Failure Analysis:
What Infrared Spectroscopy Can Tell You

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Many laboratory techniques can be used to help investigate coating failures. Certainly, spending some time at a microscope in careful examination of the samples is invaluable and should be the first step in any laboratory failure analysis investigation. A few minutes spent at a good quality stereo microscope can often yield clues that might save days of expensive laboratory time. More often than not, however, the second step in the investigation involves the use of infrared spectroscopy.

This article will present a brief introduction into the background and theory of infrared spectroscopy. Furthermore, practical examples of the usefulness of the technique will be demonstrated by presenting case histories of coating failures where infrared spectroscopy was the key technique in solving the problems.

The Basics of Infrared Spectroscopy

Spectroscopy involves the interaction of light, or electromagnetic radiation, with matter. Since the electromagnetic spectrum is composed of many different types of "light," such as ultraviolet, visible, and infrared, and since these different types of light interact with matter in different ways, it stands to reason that there are many different types or categories of spectroscopy. (See the box.)

Infrared spectroscopy relies upon the fact that molecules are in a constant state of motion. Not only can they move through space (such as a molecule of a gas diffusing across a room), but also they are constantly vibrating. It is this vibrational motion that is the basis of infrared spectroscopy.

A useful, although not particularly accurate, view of a molecule is that it consists of several balls (the individual atoms) connected by springs (the chemical bonds). Since the molecule is vibrating, both the bond length and the bond angles are constantly changing. Furthermore, these vibrations do not occur haphazardly, but at fairly well-defined frequencies. For example, consider a carbon atom bonded to two hydrogen atoms. This tiny fragment of a molecule can vibrate in several ways. For instance, the length of the bonds could change (a stretching vibration), which occurs at a frequency of approximately 2,900 cm^{-1}, or the angle between the two bonds could change, (a bending vibration), which occurs at about 1,470 cm^{-1}. (See the box on p. 69.)

The above discussion is important because when light is focused on a sample, if the frequency of that light identically matches one of the frequencies at which the molecule is vibrating, the molecule can absorb some of that light. It just so happens that the frequencies of molecular vibrations match the frequency range of infrared light. Therefore, infrared spectroscopy involves the absorption of infrared light by a vibrating molecule, resulting in what is termed an infrared spectrum.

Because even a simple molecule such as methyl ethyl ketone (MEK), a common paint solvent, can contain many different atoms bonded to one another in many different ways, it can vibrate in a fairly complicated fashion and therefore ab-
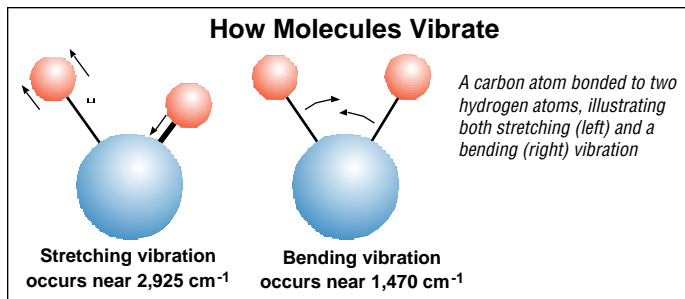

Visualization of Light Travelling through Space

direction of propagation of light
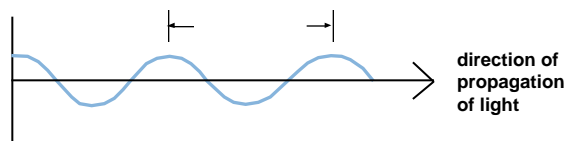
Light, as a form of electromagnetic radiation, travels through space with a wave-like motion, which has a characteristic frequency and wavelength to it, as shown above. The wavelength is the distance between successive maxima or minima and is given in various units of length, such as microns, angstroms, or nanometers. The number of complete cycles that occur in one second is the frequency of the light. One cycle per second is called a hertz, but in spectroscopy, a more convenient unit, related to frequency, is called the wave number, or reciprocal centimeter (cm^{-1}).

