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A critical evaluation of spectral library searching for the application of automotive paint database

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Abstract

Hit-and-run cases can be investigated by comparing paint traces collected from traffic scene with standard paints stored in a database. IR spectra of automobiles have been amassed in a database for searching purposes. Based on weather conditions and paints in different varying regions, this IR spectra database should be evaluated for its forensic application.

Original automotive paints were herein provided by four domestic automotive companies in Taiwan. Paint panels were naturally exposed in Taipei (north of Taiwan) and Pingtung (south of Taiwan) via JIS K-5400 9.9 standard method of natural weathering. All samples were pretreated with a series of steps including embedding, microtoming and pelleting prior to micro-fourier transform infrared spectroscopy (Micro/FTIR) analysis. Three library search programs, First Derivative Euclidean Distance, First Derivative Least Squares and Peak Table Search algorithms, were evaluated and selected by comparing their discriminating capabilities for paint analysis. IR spectroscopy and pyrolysis gas chromatography/mass spectrometry (Pyrolysis-GC/MS) were employed to identify clearcoats and basecoats.

Peak Table Search algorithm is adopted as the most appropriate approach to calculate hit quality index (HQI) and to analyze weathered paints. Compared with non-weathered paint, the HQIs of most paints containing basecoats and clearcoats, which are comprised of acrylic-melamine binders that were exposed in both Taipei and Pingtung, exceed 95 after following 36-month weathering. However, #518 paint exposed in Taipei presents an unexpected phenomenon. That is, its HQIs decrease to 75 for clearcoat (acrylic-melamine binder) and 63 for basecoat (polyester and epoxy-melamine binder). Changes in basecoat HQIs are proportional to those of the coated clearcoats. Two paints that were coated with only one topcoat layer (alkyd resin and/or blended with polyurethane) (i.e. no clearcoat) for binder composition have HQIs that significantly decrease with an increase in weathering time exposure. The observed trends in the analyses of panels that were exposed in Taipei and Pingtung are similar. In this study, changes in HQI and IR spectrum along with weathering time are discussed with regards to the application of the automotive paint database.

Keywords: Forensic Paint, Library Search Algorithm, Micro-FTIR Analysis, Naturally Weathering

Introduction

Forensic examination of automotive paints often involves either (a) comparing a paint chip or smear (evidential sample) left on the scene against a paint sample from a suspected hit-and-run vehicle (known sample); or (b) identifying potential sources of an evidential sample based on a reference collection or database.

FTIR spectroscopy is now widely used in the forensic science community for examining automotive paints. Combination of microtoming and embedding techniques greatly facilitates the use of IR spectroscopy in the microanalysis of multilayer paint samples [1-4] as well as the acquisition of IR spectra. IR spectra databases of

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automotive paints and the searching routines have also been available and utilized by the forensic science community for nearly a decade [5-8]. Typically, a search is performed to compare the spectrum of an evidential sample against all reference spectra within the database. As a result, a list of best matches is provided for further examination. Search algorithm and spectrum quality are two significant factors determining the effectiveness of this application. For example, due to aging and a difference in related processes, IR spectra from a specific automotive paint may not be identical, thus affecting the match quality [9-11]. For those reasons, the creation and use of a local database may effectively improve this application.

Three search algorithms, First Derivative Euclidean Distance, First Derivative Least Square and Peak Table Search, and parameters are herein applied to search IR spectra library that was created from domestic automotive paint samples that were subjected to varying weathering parameters in two locations with substantially different climate conditions. The weathering set was illustrated in our early study [12]. IR spectra variations caused by weathering effect and thus the resulting match quality are examined. Parameters essential to the selection and usage of search algorithms are also discussed.

Experimental

Paints, weathering methods and sample preparation

Twelve basecoats along with seven sorts of clearcoats that were applied as the original finish were obtained from four domestic automobile companies in Taiwan. Based on the manufacturer's instructions, the topcoat paints were applied to steel panels, which were pre-coated with an electrocoat and primer. Paint panels were exposed in Taipei (north of Taiwan, 23℃ of latitude) with 18℃ weathering angle and Pingtung (south of Taiwan, 22℃ of latitude) with 17℃ weathering angle by JIS K-5400 9.9 standard method of natural weathering for three years. Paint chips that were sampled as panels were weathered for 0, 3, 6,12,18, 24, 30, and 36 months, respectively. Paint chips were mounted with an embedding material (Spurr's kit, Electron Microscope Science Co. Ltd, Pennsylvania, USA). The embedded samples were sectioned in 5 μ m thick slice by a microtome technique. The sectioned layers were then pelleted with KBr crystal just as the sandwich structure.

