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Original Research Article

Forensic analysis of automobile paint of Indian company

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Abstract

The present study was done in an attempt to distinguish between paint samples of automobiles obtained from cars of same company "MARUTI". 20 samples of paint were analyzed with the help of solubility tests and 5 samples with the help of instruments such as UV Spectrophotometry each. The solubility tests were performed using 3 liquids, Chloroform, Sulphuric acid and Nitric acid. The results obtained clearly proved that the combination of both methods yields better results than when used individually. Through this research, a database has been created which can be useful in further forensic related work. It can be really helpful in hit and run cases where possibility of exchange of paint is very high.

Keywords: Solubility tests, UV Spectrophotometry, Automobile paint, Forensic analysis.

Introduction

Paint can be considered phenomenal forensic evidence or evidence that can be helpful to solve crimes. It is a type of trace evidence like glass, hairs and fibers that can be found in trace amounts on the crime scene but can be solely responsible for the conviction of the perpetrator. Automobile paint evidence can be especially relevant in hit and run cases or other cases where automobiles are involved. Car paint is one of the most received evidence in forensic laboratories. The paint chips or paint smears are generally transferred from the car to the clothing of the victim or another car during an impact with the first car. Paint chips and smears can be easily compared to a suspect's vehicle to check whether the vehicle has been involved in any hit and run accident or not. These chips can also be matched by fitting them to any missing section on the vehicle like puzzle pieces are fitted.

Automotive paint is paint which is used for protection and decoration on the automobile. The widely used paint nowadays is water based acrylic polyurethane enamel paint due to its less harmful effect on the environment.[1] Modern used automobile paint is applied with a thickness of 100 µm (0.1mm). Automobile paint consists of mainly three components; binder, pigment and additives.

There are many research articles published on paint evidence nowadays. In most of them, the primarily used method of examination is visual examination using microscopy[5,7] as in *Gothard* (1976) and *Ryland* (1978). Solubility tests and chemical tests were also used as a way of identifying various pigments present in the paint sample as done by *Cassissta* and *Sandercock* in 1994. They performed micro chemical spot tests to identify the number and type of pigments present in the paint samples.

For the confirmatory tests, Instrumentation is proven to be the best method used to identify and quantify all the elements present in the paint samples. FTIR was the most favored technique in all the current research papers.[25] This was due to the fact that it gives accurate results and is easy to use. Usually FTIR was coupled with a number of techniques; Pyrolysis gas chromatography,[9,10] SEM-EDX,[21] Raman spectroscopy.[24] Another technique used was LA-ICP-MS[19] which was sometimes coupled with FTIR but sometimes used alone. This yielded surprising good results.

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This study used UV Spectrophotometry and Solubility tests in combination to identify various elements present in the sample. Peaks were obtained which matched certain elements through which they were identified. UV Spectrophotometry proved to be really useful technique to differentiate between different samples of same company by identifying elements that were specifically present in them.

The results obtained from the analysis of paint using instrumentation yielded the results that combination of 2-3 techniques always gives accurate results rather than using single technique. Coupling of techniques is the best way to ensure that all the elements that are present in the sample are identified and quantified.

Materials and Methods

Collection of Samples

In this study, 20 samples of paint chips were collected from cars of Indian brand "MARUTI". They were collected from various sources like Police Stations, Denting and Painting shops, Showrooms located in the area of Mohali, Ludhiana and Sri Muktsar Sahib. One company was targeted due to a large number of cars of this brand only. The paint chips were collected using Surgical Blade.

Analysis

Solubility tests

Solubility tests were performed using chemicals like Chloroform, Sulphuric Acid and Nitric Acid. The chips were dipped in these chemicals for 3 days. Every day, the test tubes containing the heterogeneous mixture were observed. The changes occurring in them were carefully observed and noted down.