As it turns out, different types of light also have different energies associated with them, and this energy is directly proportional to the frequency of the light. Thus, ultraviolet (UV) light, which causes sunburn and can chemically degrade polymers and resins over time, is of relatively low frequency and hence of high energy. Visible light is, of course, the light that we see things by and is of medium frequency (energy). Infrared light is of relatively low frequency (low energy). Rather than ripping apart chemical bonds, like UV light can do, infrared light interacts with the internal vibrations occurring in molecules.

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sorb infrared light at many different frequencies. The resulting infrared spectrum (Fig. 1) shows many different bands occurring at many different frequencies. Indeed, each molecule has its own unique infrared spectrum or "fingerprint." Some spectra

How Molecules Vibrate

A carbon atom bonded to two hydrogen atoms, illustrating both stretching (left) and a bending (right) vibration

Stretching vibration occurs near 2,925 cm⁻¹

Bending vibration occurs near 1,470 cm⁻¹

are very similar to one another, with only subtle differences, but some are dramatically different, such as the spectra of an alkyd resin and an epoxy resin, shown in Fig. 2. Perhaps the most useful collection of reference spectra for the coatings industry is the *Infrared Spectroscopy Atlas,*[1] while Mirabella[2] has published an excellent volume on technique and theory.

When applied to coatings, infrared spectroscopy has a number of uses. These include the following.
- Identification of coating type
- Identification of certain pigments
- Determination of degree of cure
- Determination of mix ratio for multi-component coatings
- Detection of contamination
- Identification of batch-to-batch variations

It should be apparent from the above list that infrared spectroscopy can be a powerful tool in the field of failure analysis of coatings. The following are case histories, from the author's experience in this area, illustrating how infrared spectroscopy can be used to solve coating failures.

Blistering of a Coating System on an Offshore Oil Platform

The steel deck of an offshore oil platform was to have been coated with a three-coat system consisting of an epoxy zinc-rich primer, a white epoxy intermediate coat, and a gray urethane topcoat. The primer was specified to be 2–4 mils (50–100 micrometers) thick; the intermediate coat was to be 4–6 mils (100–150 micrometers) thick; and the urethane topcoat was to be 2–3 mils (50–75 micrometers) thick. Within a few weeks of completion, the coating system blistered. The blisters ranged up to approximately ¼ in. (6 mm) in diameter and were confined to one particular area a few hundred square feet in size. It was reported that the blisters were dry and that they were occurring within the gray urethane topcoat. In other words, not only were the backs of the blister caps gray, but gray urethane was noted remaining beneath the blistered coating. Samples that were forwarded to the laboratory included failing, blistered coating (including shavings of the intact coating beneath the blisters), non-failing coating, and a liquid sample of the specified urethane topcoat.

As usual, the investigation began at the microscope. The most obvious observation, which did not even re-

quire the use of the microscope, was that the back of the blistered coating was very rough. When examined microscopically, this roughness was due to an extensive "honeycomb" pattern in the urethane (Fig. 3). The cell walls of the honeycomb were smooth and very glossy. Furthermore, examination of shavings removed from directly beneath a blister indicated the same type of honeycomb pattern in the gray urethane that had not lifted from the deck.

In addition to the blistered urethane displaying the unusual pattern of honeycombs, it was found to have very poor solvent resistance. A properly mixed and crosslinked two-component urethane should have very good solvent resistance. However, a drop of MEK applied to the back of a blister chip immediately dissolved the honeycombed urethane. Equally surprising was the finding that the MEK had no effect on the front surface of the chip. A careful examination of the cross section of the chip sug-

Example of a modern Fourier transform infrared spectrometer
Photos courtesy of the author

gested a reason: there appeared to be two coats of gray urethane, not the single coat called for in the specification. Furthermore, both coats were thicker than specified. The thickness of the honeycombed lower coat was difficult to judge because of the peaks and valleys of the honeycomb structure, but it averaged approximately 5 mils (125 micrometers). The upper urethane topcoat was 9–12 mils (225–300 micrometers) thick, compared to the specified value of 2–3 mils (50–75 micrometers).

Chips from a good area were also examined. Only one coat of urethane was present, at approximately 4–5 mils (100–125 micrometers). There was no honeycombing, and the topcoat had good solvent resistance.