Determinations of Micro-FTIR and Pyrolysis-GC/MS

The optimal condition parameters obtained based on the evaluation of spectral quality in the Micro-FTIR (Jasco Micro/FTIR 200) were, scan mode: transmission, IR aperture: 30×30 μm, accumulation: 100 scans, and resolution: 4 cm^{-1}. The baseline within the 4000-2000 cm^{-1} range often drifted seriously and resulted in a larger deviation of matched degree. Thus, the wavenumber range of 650-2000cm^{-1} was selected for the database search. Binder composition identification for each paint layer was conducted by IR spectrum analysis via a Pyrolysis-GC/MS system. Pyrolysis was performed on a Model JHP-3S Curie-point pyrolyzer (Japan Analytical Industry Co. Ltd., Japan). A Hewlett-Packard (Palo Alto, CA) HP 5890 Gas chromatograph interfaced to a HP 5971 mass selective detector (MSD) was adopted to analyze pyrolysis products.

Selection of library search algorithms, HQI analysis and spectrum comparisons

Based on the comparison of discriminating capability, three library search algorithms, First Derivative Euclidean Distance, First Derivative Least Square and Peak Table Search, were evaluated prior to determining the weathered paints. Seven clearcoats that contained similar acrylic-melamine binders but varying monomers were compared with three additional sets of clearcoats to evaluate the Hit Quality Index (HQI), which presented the matched degree. Five paint chips were sampled from each weathered panel for IR determination. To calculate HQI, a non-weathered spectrum for each used paint was selected as the searched target. Five chips from each sample were then used to obtain the mean of HQIs. Changes in all HQIs were monitored from 0 to 36 months of weathering. IR spectra variations that produced a decrease in HQI following various weathering time were investigated.

Results and discussion

Identification of basecoat and clearcoat

All topcoat samples contained basecoat and clearcoat systems, except two, which had no clearcoats. Ten automobile clearcoats and twelve basecoats were identified by the transmission spectrum for paint composition analysis. The empirical results are shown in Table

1. All clearcoats are primarily formulated on thermosetting acrylics that are crosslinked with a melamine resin and modified by styrene. However, basecoats are more complex than clearcoats in their binder compositions. Acrylic-melamine binders were used for basecoats in most paints. However, different resins including polyester, epoxy, and acrylic, were used in various combinations to crosslink with melamine or urethane for basecoats. Alkyd-melamine binders were used in two Toyota topcoats, which were solid colours.

Table 1 Description of automotive paint system

Manufacturer	Topcoat/ thickness	Clearcoat code	Basecoat code/color	Composition of binder
Toyota	(no clearcoat)			
	Topcoat/60 μm		045/white	Alkyd-melamine; Titanium dioxide
Toyota	(no clearcoat)			
	Topcoat/60 μm		9E9/yellow	Alkyd-melamine; Polyurethane
Toyota	Clearcoat/30 μm	TC-71		Acrylic-melamine
	Basecoat/50 μm		6N7/ green	Acrylic-melamine
Toyota	Clearcoat/26 μm	TC-71		Acrylic-melamine
	Basecoat/36 μm		8G5/blue	Acrylic-melamine
Toyota	Clearcoat/32 μm	0150		Acrylic-melamine
	Basecoat/50 μm		3H4/red	Acrylic-melamine; Polyurethane
Yuelong	Clearcoat/40 μm	BF		Acrylic-melamine
	Basecoat/32 μm		235/white	Polyester and acrylic-melamine
Yuelong	Clearcoat/30 μm	BF		Acrylic-melamine
	Basecoat/20 μm		259/blue	Polyester and epoxy and trace acrylic-melamine
Yuelong	Clearcoat/40 μm	SE		Acrylic-melamine
	Basecoat/30 μm		316/yellow	Acrylic and polyester-melamine; Calcium carbonate
Yuelong	Clearcoat/24 μm	Dulux		Acrylic-melamine
	Basecoat/20 μm		518/green	Polyester and epoxy-melamine
Sanyang	Clearcoat/56 μm	Center		Acrylic-melamine
	Basecoat/30 μm		WT-09/white	Acrylic-melamine; Titanium dioxide
Ford	Clearcoat/32 μm	Ford		Acrylic-melamine
	Basecoat/20 μm		Ford-red/red	Polyester-melamine; Polyurethane
Ford	Clearcoat/22 μm	Ford		Acrylic-melamine
	Basecoat/14 μm		Ford-green/green	Polyester-melamine

Acrylic-melamine system blended with UV absorbers has been generally adopted as the main composition of clearcoats due to its excellent durability. In order to achieve the desired properties, various acrylic resin monomers and styrene were used for this purpose. Therefore, it was hard to differentiate clearcoats containing acrylic-melamine binder only by comparing their IR spectra. Fig. 1 depicts that seven IR spectra of clearcoats obtaining from various automotive companies appear very similar absorption bands of acrylic-melamine binders. The 1730 and 1160 cm^{-1} band region (1250-1050 cm^{-1}) represent the C-O ester group; 700 and 760 cm^{-1}, styrene; 1550 and 815 cm^{-1} melamine triazine. To further discriminate those clearcoats, the acrylic resin monomers used in clearcoats were determined by the Pyrolysis-GC/MS approach with 100 μg of each sample. Fig. 2 presents pyrolysate chromatograms that discernible patterns can be achieved by comparing monomers. Resins used in the basecoat binders are also recognized as having added trace acrylics, such as methyl methacrylate that is used in #235 and #259 basecoats. Definitely, Micro-FTIR combined with Pyrolysis-GC/MS is an effective method of determining binders in automotive paints.

