Motorcycle helmets: what about their coating?

Abstract

In traffic accidents involving motorcycles, paint traces can be transferred from the rider's helmet or smeared onto its surface. These traces are usually in the form of chips or smears and are frequently collected for comparison purposes. This research investigates the physical and chemical characteristics of the coatings found on motorcycles helmets. An evaluation of the similarities between helmet and automotive coating systems was also performed.

Twenty-seven helmet coatings from fifteen different brands and twenty-two models were considered. One sample per helmet was collected and observed using optical microscopy. FTIR spectroscopy was then used and seven replicate measurements per layer were carried out to study the variability of each coating system (intravariability). Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were also performed on the infrared spectra of the clearcoats and basecoats of the data set.

The most common systems were composed of two or three layers, consistently involving a clearcoat and basecoat. The coating systems of helmets with composite shells systematically contained a minimum of three layers. FTIR spectroscopy results showed that acrylic urethane and alkyd urethane were the most frequent binders used for clearcoats and basecoats. A high proportion of the coatings were differentiated (more than 95%) based on microscopic examinations. The chemical and physical characteristics of the coatings allowed the differentiation of all but one pair of helmets of the same brand, model and color.

Chemometrics (PCA and HCA) corroborated classification based on visual comparisons of the spectra and allowed the study of the whole data set at once (i.e., all spectra of the same layer). Thus, the intravariability of each helmet and its proximity to the others (intervariability) could be more readily assessed. It was also possible to determine the most discriminative chemical variables based on the study of the PCA loadings. Chemometrics could therefore be used as a complementary decision-making tool when many spectra and replicates have to be taken into account.

Similarities between automotive and helmet coating systems were highlighted, in particular with regard to automotive coating systems on plastic substrates (microscopy and FTIR). However, the primer layer of helmet coatings was shown to differ from the automotive primer. If the paint trace contains this layer, the risk of misclassification (i.e., helmet versus vehicle) is reduced. Nevertheless, a paint examiner should pay close attention to these similarities when analyzing paint traces, especially regarding smears or paint chips presenting an incomplete layer system.

Keywords

Traffic accident investigation
Fourier transformed infrared spectroscopy (FTIR)
Chemometrics
Principal Component Analysis (PCA)
Hierarchical Cluster Analysis (HCA)
Automotive coating systems
Paint evidence
Microtraces

1. Introduction

When involved in traffic accidents, motorcyclists can be very severely injured or killed [1-4], due to the lack of physical protection and to the comparatively small size of their vehicle [5,6].

Because of this, traffic accidents involving motorcycles represent an important part of the cases handled by forensic science laboratories. Many studies have been carried out in the area of traffic accident reconstruction, the majority concerning the dynamic of the accident. A large variety of traces can be collected on the accident scene for identification and/or comparison purposes for example liquids (such as oil and petrol), paint (chips or smears), glass fragments and skid marks [4,7-10]. To help in the reconstruction of the events of a traffic accident, the attribution of the different traces to each item involved is essential. It is thus important to have knowledge about the composition of these different elements that can induce traces during a traffic accident (e.g., automotive paint, tires).

Whenever a motorcyclist is injured, it is crucial to collect his equipment [4], in particular the helmet. Indeed, during the collision, traces might be exchanged between the helmet, the vehicles, road and traffic signs [11]. The role of this protective equipment is crucial, as the head is often subject to severe injuries [12]. In forensic science, the most important helmet parts are usually the external ones (i.e., those in contact with the vehicles and/or the other elements). These include the shell, visor and ventilation system pieces. The shells are often coated, can present various graphics and are constituted of thermoplastic polymers. Three types of polymers are currently used by the manufacturers: polycarbonate (PC), acrylonitrile butadiene styrene (ABS) and composite material such as Kevlar, glass or carbon fiber [5,13,14]. Although composite shells are extremely resistant, ABS shells are still frequently encountered due to their more accessible price and ease of production [13]. Literature concerning the composition and the resistivity of helmet shell is abundant [15-17]. In contrast, very little has been published on the coating systems of helmets. To the knowledge of the authors, only two studies referred to the coating system. These studies mentioned that the coating system of helmets was multi-layers, but, did not give any further details [8,18]. To overcome the lack of information in this field, this work focuses on the analysis of the coating systems applied on helmet shells.

This work focuses on two main aspects: first, twenty-seven helmets were analyzed to allow for the physical and chemical characterization of the helmet coating systems. This part allowed investigating whether helmets of different brands and/or models could be differentiated based on their coating systems. The information provided by this part of the research (e.g. occurrence of a given layer of the coating system) will assist the expert during the evaluation process. Indeed, when a paint trace recovered in a traffic accident is not differentiated from a helmet coating, it is important to assess the evidential value of this correspondence.

Secondly, as traffic accident generally involve automotive vehicles, similarities between helmet and automotive coating systems were investigated to determine whether helmet and automotive coatings could be differentiated. This knowledge is important for the investigation of traffic accident involving for example both vehicle(s) and a motorcyclist.