The next step in the investigation involved infrared spectroscopy. There are many ways to obtain an infrared spectrum, and the procedure used here was the potassi-
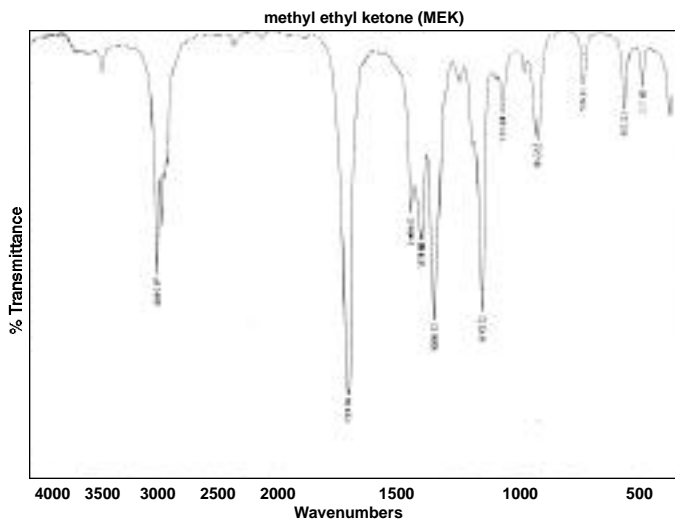
methyl ethyl ketone (MEK)

Fig. 1: Infrared spectrum of methyl ethyl ketone

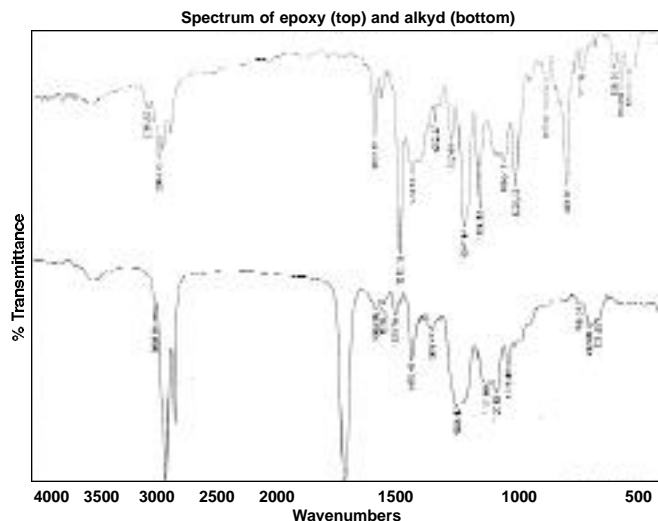**Spectrum of epoxy (top) and alkyd (bottom)**

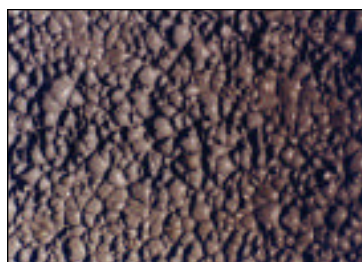*Fig. 2: Infrared spectra of an epoxy coating (top) and an alkyd coating (bottom)*

Fig. 3: Back side of disbonded urethane topcoat showing dramatic honeycomb structure

um bromide pellet technique. This involves combining a small amount of sample with potassium bromide powder (which functions as a transparent carrier), grinding in a mortar and pestle, placing the ground up sample in a die, and fusing it into a pellet under high pressure. The pellet is then placed in the optical path of the spectrometer, where infrared light is focused through it, and a spectrum is obtained over the range of 4,000–400 cm^{-1}.

Figure 4 shows spectra of both the blistered, honeycombed urethane from a failed area and urethane topcoat from a non-blistered area. Even a cursory examination shows that the two spectra are considerably different. The spectrum of the non-failing coating is typical of a urethane, with characteristic bands near 1,725, 1,690, and 1,515 cm^{-1}. To understand the origin of these bands, one must have knowledge not only of spectroscopy but also of urethane chemistry.

The type of urethane typically used in industrial maintenance coatings consists of two components: a polyol and an isocyanate. The polyol is a resin that has a number of hydroxyl (OH) groups on it. Often, the polyol is an acrylic resin. Additional bands in the infrared spectrum near 1,240 and 1,150 cm^{-1} indicate that such was the case here. In addition to hydroxyl groups, the acrylic polyol also contains a functional group known as a carbonyl group, which consists of a carbon atom double-bonded to an oxygen atom. This acrylic carbonyl group is responsible for the strong band near 1,725 cm^{-1}.

