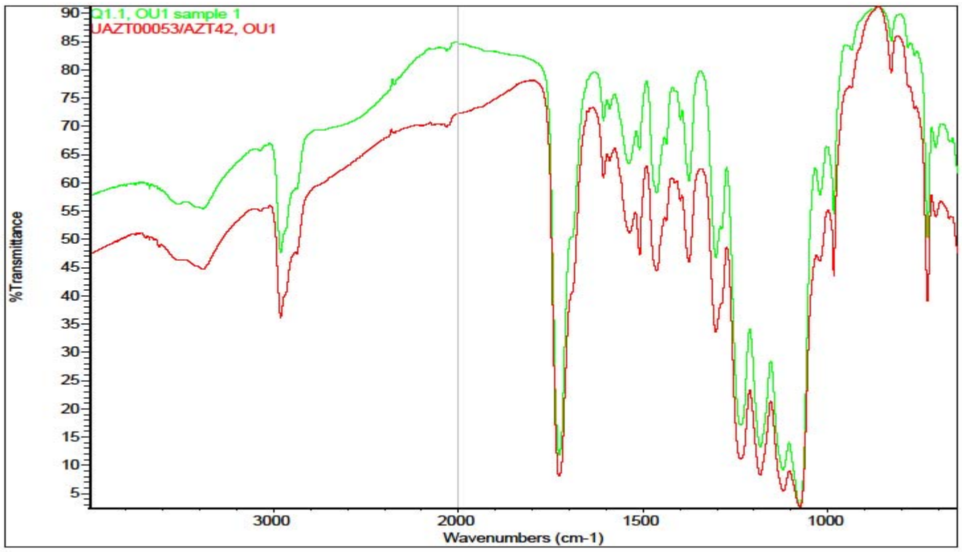

Figure 4. Comparison of the primer surfacer layer from the case sample versus a PDQ sample.

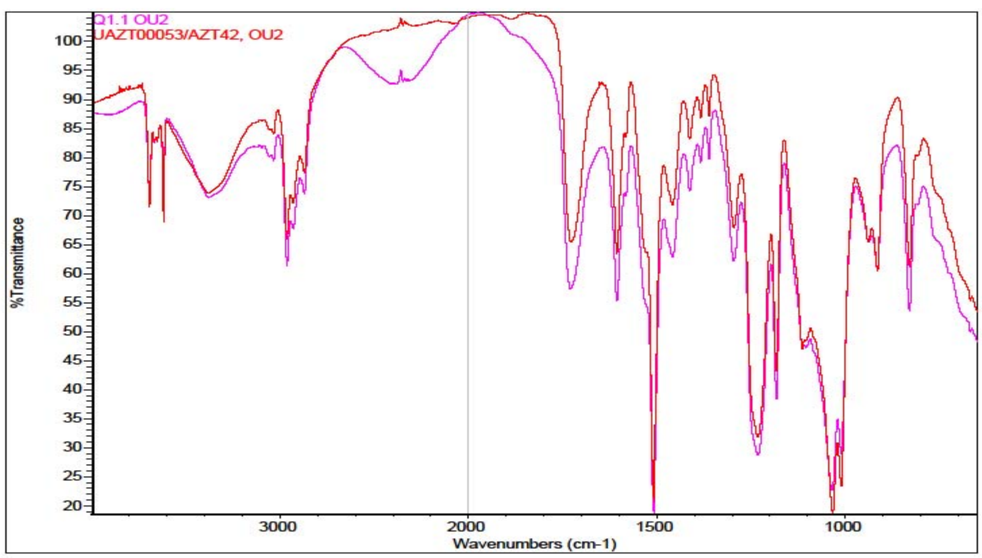

Figure 5. Comparison of the electrocoat layer from the case sample versus a PDQ sample.

