

FT-IR FINGERPRINTING OF ORGANIC COATINGS: POSSIBILITIES AND PRACTICALITIES IN INDUSTRY

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ABSTRACT

Fourier Transform Infrared Spectroscopy (FT-IR) can be used as a quality control tool to fingerprint paint and coatings. The fingerprinting of the final cured coating or the uncured liquid paint are both possible; in each case it is possible to achieve good batch to batch correlation. However the effectiveness of fingerprinting in detecting formulation changes remains to be seen. The implementation of any fingerprinting program should take into consideration the constraints and standard practices of paint formulators, as well as other factors that may affect the performance of the final coating.

1. Introduction

The characterisation of organic coatings in industry has commonly involved the testing of a number of properties, some of which include hardness, flexibility and impact resistance. The appearance, such as gloss and colour, can also be measured. For protective coatings, outdoor durability and corrosion protection performance are critical; both can be tested for in accelerated weathering machines such as the QUV (A and B) and salt fog or cyclic corrosion chambers, even though the correlation with natural weathering data can be found wanting.

The application of analytical techniques in the characterisation of organic coatings has, however, been relatively slow to be accepted as standard practice among formulators and end users of the paints, particularly in developing countries where cost concerns are high and competition is intense. Apart from concerns about the high investment costs of the instruments, there are also issues in finding suitable personnel to use them since they require a certain amount of knowledge and expertise in order to be able to correctly analyse and interpret the data generated by these machines.

In the analysis of organic materials, FT-IR is one of the most versatile and useful tools available. Its applications in the analysis of organic coatings are routinely reported in scientific journals. While it has also been reportedly used as a quality control (QC) tool in the coatings industry, both in analysing in-coming raw materials and in analysing the final product to be shipped to the customer, this does not appear to be a standard industrial practice.

This article takes a look at the possibility of using FT-IR fingerprinting as a QC tool, and whether this is practical with regard to the paint industry.

2. Related Standards For FT-IR Fingerprinting of Organic Coatings

Two related ASTM standards on FT-IR are currently available [1, 2]. The first and older standard, ASTM D2621-87 (2011), involves the separation of the different components of paint (solvents, binders, pigments) via high-speed centrifuging. The separated components are then analysed individually. The analysis requires the careful and consistent application of a uniform thin film of the separated component onto a NaCl window. As the IR transmittance depends on the thickness of the film, it is therefore possible that different operators may generate spectra of varying quality. This method is intended more as a paint solids identification tool rather than as a fingerprinting technique.

The second and relatively recent standard, ASTM D7588-11, does not require the separation of the paint components. However, it requires the availability of a multiple or single bounce horizontal Attenuated Total Reflectance (ATR) trough plate to hold the liquid sample. The complete

paint formulation is analysed, including the solvent. Sample preparation is convenient and the collection of spectrum requires minimal time and operator skill. However, solvent evaporation from the paint may occur during spectrum collection especially if the solvents are highly volatile. It is also noted in the standard that some paints may be unsuitable for this method as they may show many peak saturations (100% absorptions) which make the spectra inaccurate. This method appears to be similar to one reported much earlier [3].

3. FT-IR Fingerprinting of Liquid Paint

Despite the availability of related standards, a common method to fingerprint paints without separating the different components is by simply applying a thin film of the paint on a NaCl or KBr window, and proceeding with the scanning [4]. This is basically similar to the method of ASTM D2621-87 (2011) except without the centrifuging step. It does not require the ATR trough plate accessory as specified in ASTM D7588-11.

Figure 1 shows the spectra of seven batches of a single-pack epoxy primer for coil coating analysed as liquid samples. The samples were prepared by applying a small drop of paint onto a KBr disc. Another disc was then immediately put on top of the paint, effectively spreading it into a thin film and sandwiching it between the two discs. Scanning was then carried out and automatic baseline correction was applied on the resultant spectra.

c	Correlation
Batch 1 (Reference)	1.00
Batch 2	0.99
Batch 3	0.99
Batch 4	0.99
Batch 5	0.99
Batch 6	0.99
Batch 7	0.99

Table 1. Correlation for seven batches of uncured liquid epoxy primer on KBr disc