When the two components of a urethane coating are mixed together, the hydroxyl groups on the acrylic polyol react with the isocyanate component, forming the cured, crosslinked urethane. The urethane, or carbamate, as it is also called, also has a carbonyl group in its structure. Because the carbon atom in the urethane carbonyl group is also attached to a nitrogen atom, the urethane carbonyl absorbs at a different frequency than does the carbonyl coming from the acrylic polyol. The urethane carbonyl has its absorption band near 1,690 cm^{-1}.

With this background information in mind, it is apparent that not only are the spectra of blistered and non-blistered urethanes different from one another, but also the blistered urethane is really not a urethane at all. If it were, it would have a strong band due to the urethane carbonyl group near 1,690 cm^{-1}, as shown in the spectrum of the non-blistered topcoat. In fact, some additional laboratory work showed that the spectrum of the blistered "urethane" was quite similar to the spectrum of the Part A component of the coating (the acrylic polyol component), without the addition of any of the Part B isocyanate component.

In summary, it is apparent that the blistering of the coating system occurred in the few hundred square foot area because the contractor simply applied the Part A component of the two-component urethane, without mixing it with the Part B isocyanate component. The coating never cured because there was nothing for the acrylic polyol resin to react with. It is possible that the contractor realized this, since the topcoat was probably soft or sticky, and tried to fix it by applying a second coat of properly mixed urethane. This would explain why there were two coats of topcoat in the blistered area, rather than the specified single coat. Unfortunately, rather than fixing it, this "solution" just caused a different type of problem. The uncured, solvent-sensitive acrylic resin was partially redissolved by the solvents in the second, very thick coat (9–12 mils [225–300 micrometers] vs. the speci-
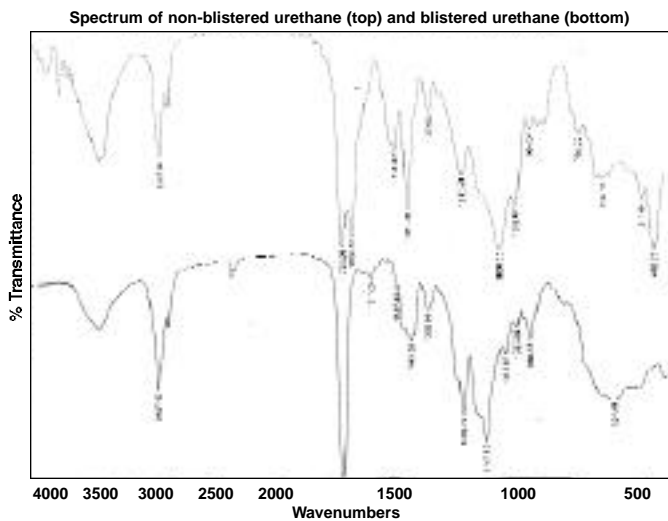
Spectrum of non-blistered urethane (top) and blistered urethane (bottom)

Fig. 4: Infrared spectra of non-blistered urethane (top) and blistered urethane (bottom)

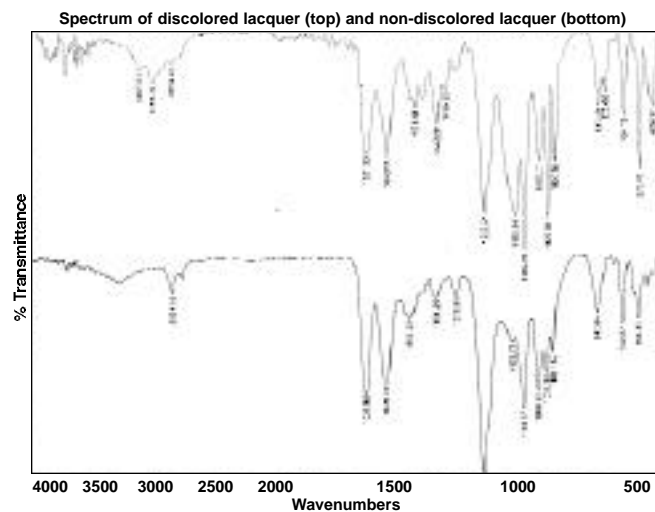**Spectrum of discolored lacquer (top) and non-discolored lacquer (bottom)**

Fig. 5: Infrared spectra of discolored lacquer (top) and non-discolored lacquer (bottom)

fied 2–3 mils [50–75 micrometers]), and it ruptured when this second coat cured and shrank. (All coatings shrink somewhat upon curing, imparting stress to lower layers.) The redissolving and rupturing of the first coat of "urethane" caused the formation of the honeycomb pattern and the blisters.