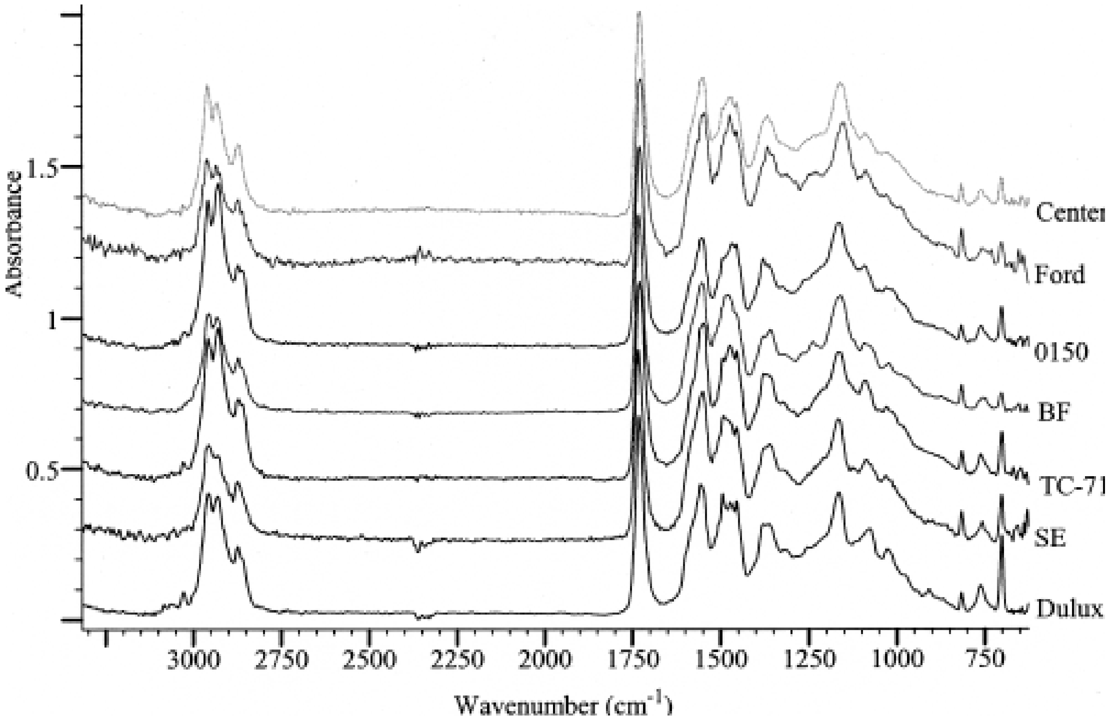

Fig.1 Similar IR spectra of seven clearcoats consisting of acrylic-melamine binders.