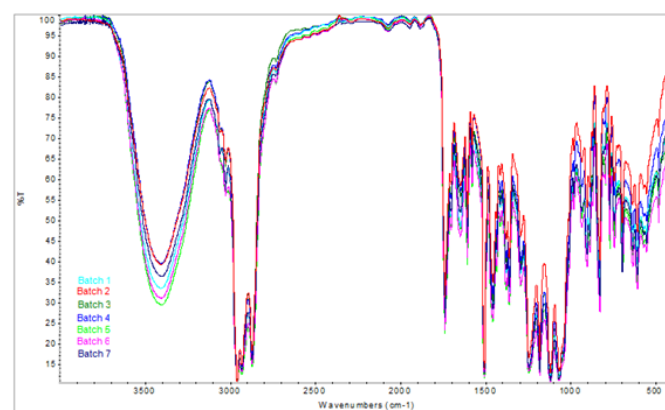


Figure 1. Transmittance spectra of seven batches of a single-pack epoxy primer for coil coating, analysed as liquid samples on KBr windows.

It can be observed in Figure 1 that the spectra are relatively consistent with each other even with the presence of solvents, which in this case were diacetone alcohol, xylene and some ester solvents. The consistency is reflected Table 1, which lists the correlations (degree of similarity) calculated by the FT-IR software. The correlations are very good at 0.99 in all cases.

The results show that it is possible to obtain good correlation by fingerprinting liquid paint. However, caution is strongly advised since the reproducibility of the method will depend on several conditions such as paint viscosity, which determines the ease of obtaining a suitable film thickness, and the operator performing the analysis. It is important that whatever method is developed must be evaluated carefully to ensure its repeatability and reproducibility before being implemented.

It is advisable to keep the maximum peak intensity in the transmittance spectrum at approximately 10% or above, or as specified by the instrument supplier. This is to ensure that there are no peak saturations which will affect the reliability of the measurement. A critical factor determining the transmittance is the film thickness of the paint applied onto the KBr discs. This is therefore a major difficulty with this method, especially if the paint has a high viscosity and is difficult to be applied into a thin film. The consistency of sample preparation could then become an issue. The alternative would be to use the ATR trough plate accessory but that is also no guarantee of eliminating peak saturations completely [2].

It should be pointed out that the most important component of a paint is the binder system because it determines the property and performance of the final coating. The solvents are there to ensure processability of the paint and that it has the right rheology to make its application as easy as possible, as well as to aid the proper film formation of the final coating. The solvents will also be eventually removed.

In practice, it is very common in the coatings industry to adjust paint rheology using solvents, thus the amount used from batch to batch may differ. Sometimes other solvents may also be added, even on site prior to applying the paint. More importantly and if done appropriately this practice does not negatively impact the quality of the final coating. Therefore the fingerprinting of a complete paint including solvents has to take this into account in order to avoid the unreasonable rejection of a batch of paint.

4. FT-IR fingerprinting of cured coating

Figure 2 shows the spectra of seven batches of the same single-pack epoxy primer, fully cured on galvanised steel substrate. The spectra were recorded on an ATR plate with ZnSe crystal. Again, it can be seen that the spectra are consistent among the seven batches, also with good correlation calculated from the FT-IR software (Table 2) at 0.98 and higher. Visually, the spectra also appear simpler compared to those of uncured liquid samples. This is because the solvents are no longer present, in addition to the lower sensitivity of the ATR technique.

While there do not appear to be any advantages of fingerprinting cured coatings over liquid paints in terms of correlation, there are good arguments to fingerprint the cured coating instead of the liquid paint.

A two-pack thermosetting paint such as an epoxy-amine system has to be mixed in the correct ratio specified by the paint supplier. The mixture is then allowed to cure and solidify into the final coating.

If fingerprinting is carried out on each component of the system separately, i.e. the epoxy and the amine, it may not ensure that the final coating is of the expected quality, since the final coating requires that the two components are added in the correct amounts and would probably need to be mixed in a certain way, for a certain duration, and to be used within a limited amount of time due to a short pot-life. In this situation, fingerprinting of the liquid paint may become almost meaningless apart from ensuring that they are consistent from batch to batch.