Discoloration of a Clear Lacquer

When it comes to naming common industrial maintenance coatings, furniture lacquers would not be on anybody's list. However, although the type of coating departs from those with which many of us are familiar, the example is included because it offers additional insight into the utility of infrared spectroscopy, especially when combined with some knowledge of coating chemistry.

As part of the remodeling of the offices of a large business firm, new desks and furniture were ordered. The furniture company used a clear catalyzed lacquer to finish the furniture. Much of the furniture was covered with thick glass tops for both decorative and protective reasons. Approximately one month after the furniture had been delivered, problems were noted in the form of a spotty, milky discoloration of the clear lacquer topcoat. The discoloration was present on the drawer fronts and sides of the furniture, but not on the tops, which were covered by the sheets of tempered glass.

Two samples of finished wood from the furniture, one displaying milky discoloration and one that was not discolored, along with liquid samples of the lacquer and catalyst, were furnished to the laboratory. As described by the client, the wood had a dark mahogany stain and had been finished with a clear lacquer. There were whitish or milky areas of discoloration on the failing sample, in a rather non-uniform, splotchy pattern. The discoloration appeared to be in or on the lacquer, rather than in the lower layers of stain.

Two techniques were used to analyze the samples: infrared spectroscopy and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS). The theory of SEM-EDS is beyond the scope of this article, but essentially, in addition to providing images at high magnification, it is an excellent tool for performing rapid multi-element analysis. Whereas infrared spectroscopy is very good at detecting organic compounds, SEM-EDS can detect virtually all of the other elements. This technique is therefore useful in detecting elements associated with inorganic or organo-metallic compounds.

The SEM-EDS analysis revealed an interesting finding. In addition to high levels of carbon and oxygen, to be expected of an organic coating, small amounts of sulfur were detected in the milky areas but not in the non-discolored areas. Initially, the significance of this finding was unclear.

Infrared spectroscopy was also performed on the various samples. Since the lacquer was thin and since the discoloration was likely even thinner, the potassium bromide pellet technique described above was not believed to be appropriate. Instead, the spectra were acquired by a technique called attenuated total reflectance, or ATR.

There are various types of ATR accessories, but essentially they all work by having a mechanism to firmly press a small sample against a crystal or other optical element, through which the beam of infrared radiation is focused. The angle of the beam hitting the crystal is such that the infrared light undergoes one or more internal reflections within the crystal. The infrared light immediately sets up what is called a standing wave at the interface of the crystal and the surface of the sample. This standing wave of infrared radiation interacts only with the surface of the sample, to a depth of perhaps one- or two-tenths of a mil (2.5–5 micrometers). Therefore, a spectrum is obtained of the surface of the sample, rather than of a bulk sample, as would be the case with a potassium bromide pellet.
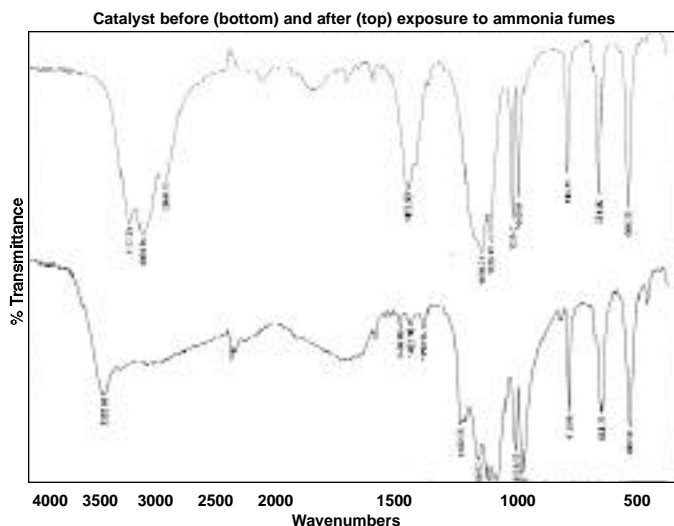
Catalyst before (bottom) and after (top) exposure to ammonia fumes