2. Material and Methods

2.1 Helmets

The sample set consists of twenty-seven helmets from fifteen different brands and twenty-two different models (Tab. 1). Three groups are of the same brand, model and color (Iota FP-03, Aero AR500 and Caberg Justissimo). Five color classes of coatings were observed: white (n=1), blue (n=2), red (n=2), grey (n=7) and black (n=12) containing both effect and solid coats. Concerning the shell compositions, determined by infrared measurements, fifteen helmets were in ABS and five were in polycarbonate (PC). The PC shells also contained the precursor monomer Bisphenol A (BPA). The other helmets (n=7) were comprised of a composite material. According to the Swiss market, it is coherent to find these three different types of shells, as they are the most common materials used in the helmet industry. Moreover, the different proportions are in accordance with the current Swiss trend in which polycarbonate is more and more replaced by ABS and where composite helmets still remain expensive. Finally, it is important to notice that these helmets were still used shortly before the present research in order to be representative of the helmets currently worn on Swiss roads.

INSERT TABLE_1.DOCX HERE

Tab. 1. Characteristics of the helmet sample set.

2.2 Sampling and optical observations

One fragment per helmet was taken with a scalpel in order to obtain the complete coating system including the polymer material of the helmet shell. However, composite shells were too rigid to be sampled by this technique and in these cases only the coating system was collected. If a graphic was present on the helmet, two fragments were taken (with and without the graphic). The fragments were included in a resin (Technovit 2000LC, Heraeus Kulzer) and cut into 5µm thin sections with a Leica Jung Supercut 2065 microtome. The cross sections were then mounted on a glass slide using Gurr's mounting medium (XAM Neutral, BDH Laboratory Supplies, Poole, UK) for microscopic observations.

Cross sections were observed and characterized in transmitted light using a Leica DM6000B microscope with a 20x Fluotar objective. As advised in the literature [19,20], bright field, dark field and crossed polars were used.

2.3 FTIR measurements

The analyses were conducted on a Nicolet 5700 FTIR spectrometer coupled with a Nicolet Continuum FT-IR microscope from Thermo Scientific equipped with a Infinity Reflachromat 32x objective and a mercury cadmium telluride detector (MCT/A). Measurements were performed in transmittance mode, using KBr pellets on which a flattened coating section was deposited, with spectral range: 4000-650 cm^{-1}, resolution: 4 cm^{-1} and 32 co-added scans. An aperture of 29 x 55 µm was used, excepted for the shells, for which an aperture of 45 x 55 µm was chosen. All spectra were obtained with OMNIC 9.2 software from Thermo Scientific. In order to evaluate the intravariability, seven replicate spectra were collected for each layer of the coating systems.

2.4 Identification and visual comparison of FTIR spectra

The chemical composition of each layer was determined using characteristic peaks wavelengths referenced in the literature [21-23] and spectral reference databases provided by the Royal Canadian Mounted Police [24].

Subsequently, a manual classification was done based on the composition of the main binders and extenders. Each category created thus represents a particular chemical class. In a second phase, the spectra within each chemical class were visually compared to see if they could be differentiated, based on major and minor absorption bands, as well as on relative intensity. When differentiations were observed, sub-categories were created. This survey mainly focuses on the external coating (clearcoat and basecoat) as they are more likely to be transferred in a road accident.

2.5 Pre-treatments, variable selection and chemometrics tools

The data set used for statistical treatments is a matrix containing the percentage of absorbance to all wavenumbers considered for each spectrum (one matrix per type of layer). A Standard Normal Variate (SNV) treatment was applied on the data in order to normalize them. Then, a detrending treatment was applied on the whole matrix to smooth the baselines. Finally, a variable selection was performed to consider only the most informative variables. The conserved spectral domain is composed of two zones: 3128 – 2750 cm^{-1} and 1830 – 650 cm^{-1}. These treatments were chosen in order to optimize the results for FTIR analyses, as advised by Muehlethaler *et al.* [25]. A total number of 810 variables (i.e., wavenumbers) were considered

Next, two multivariate analyses were performed on the data: Principal Component Analysis (PCA) and Hierarchical Clusters Analysis (HCA). These statistical methods were used to help determine the intravariability and the intervariability of the sample set. All statistical treatments were executed using the software Unscrambler X version 10.1 from Camo ASA.

PCA is a method used to graphically represent and explore a data set by reducing its dimension. The aim of this exploratory method is to define a new set of uncorrelated variables - called principal components – by calculating linear combinations of the original variables [26]. Principal components are determined in a such manner that they explain the most variation of the initial variables [27]. The aim is to consider the fewest number of principal components – generally two or three – while explaining the most possible variation. With multivariate data represented by an important number of variables (in this study the number of variables is 810), PCA can also be a very powerful tool to highlight which ones have the most significant effect on the outcome. This can be done by considering the coefficients of the linear combinations (i.e. the loadings) of each principal component.

HCA is an unsupervised grouping method that does not consider a priori any group affiliation of a given sample. Therefore, it represents a prime exploratory method for the identification of homogeneous groups of objects presenting similar characteristics in a whole data set [28]. Practically, each object is associated with another one depending on the proximity of their features. The process is repeated until all objects are grouped into one general cluster containing all the data set [27]. The result of a HCA is graphically represented by a dendrogram that allows the visualization of the successive groupings. In this work, HCA was performed using the Ward's method algorithm and Squared Euclidean distances.