Sample	Correlation
Batch 1 (Reference)	1.00
Batch 2	0.99

Batch 3	0.99
Batch 4	0.98
Batch 5	0.98
Batch 6	0.99
Batch 7	0.99

Table 2. Correlation for seven batches of cured epoxy primer, scanned on an ATR plate with ZnSe crystal.

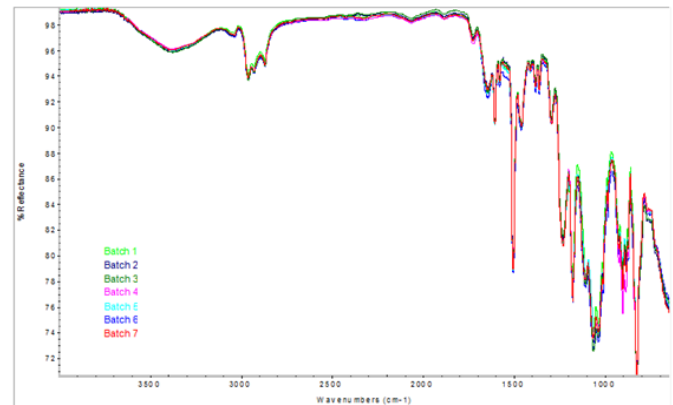


Figure 2. Reflectance spectra of seven batches of cured epoxy primer, scanned on an ATR plate with ZnSe crystal.

It is therefore desirable to complement the fingerprinting of liquid paint by also fingerprinting the final coating. If each batch of paint is mixed and cured properly, it is possible to obtain consistent spectra and any paint significantly out of specification can be detected. This is also applicable to single-pack systems since in certain cases it is possible to ascertain the degree of curing of the coating, which significantly determines the final coating performance.

A second argument in favour of fingerprinting cured coatings is that changes in formulation (not solvents) may be detected more easily, as discussed in the following section.

5. Reliability of fingerprinting in detecting changes in formulation.

The data in the previous sections shows that good correlation can be obtained between different batches of the same paint. However, if there are some changes in the formulation, could this be detected by looking at how the correlation is affected?

Figure 3 shows the spectra of one batch of the liquid epoxy primer on KBr window, and three other samples of this primer deliberately mixed with different amounts of a polyester resin. The spectra do not show obvious trending differences apart from the carbonyl region at ~1730 cm⁻¹ and the band at ~1300 cm⁻¹. The correlations are listed in Table 3.

From Table 3, it appears that the correlations are good, even with a significant 10% addition of polyester resin at 0.97. Without looking closely at the differences in the spectra themselves, one could have quite easily assumed that the paints with 2% and 5% polyester resin are acceptable and the issue would have gone undetected until a failure occurs. This obviously raises doubts about the effectiveness of fingerprinting in detecting changes in formulations.

Sample	Correlation (400-4000 cm-1)
Epoxy primer (Reference)	1.00

Epoxy primer with 2% polyester resin	0.99
Epoxy primer with 5% polyester resin	0.99
Epoxy primer with 10% polyester resin	0.97

Table 3. Full range correlation for liquid epoxy primer and three samples added with different amounts of polyester resin

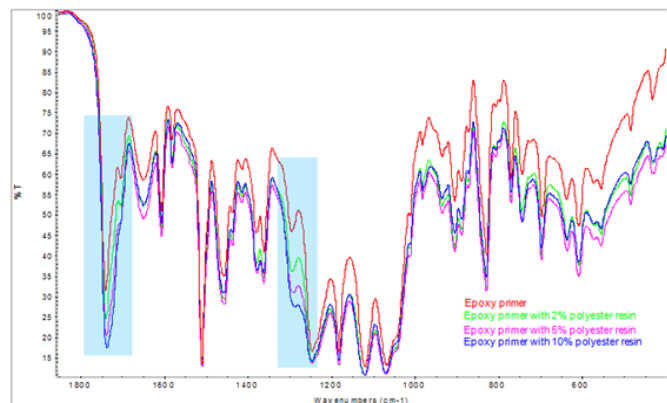


Figure 3. Transmittance spectra of liquid samples of epoxy primer and three samples mixed with different amounts of polyester resin. Regions highlighted in light blue indicate the bands most clearly affected by the addition of polyester resin. Only the wavenumber range 400-1850 cm⁻¹ is shown.