SEM/EDS ANALYSES

A portion of the paint chip was embedded in an epoxy medium (Epo-Kwik, Buehler, LTD, Lake Bluff, IL), microtomed using a rotary UCT Ultramicrotome (Leica Microsystems, Bannockburn, IL), and carbon coated by vacuum evaporation. Backscatter electron (BSE) imaging and elemental analysis were conducted using a JSM-6300 scanning electron microscope under high vacuum with a tungsten filament as the source (JEOL, Peabody, MA). For imaging purposes, the Orion software package was used. For elemental analysis, the 4pi Analytical energy dispersive spectrometer (4pi Analysis, Durham, NC) was operated with a dead time of approximately 30% and counting time of 100 s. The working distance was approximately 15 mm, the take-off angle was approximately 30°, and the accelerating voltage was 25 kV. Using SLICE (Spectral Library Identification and Classification Explorer, xK, Inc., Spokane, WA) algorithms, results for each layer were as follows:

- no elements of interest were observed in the clearcoat;
- aluminum, silicon, and titanium were readily apparent in the blue metallic layer with the possibility of chlorine, potassium, and copper also present in this layer;
- sodium, magnesium, aluminum, silicon, sulfur, barium, and titanium were all observed in the primer surfacer layer; and,
- aluminum, silicon, lead, and titanium were present in the e-coat.

According to Poth, the ban on lead usage in automotive topcoats was in effect in most countries at the time his chapter was published in Automotive Paints and Coatings in 1995 [4]. That policy was extended to include lead use in the primer layers as well throughout the latter part of the 90's resulting in its total ban by the beginning of this decade [5]. Therefore, its presence in the e-coat supported an upper limit on the model year range somewhere within the late 90's to early in this decade.

INDUSTRY CONTACTS

Discussions with the three major paint suppliers to the North American automotive industry (BASF, DuPont, and PPG) indicated that the use of benzoguanamine suggested a vehicle assembled in Europe or Asia, not North America. The spectral comparison of additional paint layers to the case sample had already ruled out the Mexico-based Volkswagen plant; this information further supported elimination of that assembly plant. One paint supplier noted that the clearcoat chemistry was indicative of a "typical one component [system], possibly old technology [from] DuPont (in the nineties)." This resource also concluded that the basecoat was a "typical solvent-based basecoat", and that the "presence of lead [in the e-coat] indicates old technology (until the end of the nineties)". Other industry contacts stated that the vehicle was manufactured pre-2003 "at the latest" since conversion to lead-free technology began in 1997 and was completed in late 2002 for most plants. It was further suggested that some residual lead might be present into 2003, but likely at levels below detection by SEM/EDS [5].

REFINISHER PAGES

The FBI Laboratory receives the color standard pages produced each model year by the paint manufacturers for sale to refinisher shops. In an attempt to identify the color code and possibly narrow the model year range, these color pages were searched for colors comparable to the case sample for "blue" entries for Volvo between MY'88-'99. This model year range was chosen to account for the information already known from the previous examinations, such as a basecoat/clearcoat layer structure, metallic effect in the basecoat, and chemistry comparable to what was obtained from the spectral searches. In other words, all monocoats, non-metallic finishes, and samples beyond MY'88-'99 were not viable candidates for the color code. All color candidates of interest were microscopically compared to the case sample basecoat color using two different light sources. Only color code 417, "Dark Blue Metallic" was a viable option. It was used from MY'93 forward, making 1993 the earliest model year under consideration for the origin of the evidentiary paint chip [6].

SETTING A MODEL YEAR RANGE

Ultimately, the model year range was reported out as MY'93-'98 based on the correlation between the color information and the chemical data present in PDQ. This approach was considered appropriate for several reasons. Firstly, Volvo is known to use a limited range of colors for its vehicle models. This information is easily documented through use of the refinisher pages generally available to law enforcement-affiliated forensic laboratories from automotive refinish paint suppliers. It can also be obtained from the internet or visits to a dealer showroom where access to historic color information (or resources of same) would also be likely forthcoming to law enforcement-affiliated personnel.