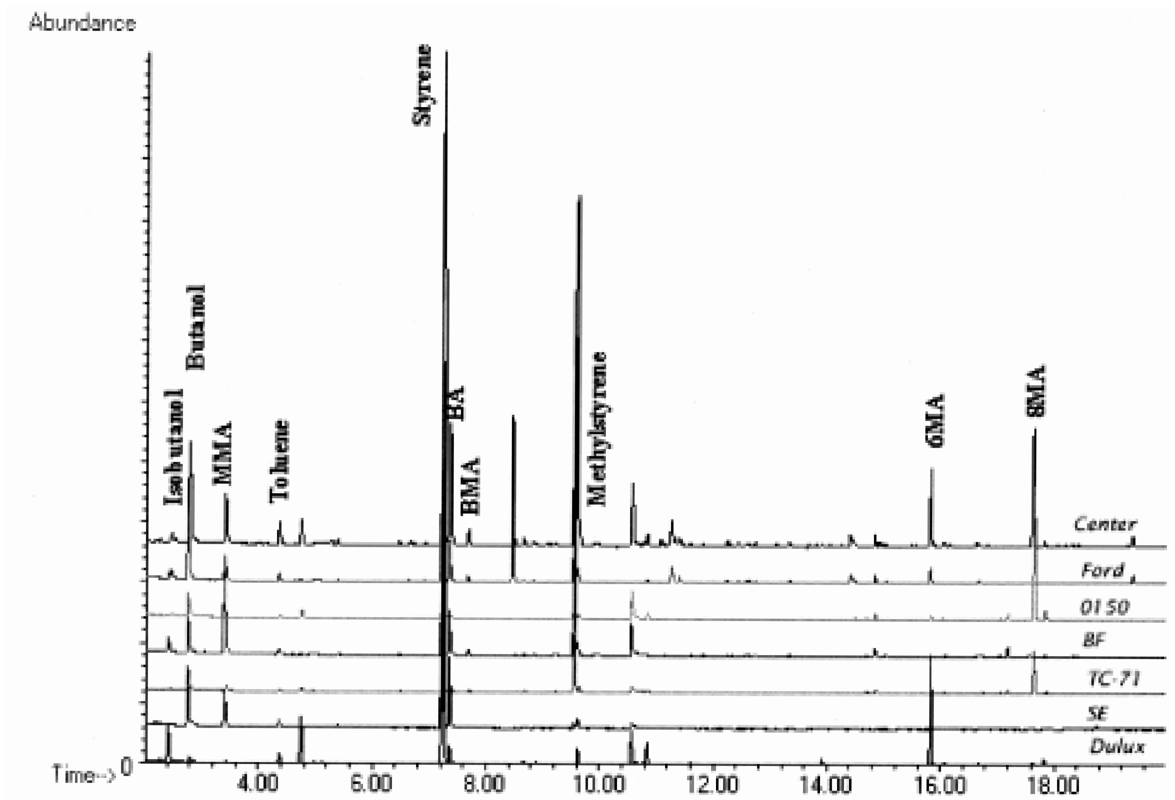

Fig.2 Seven clearcoats containing acrylic-melamine binders were determined by Py-GC/MS and shown discernible patterns (MMA: methyl methacrylate; BA: butyl acrylate; BMA: butyl methacrylate; 6MA: 6-methheptyl acrylate; 8MA: octyl methacrylate).

Selection of library search algorithm

The clearcoat of #Center was initially selected as an example to evaluate the excellent discriminating capability via comparing HQIs with other clearcoats. Based on the equations from three algorithms, HQIs were obtained by using the #Center as the base spectrum for the calculations. Fig. 3 depicts the means (n = 5) and the range of error bar (mean ±95%) of HQIs for First Derivative Euclidean Distance algorithm (A), First Derivative Least Squares algorithm (B), and Peak Table Search algorithm (C), respectively. By using Peak Table Search algorithm, among the six comparisons, four HQIs from the compared pairs appear significantly different. However, in First Derivative Euclidean Distance and First Derivative Least Squares algorithms only two HQIs differ significantly. As a result, HQIs that were derived from Peak Table Search algorithm not only indicate a smaller deviation but also present a better discriminating capability among all the samples. Two samples, #BF and #Dulux, were further evaluated via the same protocol described as above. The empirical results also indicate the same phenomenon. Although every algorithm could rank a few candidates for further spectra comparison after searching, one with good discriminating capability not only shortens search time but also improves match accuracy. Peak Table Search algorithm are proved to be superior to both First Derivative Euclidean Distance and First Derivative Least Square within the IR spectra search.