Figure 4 shows the spectra (ATR plate, ZnSe crystal) of one batch of the cured epoxy primer, similarly mixed with different amounts of the same polyester resin. The spectral differences are now clearer especially at the carbonyl region at ~1730 cm⁻¹ which is significantly affected by the polyester resin. In the previous example with liquid paints, ester solvents and those with carbonyl groups such as diacetone alcohol have a significant absorption at the carbonyl region. These were no longer present in the cured coating, making the differences in this region more visually obvious. However, the full range correlations listed in Table 4 again do not show significant differences except for the sample with 10% polyester resin at 0.95.

Sample	Correlation (650-4000 cm ⁻¹)	Correlation (1690-1780 cm ⁻¹)
Epoxy primer (Reference)	1.00	1.00
Epoxy primer with 2% polyester resin	0.99	0.81
Epoxy primer with 5% polyester resin	0.98	0.71
Epoxy primer with 10% polyester resin	0.95	0.63

Table 4. Correlation for cured epoxy primer and three samples added with different amounts of polyester resin

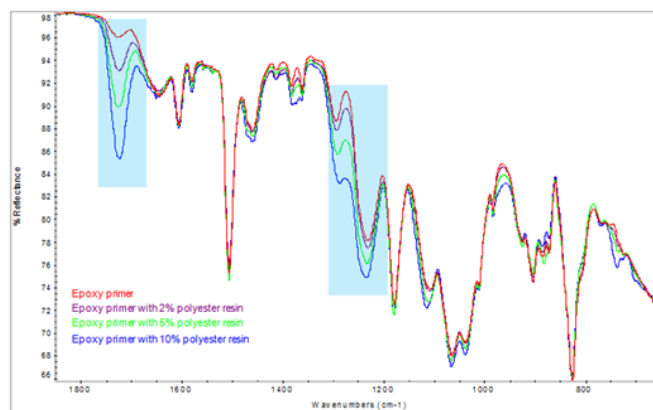


Figure 4. Reflectance spectra of cured samples of epoxy primer and three samples mixed with different amounts of polyester resin. Regions highlighted in light blue indicate the bands most clearly affected by the addition of polyester resin. Only the wavenumber range 650-1850 cm⁻¹ is shown.

One way to overcome this difficulty is to calculate the correlation only at certain regions, in this case at the carbonyl region which shows up the differences in correlation much more tellingly (Table 4). However, this requires that the analyst is very familiar with the paint spectrum in order to pick up unusual and sometimes tiny differences and then proceed to carry out further analysis and comparisons. A certain level of skill in FT-IR interpretation and knowledge of paint formulations are needed in order to do this effectively.

Another alternative is to carry out high sensitivity correlation comparison over the full spectrum range, if this option is available in the FT-IR software. When using this, one has to be extremely careful in determining the acceptable threshold since very similar materials may show large differences in correlation. There is a danger that perfectly good batches may be unnecessarily rejected.

There are techniques which allow the detection of small changes by analysing and comparing specific bands in the FT-IR spectrum. However, this again requires skilled personnel and would not be a simple and routine QC procedure.

6. Practicalities in Industry

A thorough discussion about the practicality of introducing an FT-IR fingerprinting program in the paint industry is difficult, since many manufacturing and application practices need to be considered, and these may differ considerably among formulators and end users. Some of these practices have been pointed out in the previous sections. Very importantly, different types of paint may require different preparation techniques for analysis, and some knowledge of the paint formulation needs to be available in order to obtain a meaningful interpretation. Furthermore, as can be seen in section 5, a certain level of skill is required to compare spectra visually and effectively instead of relying completely on the software to calculate correlations which may not clearly reveal that changes have been made to the formulation.

Before implementing a fingerprinting program, it is important to understand how to use this tool appropriately in accordance with the situation and also to understand its limitations with regard to reducing the problems observed in the field.

In the industry, it is always very easy and natural for the coating to be blamed if it fails since it is the most obvious thing on the surface of a substrate. However, things are not always what they seem and it is usually necessary to look beyond the surface in order to find out the root cause of a failure.

Apart from ensuring that the paint supplied is of the expected quality and consistency, there are several important factors that must be

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