3. Results and Discussion

3.1 Physical characteristics

3.1.1 Number of layers

For each helmet coating, the number of layers was counted under the microscope on thin sections. The majority of helmets (n=24) possessed a coating system (Fig. 1). The remaining helmets (n=3) were not coated and presented a raw shell of polycarbonate (PC). Nevertheless, the probability to observe a helmet without coating system is likely to decrease in the near future as acrylonitrile butadiene styrene (ABS) tends to replace PC shells due to its higher resistivity [13]. Beyond their appealing design, coatings also provide protection to thermoplastic polymers against UV degradation [29]. The uncoated helmets were not considered for the remainder of the survey.

INSERT FIGURE_1.JPG HERE

Fig. 1. Number of layers observed for the coating systems of the motorcycle helmet classified according to the composition of the shell (N=27).

It is interesting to notice that no monolayer system was observed. The most common coating systems include two (n=9) or three (n=7) different layers, independently of the basecoat type (effect or solid). These systems are composed of a clearcoat, a basecoat (effect or solid) and – for the three layers systems – of a primer. This observation is consistent with the actual coating technics used on automotive plastic substrates [29]. Some basecoats presented an irregular junction with the shell, resulting presumably from a sanding process for some polycarbonate (PC) and ABS shells. Otherwise the layers were generally regularly applied.

For the three helmets composed of ABS shells and presenting more than three layers, two of them were repainted (replicates of the outer layers) and one presented three inner layers. For the helmets with composite shells, a minimum of three layers was observed: clearcoat, basecoat - effect or solid - and primer.

3.1.2 Layer thicknesses

Optical examination allowed the measurement of the thickness of the paint layers. No differentiation between effect and solid basecoat was observed. Save for helmet n°08, the majority of clearcoats and basecoats each presented a layer thickness comprised between 20 and 40 µm (with extreme values of 14 and 63 µm for clearcoats, and of 18 and 70 µm for basecoats).

Helmet n°08 presented the thickest coating system, with four layers constituting an overall thickness of about 600 µm. Its clearcoat measured around 130 µm, while the thickness of the primer was larger than 250 µm. Such a thick coating system was attributed to the fact that this helmet was coated by a private designer.

It is interesting to note that the primer thickness depended on the shell composition. It was observed that primers used on composite shells were thicker (up to 160 µm) than those applied on ABS shells (about 30 µm). Moreover, within the composite shells, the thickness of the coating systems varied considerably from one helmet to another. Finally, the primers of the composite shells contained talc and were friable during the preparation process.

It is important to point out that the thickness of the layers is influenced by the sample preparation such as flattening process, but also by the friability of the layers and the cutting angle of the inclusions. Layers could thus appear thicker or thinner than reality and this factor should be used carefully for comparison purposes. Moreover, layer thickness cannot be compared when smear traces are encountered. Hence, in the present study, no discrimination was done on the basis of thickness alone.

3.1.3 Discriminating power of microscopic examinations

Using the microscopic characteristics of the entire helmet coating system (color and layer sequence) the majority of the helmets were differentiated, with only six pairs of helmets out of 276 possible pairs being non differentiable (Tab. 2). Within these not differentiated pairs, three came from helmets of the same brand, model and color: Iota FP-03 (helmets n°03-04), Aero AR500 (helmets n°06-07) and Caberg Justissimo (helmets n°10-11). The three remaining pairs were three black helmets that had coating systems composed of only two layers. Using Smalldon and Moffat formula [30], the discriminating power of the optical examination is 0.98. It is also interesting to notice that even if only the two outer layers were considered – representing an incomplete transfer – nine pairs would be non-differentiated, among which five were of the same brand and model. In this case, the discriminating power would be of 0.97.

INSERT TABLE_2. DOCX HERE

Tab. 2. Discriminating power of microscopic examinations calculated for the helmets (N=24). Pairs from helmets of the same brand and model are underlined.

3.2 Chemical composition

3.2.1 Clearcoats

A clearcoat was observed on all helmets which presented a coating system (N=24). These clearcoats were analyzed by infrared spectroscopy and five main chemical classes were identified according to the visual interpretation of the different infrared spectra (Tab. 3). The most common binder type (n=20) was acrylic urethane (ACR-PUR) often used with styrene (STY). Besides, some alkyd urethane (ALK-PUR) and acrylic (ACR) binders were identified, both with styrene. A figure containing representative FTIR spectra of the different chemical classes identified on the clearcoats of the helmet coatings is proposed (Fig. 2). After the visual comparison of the spectra, seven pairs were not differentiated. The discriminating power calculated for clearcoats is thus 0.97.

INSERT TABLE_3.DOCX HERE

Tab. 3. Number of helmets per chemical class of the clearcoats and number of non-differentiated pairs. Pairs of clearcoats from helmets of the same brand and model are underlined.

INSERT FIGURE_2.DOCX HERE

Fig. 2. Representative FTIR spectra of the different chemical classes identified on the clearcoats of the helmet coating systems.