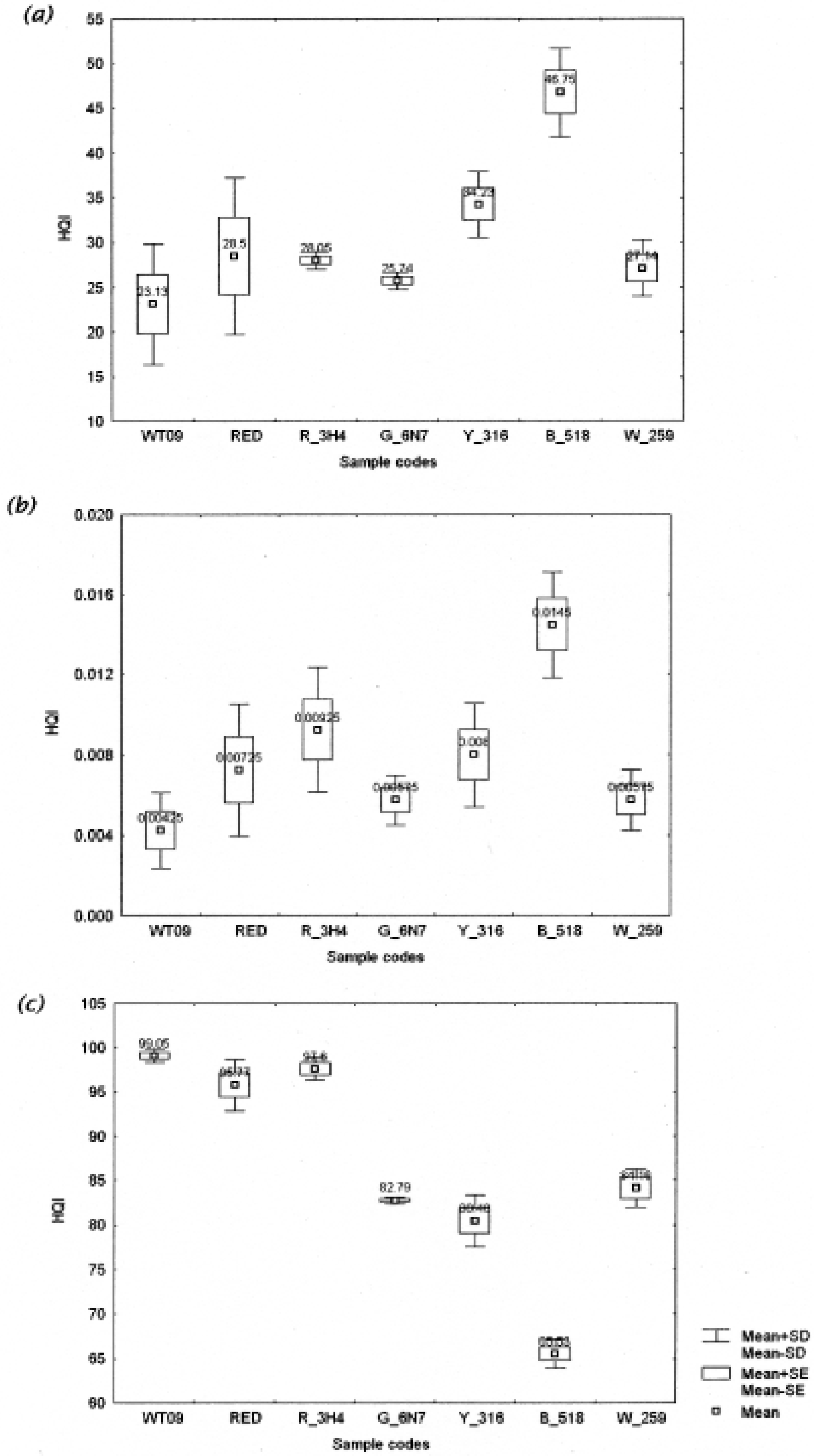

Fig.3 Comparisons between spectrum of #Center clearcoat and spectra of 7 clearcoats by the use of HQIs derived from (A) First Derivatives Euclidean Distance, (B) First Derivative Least Squares, (C) Peak Table Search algorithms.

Within the different experiments conducted, IR spectrum quality was commonly affected by the instrument and the specimen conditions. Thus, the HQIs deriving from varying spectra within the same samples vary slightly despite the identical procedures. To obtain the reproducibility of the determinations, the guidelines of the peak selection for the Peak Table Search algorithm that was evaluated prior to determining HQIs are listed as follows:

1. The absorbency of the maximum peak in IR spectrum needs to exceed 0.5. That is, small peaks may not be picked if the absorbency was too low.
2. The peak-picking step is automatically conducted with the noise level of 0.005, and then deleted or added by manual.
3. Peak Table Search Algorithm recognizes two bands that have less than 15 cm^{-1} absorption as the same one. The bigger of two peaks is then selected as the candidate in this situation.
4. All peaks having reproducible picking results after following three determinations are selected for HQI calculation.
5. Owing to the baseline drift, the wavelength range of 650 to 2000 cm^{-1} is used for HQI calculation. However, the range of 650 to 800 cm^{-1} is not used when a large amount of titanium dioxide pigment is found. The significantly broad peak may unavoidably interfere with other peaks within the absorption range.