Instrumental analysis

Instrumental analysis was also done with the help of UV Spectrophotometer. This instrument was chosen because it gives the most accurate result in combination as to which elements are present in the given paint sample. Also the results are precise and provide us with even the smallest element present in the paint sample. UV Spectrophotometer gives results in the form of peaks in the ultraviolet range that is 10nm to 400nm.

Results and Discussion

In this study, 3 chemicals were used for the purpose of solubility tests; Sulphuric acid, Nitric acid and Chloroform.

With Sulphuric acid, the samples interacted the most. Slight Shrinkage and curling was seen on the very first day. Another important thing was formation of dark brown/ black rings on the surface of solution in which the sample floated whereas rest of the solution was clear. Fragmentation was also seen starting on first day in many samples. By the second day, the rings formed were still intact in many but in some samples, It was replaced by muddy or brown colored liquid in which the samples were either floating or were settled down. Another thing was separation of layers of samples. On the second day, only top layer was seen separated from the sample whereas by the third day, every layer was separated from each other.

Table 1: Showing changes occurred in various samples when dissolved in Sulphuric acid (H_2SO_4)

Sample No.	Day 1	Day 2	Day 3
1.	Shrinkage, Bleeding brown, Top layer removed which floated	Dark brown ring formed on upper side of solution while rest of the solution is slight yellow, Fragmented sample	Dark brown colored solution with sample floating in it, NOC
2.	Slight shrinkage, Dark brown ring formed on upper side of solution while rest of the solution is clear	Floating sample, Complete shrinkage of sample	Dark brown colored solution, NOC
3.	Bleeding light yellow,	Urine colored solution	NOC

	Floating, Slightly shrinked		
4.	Sample gets enlarged, Dark brown ring formed on upper side of solution while rest of the solution is clear	Sample floating, papery, soft and curled, Muddy colored and dense solution	Layers of sample gets separated, NOC
5.	Bleeding light brown, Dark brown ring formed on upper side of solution while rest of the solution is clear	Dark brown ring formed on upper side of solution while rest of the solution is slight yellow, Fragmented sample	Ring remain intact with pieces of sample floating in it
6.	Dark brown ring formed on upper side of solution while rest of the solution is slight yellow, Fragmented sample	Ring intact with sample floating in it.	NOC
7.	Slightly curled, Top layers gets separated and starts floating	Sample became soft and papery, Solution becomes dark brown	All the layers gets separated, NOC
8.	Fragmentation begins, Dense liquid	Muddy colored dense solution, Sample curled and floating	Fragmentation completes, Slightly curled fragments
9.	Shrinkage, Bleeding brown, Top layer removed which floated	Sample floating, papery, soft and curled, Muddy colored and dense solution	NOC
10.	Black colored solution with sample floating in it, Sample slightly curled, Floating	Black colored ring with fragments of sample formed on upper side while rest of the solution is yellow	Sinking of sample, black ring remain intact
11.	Fragmentation begins, Brown colored solution, Dense liquid	Sample became soft and papery, Dark brown color occurred	Complete fragmentation of sample, NOC
12.	Fragmentation begins, Floating sample	Black colored solution	Sample almost dissolved and visible only when shaked
13.	Fragmentation begins, Dense liquid	Muddy colored dense solution, Sample curled and floating	Fragmentation completes, Slightly curled fragments
14.	Bleeding light yellow	NOC	NOC
15.	Slight shrinkage, Dark brown ring formed on upper side of solution while rest of the solution is clear	Ring intact with sample floating in it	Dark brown colored solution, NOC
16.	Slightly curled, Dark brown ring formed on upper side of solution which contains sample, while rest of the solution is clear	Fragmented sample, Dense muddy colored solution with fragments floating in it	NOC