Multivariate analyses

Both PCA and HCA performed on the data from clearcoats (168 spectra) presented similar results to the classification proposed by the authors (after visual comparisons and identifications of the different spectra). For PCA, the plotted scores of the first two principal components showed that the seven replicates per clearcoat were very close to each other (Fig. 3). This observation supports that the repeatability of the measurements for each helmet was good. It also means that this layer (within the fragment of the helmet) is homogenous. The replicates of each clearcoat thus constituted groups, which were generally well separated (Fig. 3). The clearcoats that were differentiated from one another by visual classification were also well separated by PCA, while the non-differentiated pairs of samples presented very close or even superimposed groups. Finally, the PCA results indicate that the variability between the helmets (i.e., intervariability) was generally greater than the variability within each helmet (i.e., intravariability). Study of the loadings of the first principal components revealed that styrene was one of the most influential variables for the model.

INSERT FIGURE_3.JPG HERE

Fig. 3. Scores of the first and second principal components of the PCA realized on the FTIR spectra of clearcoats (N=24; 168 spectra).

For HCA, when twenty-four clusters were considered, each of them only contained the seven replicates of one particular helmet. This result highlights the possibility to differentiate all the clearcoats of the sample set. However, the helmets superimposed or close from each other on the plotted scores of the PCA (i.e., helmets with very similar chemical composition) had their cluster grouped together at a subsequent level. This is why the complete discrimination of the sample set proposed by the HCA has to be considered cautiously. In light of the PCA results, it is thus reasonable to put aside the new differentiation proposed by HCA.

3.2.2 Basecoats

All clear-coated helmets presented a basecoat (N=24). For these twenty-four basecoats, eight main chemical classes were identified according to their binder type (Tab. 4) based on the visual comparisons of spectra. The most frequent composition encountered was urethane (n=21). Of these twenty-one urethane basecoats, thirteen were acrylic urethane (ACR-PUR, n=13) and eight alkyd urethane (ALK-PUR, n=8).These binders were sometimes encountered with styrene (n=9) or talc (n=7) as extender pigment. Other chemical classes identified were alkyd orthophthalic (ALK OPH, n=1) and acrylic (ACR, n=2). Unmodified acrylics were encountered with styrene (n=1) or talc and titanium dioxide (n=1). A figure with representative FTIR spectra of the different chemical classes identified on the basecoats of the helmet coatings is given in Figure 4.

INSERT TABLE_4.DOCX HERE

Tab. 4. Number of helmets according to the chemical class of the basecoats and the number of non-differentiated pairs. Pairs of basecoats from helmets of the same brand and model are underlined.

Visual comparisons of infrared spectra of basecoats from the same chemical classes were performed only for layers presenting similar physical features (i.e., color and effect or solid type). The aim was to investigate possible differences within each of these groups. Then, by considering the color and type of basecoat in addition to the visual comparisons of their infrared spectra, five pairs out of 276 were not differentiated (Tab. 4). It should be emphasized that these pairs were different from the ones observed on clearcoats, with the exception of the pair constituted by helmets n°03-04 (Iota FP-03), which remained not differentiated. The combined discriminating power based on physical features and FTIR spectra for the basecoats is 0.98.

INSERT FIGURE_4.DOCX HERE

Fig. 4. Representative FTIR spectra of the different chemical classes identified on the clearcoats of the helmet coating systems.

Multivariate analyses

It is important to point out that, for multivariate data analyses, basecoats were separated according to their color (i.e., they were put into different matrixes). The color groups that contained only two samples (blue, red and white) were not considered for statistical treatments. PCA were thus performed separately on black (n=12) and grey (n=7) basecoats.

Black basecoats

The number of black helmets sharing the same physical features (i.e., effect or solid type) was relatively low. Thus, the authors decided to consider the effect and solid black basecoat together.

The scores of the first two principal components of the PCA performed on black basecoats (n=12; 84 spectra) can be viewed on Figure 5. On this figure, four main groups were determined. These were formed by basecoats belonging to the same chemical class (i.e., main binders and extenders). These are the same classes previously identified on spectra (Tab. 4). The four helmets with an effect basecoat were grouped together (group III).

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Fig. 5. Scores of the first and second principal components of the PCA obtained from the FTIR spectra of black basecoats (n=12; 84 spectra). Items are grouped into four main chemical classes: ALK-PUR (I), ACR-PUR + STY (II), ACR-PUR + Talc (III) and ALK OPH (IV).

As for clearcoats, the seven replicates per helmet were well grouped together, even if some basecoats presented a higher dispersion of measurements (i.e., higher intravariability). Indeed, some basecoats were more difficult to analyze due to their small size which could influence the repeatability of the measurements and thus increase the intravariability. Study of the loadings indicated that all characteristic peaks of the talc were the most influential variables for the first principal component.

When the first three principal components were used, a complete separation of the twelve black basecoats was obtained, with the exception of two basecoats of the ACR-PUR + STY chemical class (group II). The replicates performed on helmets n°12 and n°18 remained overlaid, but the basecoat of the helmet n°07 was differentiated from this pair. Compared to the classification based on visual spectra comparisons, this resulted in a new discrimination.