Secondly, while the hit obtained from the PDQ database (a MY'95 Volvo 850 assembled in Ghent, Belgium) was a good fit for the three layers directly compared to the case sample, it was the only such hit in the database. As compared to North American-based automotive manufacturers, Volvo is not well represented within PDQ. This is understandable given that it is a relatively low volume participant in the domestic marketplace. Moreover, some of the Volvo entries from the Ghent plant within the MY'92-'95 window developed from the initial searches differed physically or chemically from the case sample in at least one of the layers compared. While the number of differing samples does not affect how well the PDQ entry from MY'95 compares to the case sample, it may have been possible to narrow the model year range further if additional samples were present. In the absence of such samples, the lower limit of the model year range was held at MY'93, which was when the color of interest was first introduced. For the upper limit, chemical differences in MY'99 forward provided a basis to conclude that MY'98 was a reasonable cut-off.

INTERNET SEARCHES

As a starting point to determine automotive plant production sites, years of production, and manufacturing volume estimates, a common search engine is a useful tool. However, when attempting to verify or concentrate information into a more specific assessment, Wikipedia has proven useful. Since data entry into this utility is open-ended, the information obtained should be verified through other resources and contain the proper precautions. For this specific case example, Wikipedia listed the 850 as a "mid-90's bestseller for Volvo", stating that it was produced between MY'92-'97. It also listed the S70/V70 model under a different tab within the Volvo summary pages. The production of these models was reportedly begun in MY'98 [7].

When a general search for information on Volvo was conducted on the internet, a press release from Volvo was also found. It provided production figures for vehicles assembled at Ghent. For the 1993-1998 model year range of interest, only the Volvo 850 and S70/V70 remained viable models. The 850 was produced at Ghent from MY'91-'96 and the S70/V70 was produced there from MY'96-'00. These two models totaled just over 1 million vehicles between 1991-2000 [8].

CONSTRUCTING A VIN

Several websites exist for deciphering the first twelve characters used in a seventeen character Vehicle Identification Number (VIN). For this particular case, a Wikipedia link was found specific to VIN numbers [9]. Another website was found and searched for Volvo 850, S70, and V70 models between MY'93 - MY'98 [10].

Summarizing all of the information that was able to be obtained from the various sources already discussed, the following partial VIN was constructed and provided to the investigator:

Position:	1-3	4	5	6-7	8	9	10	11	12-17
Character:	YV1	L	S/W	52/53/55/57	?	?	P/R/S/T/V/W	2	?

where,
YV1 = Europe/Volvo/cars
L = vehicle code; L = 850/S70/V70
S/W = safety equipment, body style, platform code; S = sedan; W = wagon
52/53/55/57 = engine codes
? = emission control equipment
? = check digit
P/R/S/T/V/W; P = MY93; R = MY94; S = MY95; T = MY96; V= MY97; W = MY98
2 = plant ID: 2 = Belgium, Ghent plant (VCG22)
? = individual to a specific vehicle

CONCLUSIONS

From this case, it is clear that melamine cannot be assumed to be the only crosslinker used in all automotive OEM formulations, particularly underlying layers such as primer systems. Also, it has been demonstrated that the information available from the internet is plentiful and can supplement information from other resources to aid in developing investigative lead information. This statement may be particularly true in investigations that develop leads for models that are less commonly available in the marketplace at the time of the incident under investigation. Lastly, the importance of maintaining PDQ as a viable resource for spectral and database searches in make-model-year cases cannot be overemphasized. It is also a repository of physical reference samples that can be readily accessed by participants from partner laboratories with a phone call to either the FBI Lab (for US lab submissions only) or to the RCMP for any sample in the database.

Consistent contribution of appropriately vetted street samples to this database by participating laboratories has dwindled in recent years as economic realities have continued to impact many laboratory systems. By presenting the utility and limitations of PDQ as observed in this case example, it is anticipated that interest in sustaining and growing the capabilities that PDQ has to offer the forensic paint community will encourage less frequent contributors to renew efforts to populate this database for the benefit of all partner laboratory systems.

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