17.	Fragmentation begins, Dense brown colored liquid	Muddy colored dense solution, Sample curled and floating	Fragmentation completes, Slightly curled fragments
18.	Slight shrinkage, Dark brown ring formed on upper side of solution while rest of the solution is clear	Floating sample, Complete shrinkage of sample	Dark brown colored solution, NOC
19.	Slightly curled, Top layers gets separated and starts floating	Sample became soft and papery, Solution becomes dark brown	All the layers gets separated, NOC
20.	Bleeding light yellow, sample floating and slightly curled	Urine colored solution	NOC

In Nitric acid, the samples reacted mildly. The samples either slightly curled or shrank on the first day. Some of the samples even got swollen. Slight fragmentation was also seen. The second day was when most of the bleeding occurred. Most samples bleeded yellow / urine color whereas 2-3 were seen bleeding light green color. Fragmentation was seen reaching its peaks. Curling and shrinking of the samples was also seen. By the third day, most of the samples did not show any further changes but some samples bleeded yellow. An interesting thing to note was that this was the only liquid in which some samples do not reacted at all on any day.

Table 2: Showing changes occurred in various samples when dissolved in Nitric acid (HNO_3)

Sample No.	Day 1	Day 2	Day 3
1.	Slight color change to light yellow	Urine colored solution, Sample shrank and sank	NOC
2.	Fragmentation starts and slight bleeding	Urine colored solution, Fragmentation complete	NOC
3.	No visible changes	No visible changes	No visible changes
4.	Slightly curled, Settled down, Shrinking done	Sample curled and solution is cloudy in nature	Sample fragmented into large pieces
5.	Curled, bleeding slight yellow, Fragmentation and shrinking starts	Sample curled, fragmented and settled down	NOC
6.	Sample curled, float, and bleed white	Sample settled down	No other visible changes
7.	Sample curled and swollen, Top layer gets separated	Top layer fragmented while other layers still intact, Sample swollen and bleeds light yellow	Sample floats and starting to get fragmented into further very little pieces
8.	Slight color change to light yellow	Fragmentation starts	Fragmentation completes, NOC
9.	Sample curled, float, and bleed white	Sample settled down	NOC
10.	Bleeding slight yellow, Fragmentation and	Sample curled, fragmented and swollen, Bleeds light	Some of the sample float and some sank

	shrinking starts	green color	
11.	Swollen and curled sample, Top layer gets separated and floats	All the layers gets separated, Fragmentation starts, yellow colored solution	Sample settled down, NOC
12.	Sample gets swelled and floats, Fragmentation starts	Sample swollen and fragmented, Bleeds light green	Sample settled down, NOC
13.	Sample curled and swollen, Top layer gets separated	All the sample gets fragmented	Bleed slight yellow
14.	Bleeding slight yellow, Fragmentation and shrinking starts	Sample curled, fragmented and swollen, Bleeds light green color	Some of the sample float and some sank
15.	Sample curled and solution is cloudy in nature	Sample fragmented into large pieces	NOC
16.	Sample curled, float, and bleed white	Sample settled down	No other visible changes
17.	Solution slight yellow and opaque in nature	Sample curled, swollen and settled down, Solution a bit cloudy	Bleeds yellow, and float
18.	Fragmentation starts and slight bleeding	Urine colored solution, Fragmentation complete	NOC
19.	Sample curled and swollen, Top layer gets separated	Top layer fragmented while other layers still intact, Sample swollen and bleeds light yellow	Sample floats and starting to get fragmented into further very little pieces
20.	No visible changes	No visible changes	No visible changes

In Chloroform, almost all the samples floated on the first day but by the third day, they were settled down. Slight Curling and shrinking was seen on first day where as Bleeding happened rarely. On the second day most of the samples were curled and shrank completely. Bleeding occurred in few samples on the third day whereas most of the samples did not undergo any disastrous change from second to third day. Fragmentation also occurred rarely.