For HCA, when considering twelve clusters, each only contained the seven replicates made on the same helmet (Fig. 6). This result supports that replicates of each item are more similar to each other than to all other spectra of the sample set. The HCA results also supports that it is possible to differentiate all the black basecoats of the sample set. The investigation of the dendrogram showed that this one was constructed given the main chemical classes. Indeed, the first separation proposed by HCA occurred between basecoats composed of ACR-PUR + Talc (Fig. 6 – group III) and the three others chemical classes (Fig. 6 – group I, II and IV). The first principal component of the PCA also gave the same repartition (Fig. 5). The next separation observed on the dendrogram differentiated ALK-PUR (group I), ACR-PUR + STY (group II) and ALK OPH basecoats (group IV), as also suggested by the second principal component of the PCA.

INSERT FIGURE_6.JPG HERE

Fig. 6. Dendrogram of the HCA performed on the black basecoats (n=12; 84 spectra). All replicates of a given helmet are grouped together in the same cluster.

Despite the differentiations proposed by the chemometrics tools for helmets n°7, 12 and 18, more analyses should be performed before considering this information, as the spectra of these helmets are visually very close (Fig. 7). Moreover, only one sample per helmet was analyzed in this study. To take into account this new differentiation proposed by chemometrics, more analyses on several samples per helmet should be conducted in order to fully study the variability of each helmet.

INSERT FIGURE_7.JPG HERE

Fig. 7. FTIR spectra of the black solid basecoats from helmets n°07 (top), n°12 (center) and n°18 (down). Spectra are judged non-differentiable.

Grey basecoats

All the grey helmets were effect basecoats. As for the black helmets, the scores of the first two principal components allowed to group the basecoats (n=7; 49 spectra) according to the chemical classes previously identified on spectra (Tab. 4.). Thus, four main groups were constituted based on the main binders, modifiers and extenders of each basecoat (Fig. 8).

INSERT FIGURE_8.JPG HERE

Fig. 8 Scores of the first and second principal components of the PCA performed on the FTIR spectra of grey basecoats (n=7; 49 spectra). Items are separated into four main chemical classes: ACR-PUR + STY (A), ALK-PUR (B), ALK PUR + Talc (C) and ACR-PUR + Talc (D).

The replicates of each helmet were well grouped together, with the exception of the helmet n°04, which was more spread out. This can be explain by the fact that helmet n°04 presented a high density of effect particles leading to noisy spectra (due to the low signal-to-noise ratio). These spectra were thus less repeatable and increased the intravariability for helmet n°04. Considering the loadings, it was determined that all the characteristic peaks of styrene and of talc were important variables for the first principal component.

Despite the use of the first four principal components, it was not possible to differentiate the pair composed by helmets n°03 and n°04. Helmets n°10 and n°11 were also superimposed and could thus not be separated.

HCA first allowed the separation of helmets with ACR-PUR + STY basecoats (Fig. 9 – group A) from helmets of the other chemical classes (Fig. 9 – group B, C and D). This led to the same grouping proposed by the first principal component of the PCA (Fig. 8). The group B (ALK-PUR) was then separated from groups C and D. These were finally divided at the subsequent level. The second principal component of the PCA also conducted to this separation. In the end, when seven clusters were considered, each of them was composed by replicates of one particular helmet. This supports that the replicates of each helmet are more similar to each other than to all other spectra of the sample set. The observation also supposes that all the grey basecoats could be differentiated. However, helmets n°03 and n°04, which presented very similar infrared spectra (see section 3.3) had their cluster grouped together, as it was the case for helmets n°10 and n°11 (Fig. 10). The chemical compositions of these helmets are very similar, and were superimposed on the PCA results. It is thus reasonable not to consider the new differentiation proposed by HCA.

INSERT FIGURE_9.JPG HERE

Fig. 9. Dendrogram of the HCA performed on the grey basecoats (n=7). All the replicates of one particular helmet are grouped together in the same cluster.

INSERT FIGURE_10.JPG HERE

Fig. 10. FTIR spectra of the grey effect basecoats from helmets n°10 (top) and n°11 (down). Spectra are judged non-differentiable.

Hence, considering the chemometrics tools applied on the basecoats of the sample set (N=24), only five pairs out of 276 remained not differentiated. This represents a discriminating power of 0.98.

3.3 General discriminating power

The microscopic examinations and FTIR analyses of all layers, allowed the differentiation of all but one pair of helmets of the same brand, model and color. This concerns helmets n°03 and n°04 from the French manufacturer Iota®, whose coating systems presented three layers – a clearcoat, an effect basecoat and a primer – applied on an ABS plastic shell (Fig. 11 and Fig. 12). Thus, on the sample tested (N=24), the general discriminating power of the sequence of examination is 0.99 (microscopy and FTIR). It is important to highlight that this result was also obtained even when only considering the clearcoat and the basecoat of the helmets.

It is also of interest to note that coatings from the other helmets of the same brand, model and color – for example helmets n°06-07 and n°10-11 – could be differentiated based on the chemical composition of their basecoat and/or clearcoat. However, no information about the date of manufacture and the production plant were available. Therefore, no hypothesis about the discrimination of these pairs can be formulated

INSERT FIGURE_11.JPG HERE

Fig. 11. Coating systems of helmet n°03 (left) and n°04 (right) of the same brand, model and color namely two grey Iota® FP-03. The layers sequence is thin clearcoat (a), effect basecoat (b) and primer (c) applied on ABS plastic shell (d).