Analyses of weathered paints

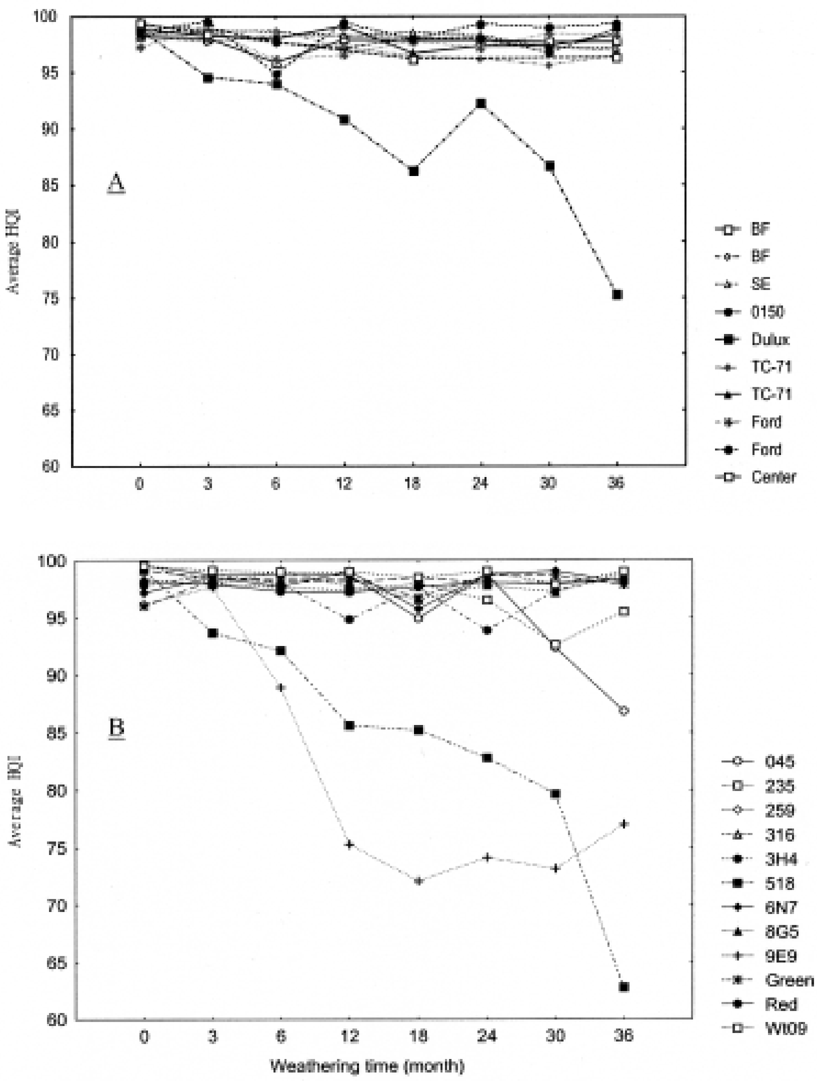

Fig.4 The trends plotted by average HQIs (n = 5) and weathering time for (A) clearcoats and (B) basecoats exposed in Taipei area.

HQIs of the non-weathered and weathered paints were monitored to determine the trends along with the weathering time. Fig. 4A reveals that panels exposed in Taipei present two phenomena. First, nine HQIs of ten clearcoats barely change despite their basecoat and remain above 95 after following three years weathering. The result also indicates that there is no obvious correlation among the clearcoat thickness, basecoat color and HQIs. Second, HQIs of #Dulux clearcoat solely decrease with an increase in weathering time. Although acrylic-melamine binder clearcoats generally had excellent weathering resistance [13], they were easily degraded due to photo-oxidation of the polymer [14] under natural weather conditions as it might have contained insufficient UV absorber or light-stabilizer [15]. This unexpected result reveals that the searched target should be examine by other additional data. That is, the highest HQI of all searched results might not be the right target. Based on the design of original finish system, clearcoat layers generally protect basecoats. Due to the consideration of expense, weathering resistance additives were not included in this layer. Thus, as long as the clearcoat was not degraded, the basecoat was theoretically not degraded. Excluding #518, #045 and #9E9, HQIs of nine basecoats (Fig. 4B) change slightly and remain above 95 value along with the weathering time. However, HQIs of #518 basecoat presents greater changes due to lack of clearcoat protection. That is, after three years of weathering, the clearcoat and basecoat's HQIs of #518 decrease to 75 and 63, respectively. Thus, the fragile property of the #518 topcoat was observed while sampling the weathered paint panel. Fig. 5 illustrates the degradation of the binder compositions, which result in a decrease in the HQIs. Intensities of the absorption bands for 1550, 1450, 1370, 1070, 1020, 815, 760, and 700 cm^{-1} reduce gradually, however 1730 and 1160 cm^{-1} remain constant throughout weathering time. In contrast, 1230 cm^{-1} band heightens gradually after undergoing 3 years of weathering.