Table 3: Showing changes occurred in various samples when dissolved in Chloroform ($CHCl_3$)

Sample No.	Day 1	Day 2	Day 3
1.	NVCC, Floating	Settled down	Complete shrinkage
2.	NVCC	Slight color change	NOC
3.	Floating	NVCC	NOC
4.	Curled, NOC	Floating	NOC
5.	NVCC, Floating	Curled Completely	Milky appearance
6.	NVCC, Floating	Curled slightly	Curled completely
7.	NVCC	NOC	NOC
8.	Slightly curled	NVCC	NOC
9.	Bleeding yellow	Floating	NOC
10.	NVCC	Sinking	Bleeding yellow
11.	Bleeding white, Floating	Complete shrinkage	Curled completely

12.	Slight color change, Floating	Slightly shrinked	Shrinkage, Bleeding yellow
13.	Floating	NVCC	NOC
14.	Slightly curled	Sinking	NOCC
15.	NVCC, Floating	NOC	NOC
16.	Shrinkage, Floating	Settled down	Slightly curled
17.	Slight Shrinkage, Floating	Complete shrinkage, settled down	NOC
18.	NVCC, Floating	Shrinkage	Milky appearance
19.	Slight bleeding, Floating	Curled, Fragmentation begins	Fragmentation completes
20.	NVCC, Floating, Slightly curled	Curled completed	NOC

The present study contrasts with a study performed by Cassissta and Sandercock in 1994 in which they used chemicals like Acetone, Toluene, Acetic acid etc to check whether the samples are soluble in these chemicals or not. The samples were not put for more than a few hours as Micro chemical Spot tests were performed. The result was that most of the samples were soluble in these chemicals.

Table 4: Showing results of UV spectrophotometry

Sample No.	Wavelength	Absorption
5	267.55	0.894
16	245.96	0.722
17	271.25	0.988
18	250.07	0.925
20	254.99	0.993

5 samples of automobile paint were analyzed under UV Spectrophotometry. All the samples show maximum absorption at wavelength 240 – 270 nm. The maximum absorption of 0.993 at wavelength of 254.99 nm was seen by sample 20. Another sample named 17 also showed a maximum absorption of 0.988 at wavelength of 271.25 nm. Almost all the samples showed good absorption peaks in the UV. This study can be a very good basis of forming a handbook which contains all the peaks generated by particular constituent in particular solvent.

The main techniques applied analysis of paint are generally FTIR, RAMAN spectroscopy, IR Spectroscopy, GC-MS and SEM-EDX. In most of the cases it has been seen that, a single technique has never been good at identifying all the elements present in a sample. A combination of 2-3 techniques is best if we want to identify and quantify nearly all the elements. This statement is supported by facts presented by Burke *et al.* (1985), Giang *et al.* (2002), Chen *et al.* (2014) and Kruglak *et al.* (2019).