INSERT FIGURE_12.JPG HERE

Fig. 12. FTIR spectra of the helmet n°03 and n°04 of the same brand model and color. Spectra of the clearcoat (top), basecoat (center) and primer (down) were judged non-differentiable.

3.4 Similarities between helmet and automotive coating systems

Automotive vehicles are frequently involved in traffic accidents and, it is common to recover paint chips or smears coming from that type of vehicles in forensic investigations. We therefore decided to investigate how similar helmet and automotive coating systems were, and if they could be differentiated. Indeed, when no potential source is available, it is crucial to properly attribute a paint trace (i.e., chips or smears) to the potential type of source. Obviously, beside the physical and chemical characteristics of the traces, the circumstances of the case (e.g., if a motorcyclist is involved or not), the localization of the trace and the propositions given by the different parties involved (i.e., the accusation and the defense allegations, as used in the Bayesian framework) have to be considered. This type of information is crucial for the interpretation of a questioned paint trace. Indeed, if a transparent trace identified as a clearcoat is found in the middle of a car hood, because of its localization, the possible source is more likely a helmet than a vehicle, provided that the case implies a motorcyclist. However, if the trace is found near the bumper, it is important to determine the motorcyclist position as the trace could come from a helmet, another vehicle, or any other coated objects.

3.4.1 Optical similarities

The microscopic observations showed that the majority of the helmet coating systems presented two or three regular, homogeneous and properly applied layers. In the automotive industry, vehicles are typically coated with three or four layers on metallic substrates [31]. Depending on the process used and the category of the vehicle, the number of layers can increase. If we compare automotive plastic substrates and helmet coating systems, they might share similar characteristics. Indeed, automotive plastic substrates are commonly coated with a three – sometimes two – layers system, with a sequence of clearcoat, basecoat and primer [29,31]. This type of substrate is currently used for some automotive body parts, notably bumpers, spoilers, and fenders. Automotive and helmet coating systems also present similar layer thicknesses, except for the primers of composite shell helmets which are much thicker [32]. However, as already noted, thickness information is not always exploitable. Hence, it might be difficult to infer – based on microscopy only – the type of source (i.e., automotive vehicles or helmets) from which the multilayer paint chip or smear originated.

3.4.2 Chemical characteristics

Based on chemical composition (FTIR), searches were performed using the European Collection of Automotive Paints (EUCAP) spectral references databases provided by the European Network of Forensic Science Institute (ENFSI). Requests were focused on clearcoats and basecoats independently of the type of support (i.e., plastic or metallic substrates). Based on infrared spectra, several helmet clearcoats proved to be very similar to automotive clearcoats applied on plastic or metallic substrates. The clearcoats showing the highest similarity between helmets and vehicles were acrylic urethane binders with styrene. Misclassification could occur with many European car brands – including Volkswagen, BMW, Peugeot and Opel – but also with Asian ones, like Honda or Kia. Helmet n°20 – composed of an alkyd urethane and styrene clearcoat – also presented similarities to Renault manufactured vehicles. No other similarity was observed with remnant clearcoats.

For basecoats, the risk of misclassification (i.e., helmet versus vehicle) was lower than for clearcoats. Helmet basecoats contained generally much more talc than automotive ones. However, significant similarities were observed on black solid basecoats presenting a urethane (both alkyd and acrylic urethane) binder and a styrene modifier. Several brands were concerned, including Volkswagen, BMW, Mercedes, Ford and Nissan.

According to these observations, new searches combining the results for the clearcoat and the basecoat of the same helmet were conducted. Results indicated that the risk of misclassification decreased when considering the two layers. However, the coating systems of three helmets still presented similar chemical composition to some automotive brands. These samples were all black helmets presenting solid acrylic urethane with styrene basecoats (helmets n°07, n°12 and n°18). The automotive brands concerned were respectively Volkswagen, BMW and Kia. As helmet n°07 had no primer, it was not possible to proceed to additional comparisons. Contrariwise, helmets n°12 and n°18 presented a primer (i.e., the first layer applied on the shell) and when this one was considered, no more candidates from the databases were found.

All the primers of the helmets of this study were compared to the automotive primers of the data bases. These searches clearly showed that the chemical compositions of the helmet primers were different from those observed on automotive coating systems. However, one must take into account the fact that databases are not necessarily representative of the current vehicles in circulation. Besides, it is also important to specify that these databases are not exhaustive, especially for plastic substrates.

The presence of an electro dip primer and/or a phosphating layer [32] is additional information that can help to determine the source of a paint trace. Indeed, this coating procedure is only applied on metallic surfaces and is thus not encountered on helmets.

3.4.3 Plastic shells

Plastic shells were also compared with polymers used in the automobile industry. As mentioned previously, plastic shells were either polycarbonate (PC) or ABS. These thermoplastic polymers are also encountered on some automotive body parts, but are not the most common. Indeed, the majority of recent vehicles possesses polypropylene (PP) or polyethylene (PE) plastic substrates [29,33]. However, with PC or ABS, no differences were observed between FTIR spectra from helmet plastic shells and automotive plastic substrates.