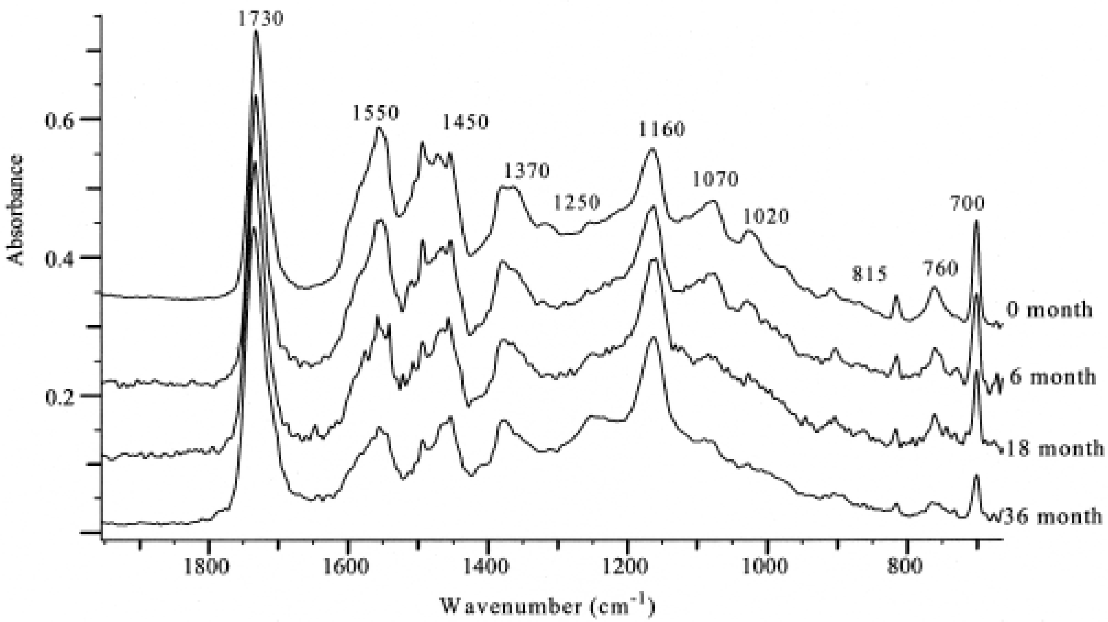

Fig.5 Intensity Changes of IR absorption bands undergoing different weathering time for #518 clearcoat.

HQIs of #9E9 and #045 topcoats (no clearcoats) decrease dramatically after 3 and 24 months of weathering in Fig 4B, respectively. Compared with the acrylic binders, alkyd resin ones significantly deteriorate after weathering due to their less weathering resistance. HQIs of #9E9 topcoat which contained alkyd-melamine and polyurethane, therefore, decrease faster than those of the #045 topcoat containing alkyd-melamine. Thus, automotive paints containing an alkyd resin for the use of topcoats are not applicable to the library search. Prior to establishing the standard database, spectra of binder or resin types should be examined and noted. The interpretation of searched results from an alkyd binder must consider a decreasing HQI due to the weathering factor. Compared with the spectra of the alternately weathered #045 topcoat in Fig. 6, absorption bands (1280, 1120, and 1070 cm^{-1}) of alkyd resin decrease intensities with an increased weathering time. Conversely, absorption band of 1120 cm^{-1} at the left side splits into 1138 cm-1 after weathering. These results produce the decrease in HQIs as shown in Fig.4B.

Panels exposed in the Pingtung area (Fig. 7) present experimental results that were similar to those described above. Experimental results from these two regions indicate that not only two sets of the experimental protocols are reproducible, but also degradations from exposure in both the north and south of Taiwan are similar.

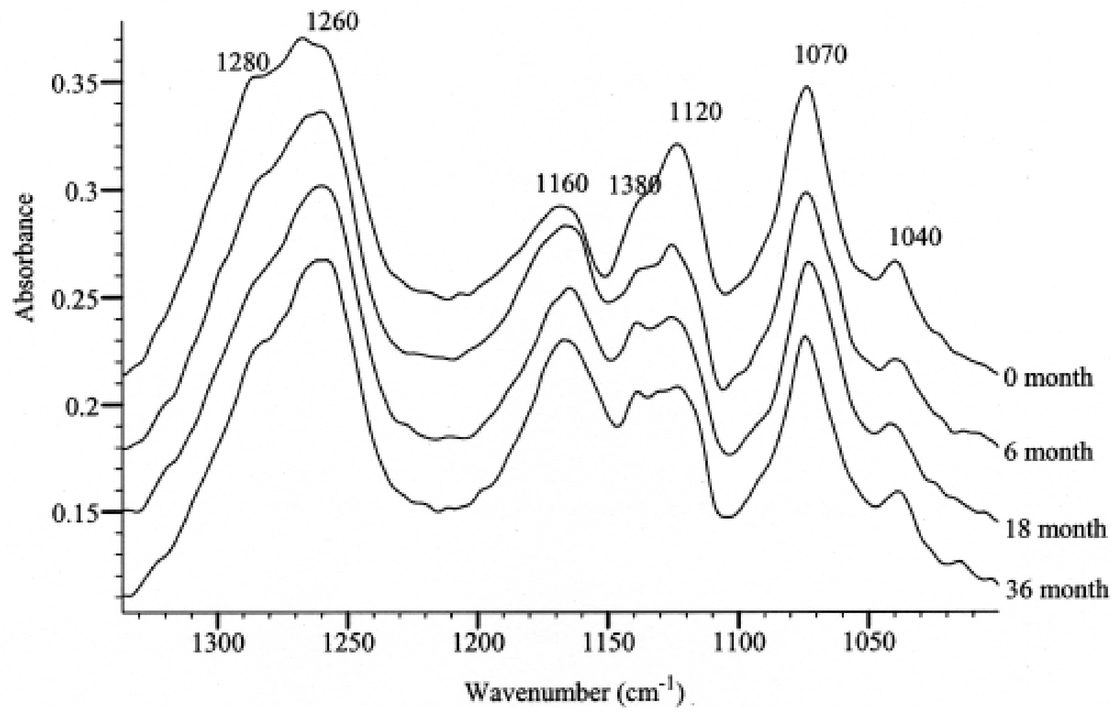

Fig.6 Intensity Changes of IR absorption bands undergoing different weathering time for #045 topcoat.