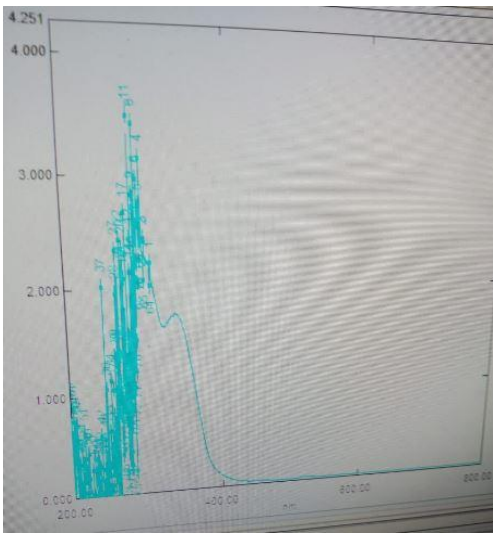

Fig. 1: Results of UV Spectrophotometry of sample 5

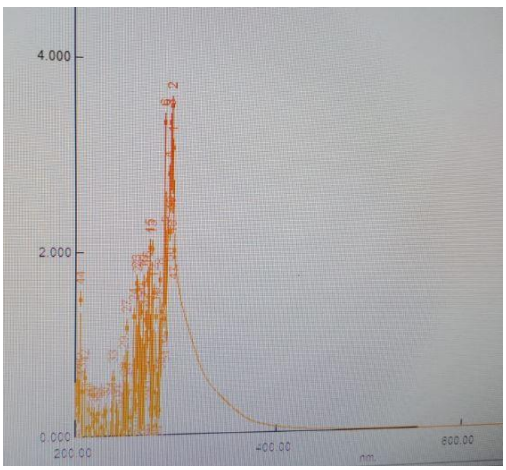

Fig. 2: Results of UV Spectrophotometry of sample 16

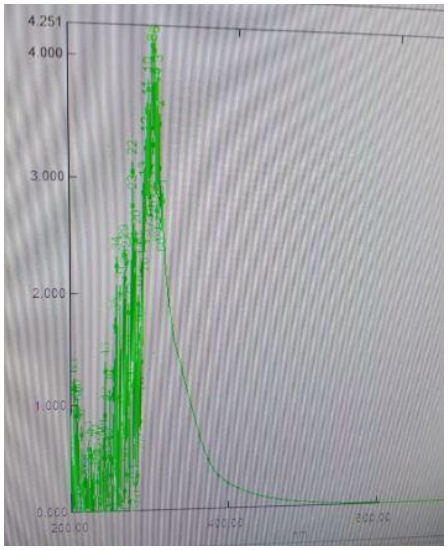

Fig. 3: Results of UV Spectrophotometry of sample 17

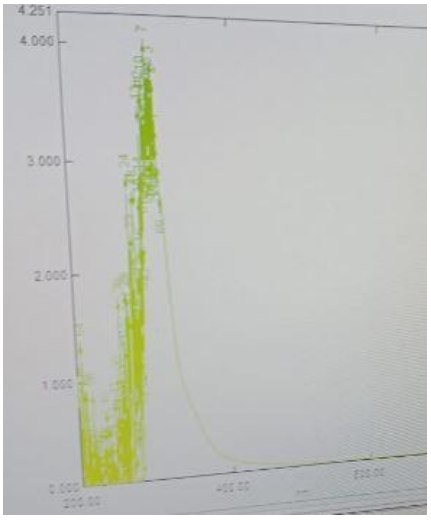

Fig 4: Results of UV Spectrophotometry of sample 18

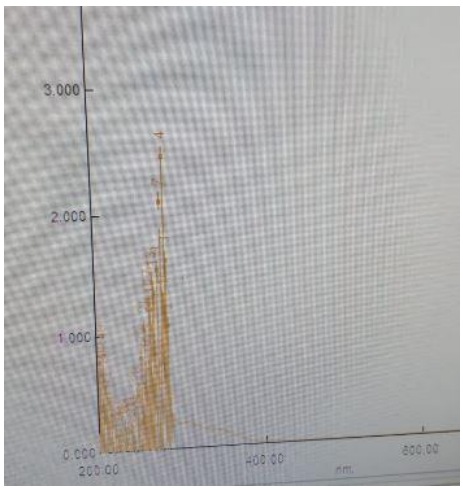

Fig 5: Results of UV Spectrophotometry of sample 20

Conclusion

Using solubility tests and instrumentation like UV-Vis Spectrophotometry, all the 20 samples were analyzed and differentiated. Solubility tests act as preliminary tests while instrumentation act as confirmatory test. Nearly all the samples were distinguished using chemicals like Sulphuric acid, Nitric acid and Chloroform. All the samples reacted differently to different chemicals while some reacted to Sulphuric acid very well; others show positive reaction in Nitric acid. UV Spectrophotometry was used to analyze 5 samples but due to unavailability of data, they were not able to get matched with reference. Through this research, a database has been created which can be useful in further forensic related work. It can be really helpful in hit and run cases where possibility of exchange of paint chips is very high.

Source of Funding

None.

Conflict of Interest

None.

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