3.4.4 Stickers inside the coating systems

It is important to note that this research focused on fragments without graphics. However, the latter might be very useful to differentiate traces originating from helmets and traces originating from automotive vehicles. Indeed, it has been observed that the stickers/decals used for helmet decoration are included in the coating system, between the basecoat and the clearcoat (Fig. 13). Stickers are rarely encountered on automotive vehicles and if they are – to the knowledge of the authors – they are pasted over the clearcoat. Besides, when someone wishes to custom his/her vehicle, stickers are generally placed over the coating system.

INSERT FIGURE_13.JPG HERE

Fig. 13. Cross-section of the coating system of helmet n°25 containing a blue sticker between the basecoat and the clearcoat (designated by the thin red arrow). The end of the sticker is clearly visible on the left of the picture.

4. Conclusion

This research brings new knowledge about the coating systems of helmets, which will be useful for the investigation of traffic accident involving motorcyclists.

The majority of the helmets considered in this research presented multi-layer coating systems that were generally constituted of two or three layers. A clearcoat and a basecoat were always observed. In accordance with the current market, a majority of ABS helmet shells were encountered. Coatings systems of composite shells always showed a minimum of three layers. Microscopic comparisons of the coating systems were sufficient to discriminate most of the studied helmets. FTIR spectroscopy results showed that acrylic urethane and alkyd urethane are the most common type of binder used for clearcoats and basecoats. Unmodified acrylics were also observed but were less common. Binders are frequently encountered with styrene or – for basecoats – with talc. The use of microscopy and FTIR allowed the differentiation of all but one pair: these two helmets were of the same brand, model and color (i.e., two effect grey Iota FP-03).

The chemometric tools applied corroborated the visual comparisons and classification of the spectra, but were more efficient as it allowed the study of the whole data set (i.e., all spectra of a same layer) at once. Chemometrics could therefore be used as a complementary decision-making tool when the practitioner has to deal with many spectra and replicates. It is however important to remain vigilant as non-relevant information (e.g., with noisy spectra) might lead to a separation that cannot be chemically explained.

PCA offered a straightforward visual display of the intra- and intervariability of the whole data set. The intravariability was found to be smaller than the intervariability for each considered layer. For the basecoats, the first two principal components allowed to group the samples given their chemical compositions (i.e., main binders, modifiers and extenders). The study of the loadings of the PCA is also useful to determine the discriminative variables.

HCA is a non-supervised method that helps investigate the proximity of each object of the whole data set without any a priori. The obtained results showed that the replicates of each helmet were firstly aggregated together and then grouped with the replicates of other helmets. It supports that spectra from the same helmet are more similar to each other than to the spectra of all the other helmets of the entire sample set. As for PCA, the study of the dendrogram of the basecoats clearly showed that its structure represented the chemical classes of the data.

Similarities between automotive and helmet coating systems were highlighted, especially with automotive coating systems on plastic substrates. These similarities are based both on microscopic observations and chemical composition. Therefore, paint examiners should pay close attention to this point while examining paint traces when motorcyclists are involved in the accident. This is especially true for smear traces or paint chips presenting an incomplete layer system. However, none of the helmets presented a primer layer similar to the primers of the vehicles present in the database. Thus, when a primer layer is present, it is easier to identify the source of the trace. Indeed, the presence of an electro dip primer or a phosphating layer remains characteristic of coating systems present on metallic substrates, such as vehicles. Finally, the observation of a sticker inside the coating system of a paint trace is an interesting element, as it seems more frequently encountered in helmet coating systems than in automotive ones.

More research should be carried out especially on composite shells, as they may become more common on the market. The plastic substrates of helmets, such as the ventilation system and visor should also be investigated, as they can be a source and/or support of traces during a traffic accident.

5. References

[1] Office Fédéral de la Statistique, Accidents de la Circulation Routière. http://www.bfs.admin.ch/bfs/portal/fr/index/themen/11/06/blank/01/aktuel.html (last time consulted 22.05.2013), 2013.

[2] J.L. Forman, F.J. Lopez-Valdes, K. Pollack, R. Heredero-Ordoyo, A. Molinero, A. Mansilla, B. Fildes, M. Segui-Gomez, Injuries among powered two-wheeler users in eight European countries: A descriptive analysis of hospital discharge data. Accident Analysis & Prevention 49 (2011) 229-236.

[3] M. Peden, R. Scurfield, D. Sleet, D. Mohan, A.A. Hyder, E. Jarawan, C.D. Mathers, World report on road traffic injury prevention, World Health Organization Geneva, 2004.

[4] D.J. Van Kirk, Vehicular Accident Investigation and Reconstruction, CRC Press LLC, Boca Raton, USA, 2001.

[5] F. Fernandes, R. De Sousa, Motorcycle helmets-A state of the art review. Accident Analysis & Prevention 56 (2013) 1-21.

[6] T.C. Lee, J.W. Polak, M.G.H. Bell, M.R. Wigan, The kinematic features of motorcycles in congested urban networks. Accident Analysis and Prevention 49 (2012) 203-211.

[7] L.B. Fricke, Traffic Accident Reconstruction (The Traffic Accident Investigation Manual, Vol. 2), Northwestern University Center for Public, Evanston, Illinois, 1990.

[8] S. Hafsi, L'exploitation des traces dans les accidents de la circulation, Ph.D. Thesis, School of Criminal Justice, University of Lausanne, Switzerland, 2011.