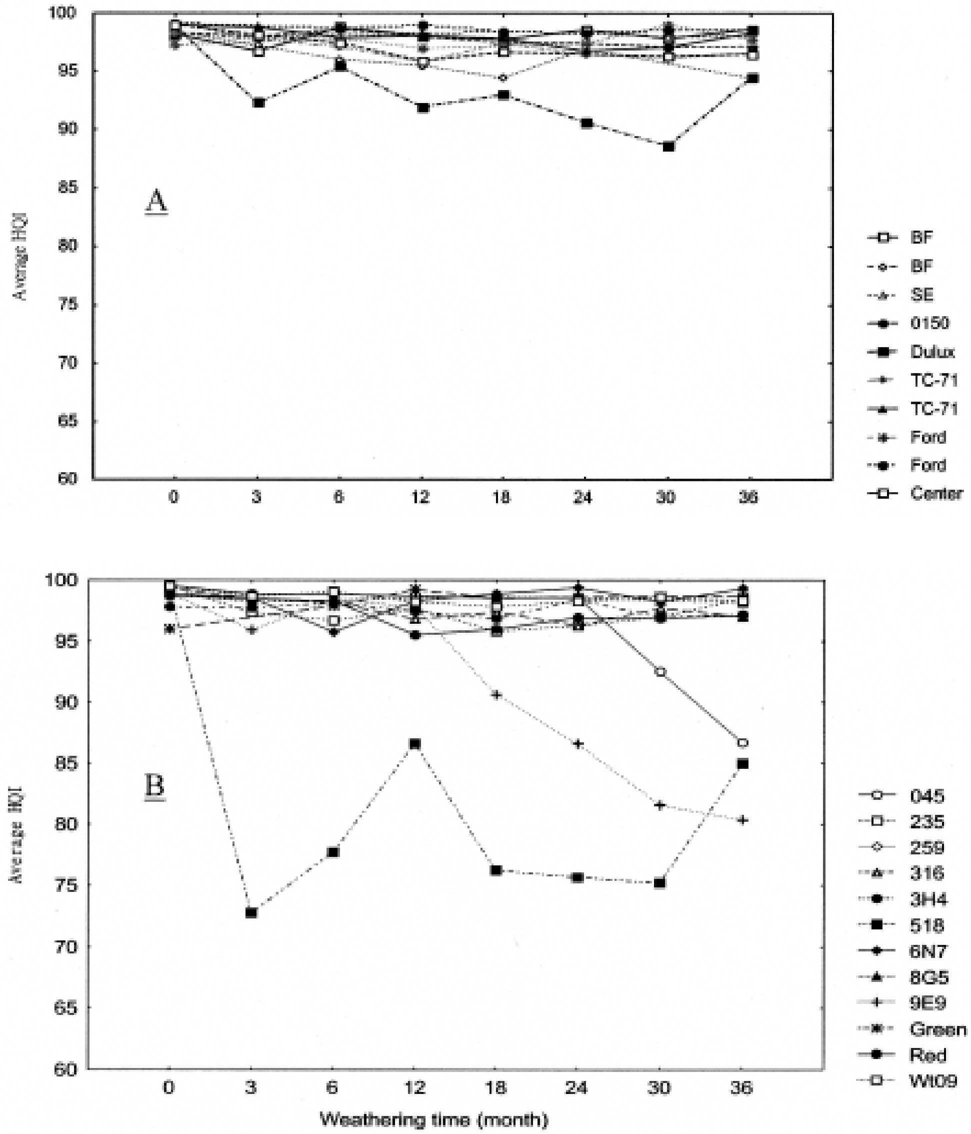

Fig.7 The trends plotted by average HQIs (n = 5) and weathering time for (A) clearcoats and (B) basecoats exposed in Pingtung area.

Conclusion

Acrylic-melamine binders are mainly used in clearcoats of automotive topcoats in Taiwan. Versatile compositions of binders in basecoats provide more characteristic possibilities for forensic examinations. Micro-FTIR assisted by Pyrolysis-GC/MS was proved effective in binder identification. In this study, Peak Table Search method was selected as the ideal algorithm to conduct library searching for the forensic application of automotive paints. To acquire more reproducible results, guidelines for peak selection should be established in a library search algorithm. Most basecoats and their coated clearcoats retain 95 HQIs after undergoing 3 years of weathering. Hence, this experimental result when HQI is greater than 95 is recognized as the nearest target. However, some acrylic- and alkyd-melamine binders that were used for topcoat or clearcoat have been proved to reduce HQI value due to aging effect. Therefore, aging effects should be considered when interpreting searched results, especially for the topcoat. Compared with automotive paints that are generally used in real vehicles, paint panels were placed outdoors for more critical exposure in this study. Thus, the spectrum database of automotive paints is intended to be used for more than three years.

Acknowledgements

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