Fig. 6: Infrared spectra of catalyst before (bottom) and after (top) exposure to ammonia fumes

Spectra were obtained of both discolored and non-discolored lacquer (Fig. 5). The spectrum of the non-discolored lacquer is rather complicated, but it is consistent with a coating consisting of an alkyd resin and a urea formaldehyde resin, which is a common recipe for a catalyzed or "conversion" varnish. These two resin types react upon the addition of a catalyst, often aided by a low-temperature bake.

An examination of the two spectra in Fig. 5 shows that there are marked differences between the discolored and non-discolored lacquers. The discolored sample has additional bands near 3,170, 3,060, 1,450, 1,150, and 1,025 cm^{-1}.

At this point, the results seemed a bit puzzling. Although infrared spectroscopy clearly showed a slightly different composition between discolored and non-discolored lacquer, it was unclear what type of chemical or resin was responsible for this difference. SEM-EDS also showed small amounts of sulfur in the discolored lacquer and not in the non-discolored lacquer. But what was the source of the sulfur, and was it related to the problem?

It seemed almost impossible that there would be a source of sulfur in the clean, air conditioned offices where the furniture was located. Therefore, the sulfur was likely coming from the lacquer. It is common to catalyze such lacquers with p-toluenesulfonic acid (pTSA), which was confirmed once the material safety data sheets for the lacquer were obtained. However, the infrared spectrum of pTSA (Fig. 6) does not have any prominent bands that match the "new" bands present in the spectrum of the discolored lacquer.

Two chemical structures that would be expected to have bands similar to those found in the spectrum of the discolored lacquer are sulfonamides and salts of sulfonic acids. However, these materials are not used in lacquers, and they certainly would not be expected to be present in the office building. So what could possibly explain the SEM-EDS and infrared results? Perhaps there was a chemical reaction between something in the environment and the pTSA in the lacquer that converted it to either a salt of the acid or to the sulfonamide. But what could that possibly be?

It has been the author's experience that it is sometimes necessary to get away from a problem in order to solve it. One evening, mulling over the chemistry, the author thought it was likely that a strong base, such as ammonia, could react with pTSA to form either an acid salt or a sulfonamide. Then the thick glass tops used to protect the desks came to mind. What if they used ammonia, or a glass cleaner with ammonia, to clean the glass tops? Could fumes of ammonia or overspray of glass cleaner react with localized areas of lacquer that were rich in catalyst and cause the discoloration?

Figure 6 is the spectra of the catalyst component that was applied to a glass slide and allowed to dry, obtained both before and after exposure to ammonia fumes. The exposure to ammonia fumes resulted in dramatic changes to the spectrum, which included the appearance of strong bands near 3,170, 3,060, 1,450, and 1,150 cm^{-1}, the same locations of the "new" bands in the spectrum of the discolored lacquer. Furthermore, after exposure to the ammonia fumes, the catalyst changed from a clear material to a white material.

Based on the above observations and testing, the lacquer developed the milky white discoloration because of a reaction between the pTSA catalyst added to the lacquer and ammonia or an ammonia-based glass cleaner used by the office cleaning staff. Although it would take a fair amount of additional work to prove, it seemed likely that the catalyst was either added in excess or was not evenly distributed throughout the lacquer, and that the problem occurred in catalyst-rich areas.

Summary

The above case histories demonstrate the usefulness of infrared spectroscopy as a failure analysis tool and provide some insight into the procedures and thought processes involved in failure analysis. Although infrared spectroscopy is indeed a powerful technique, it must be kept in mind that it, like any analytical technique, has both advantages and limitations. In fact, it is sometimes necessary to employ more than one technique in the investigation of a coating failure.

References

1. *An Infrared Spectroscopy Atlas for the Coatings Industry* (Blue Bell, PA: Federation of Societies for Coatings Technology, 1980).
2. Francis M. Mirabella, *Modern Techniques in Applied Molecular Spectroscopy* (New York, NY: John Wiley & Sons, Inc., 1988).