[9] R.W. Rivers, Traffic Accident Investigation - A Training and Reference Manual, Institute of Police Technology and Management, University of North Florida, Jacksonville, 1988.

[10] L. Gueissaz, G. Massonnet, Tire traces – Discrimination and classification of pyrolysis-GC/MS profiles. Forensic Science International 230 (1–3) (2013) 46-57.

[11] F. Berg, P. Rücker, J. König, Motorcycle crash tests—an overview. International Journal of Crashworthiness 10 (4) (2005) 327-339.

[12] C. Peek-Asa, J.F. Kraus, Injuries sustained by motorcycle riders in the approaching turn crash configuration. Accident Analysis & Prevention 28 (5) (1996) 561-569.

[13] F.M. Shuaeib, A.M.S. Hamouda, M.M. Hamdan, R.S. Radin Umar, M.S.J. Hashmi, Motorcycle helmet: Part III. Manufacturing issues. Journal of Materials Processing Technology 123 (3) (2002) 432-439.

[14] V. Tinard, C. Deck, R. Willinger, Modelling and validation of motorcyclist helmet with composite shell. International Journal of Crashworthiness 17 (2) (2012) 209-215.

[15] P.K. Pinnoji, P. Mahajan, N. Bourdet, C. Deck, R. Willinger, Impact dynamics of metal foam shells for motorcycle helmets: Experiments & numerical modeling. International Journal of Impact Engineering 37 (3) (2010) 274-284.

[16] G.D. Caserta, L. Iannucci, U. Galvanetto, Shock absorption performance of a motorbike helmet with honeycomb reinforced liner. Composite Structures 93 (11) (2011) 2748-2759.

[17] L. Di Landro, G. Sala, D. Olivieri, Deformation mechanisms and energy absorption of polystyrene foams for protective helmets. Polymer testing 21 (2) (2002) 217-228.

[18] N.J. Mills, S. Wilkes, S. Derler, A. Flisch, FEA of oblique impact tests on a motorcycle helmet. International Journal of Impact Engineering 36 (7) (2009) 913-925.

[19] W. Stoecklein, The role of colour and microscopic techniques for the characterisation of paint fragments, in: B. Caddy (Ed.), Forensic Examination of Glass and Paint – Analysis and Interpretation, Taylor & Francis, London and New York, 2001.

[20] B. Wheeler, L.J. Wilson, Practical Forensic Microscopy: A Laboratory Manual, John Wiley & Sons, Chichester, 2008.

[21] D.R. Brezinski, An Infrared Spectroscopy Atlas for the Coatings Industry, 4th ed., Federation of Societies for Coatings Technology, Blue Bell, Pennsylvania, 1991.

[22] A. Beveridge, T. Fung, D. MacDougall, Use of Infrared Spectroscopy for the Characterisation of Paint Fragments, Forensic Examination of Glass and Paint, Taylor & Francis, London and New York, 2001, pp. 183-241.

[23] D.O. Hummel, Polymers, Additives, Surfactants and their Mixtures: Computer-based Search with Special FTIR Libraries. Macromolecular Symposia 119 (1) (1997) 65-77.

[24] P. Rodgers, R. Cameron, N. Cartwright, W. Clark, J. Deak, E. Norman, The Classification of Automobile Paint by Diamond Window Infrared Spectrophotometry Part I: Binders and Pigments. Canadian Society of Forensic Science Journal 9 (1) (1976) 1-14.
[25] C. Muehlethaler, G. Massonnet, P. Esseiva, The application of chemometrics on Infrared and Raman spectra as a tool for the forensic analysis of paints. Forensic Science International 209 (1-3) (2011) 173-182.
[26] B. Everitt, T. Hothorn, An introduction to applied multivariate analysis with R, Springer, New York, 2011.
[27] R. Wehrens, Chemometrics with R: Multivariate Data Analysis in the Natural Sciences and Life Sciences, Springer, Berlin Heidelberg, 2011.
[28] O. Guéniat, P. Esseiva, Le Profilage de l'Héroïne et de la Cocaïne - Une Méthodologie Moderne de Lutte contre le Trafic Illicite, Presses Polytechniques et Universitaires Romandes, Lausanne, 2005.
[29] H.-J. Streitberger, K.-F. Dossel, Coatings for Plastic Parts, Automotive Paints and Coatings, Wiley-VCH, Weinheim, Germany, 2008, pp. 305-339.
[30] K. Smalldon, A. Moffat, The calculation of discriminating power for a series of correlated attributes. Journal of the Forensic Science Society 13 (4) (1973) 291-295.
[31] S.G. Ryland, E.M. Suzuki, Analysis of Paint Evidence, in: L. Kobilinsky (Ed.), Forensic Chemistry Handbook, John Wiley & Sons, Ltd, Hoboken, New Jersey, 2012, pp. 131 - 224.
[32] J. Bentley, Composition, manufacture and use of paint, in: B. Caddy (Ed.), Forensic Examination of Glass and Paint, Analysis and Interpretation., Taylor & Francis, London and New York, 2001.
[33] J. Maxwell, Plastics in the automotive industry, Woodhead Publishing, 1994.