Failure Analysis and Degree of Cure

Fig. 1: Catastrophic failure of undercured zinc-rich primer topcoated with epoxy
All figures courtesy of the author

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As anyone involved in failure analysis soon realizes, there are many different reasons why a coating can fail prematurely. This article will focus on one common and preventable cause of premature coating failure—degree of cure.

What Is "Cure"?

Before discussing cure, it may be helpful to discuss the concept of molecular weight. The molecular weight of a substance refers to how much a molecule of that substance weighs and is related to the size of the molecule. Most of the common chemicals which we routinely encounter are small molecules of low molecular weight, such as salt (sodium chloride), which has a molecular weight of 58, or methyl ethyl ketone, which has a molecular weight of 72. However, the molecules which make up the binder of a coating are very large, very high molecular weight polymers and resins. Some acrylic resins have molecular weights of well over 100,000. Two very important factors related to the chemical and physical properties of a coating include the type of resins or polymers composing its binder, and the molecular weight of these polymers and resins.

Coatings are broadly grouped into one of two classes: thermoplastic and thermoset. A thermoplastic coating dries by solvent evaporation.

Common examples of such a coating would be a vinyl acrylic latex house paint or a solvent-borne acrylic lacquer. The molecular weights of the resins or polymers in such coatings are as high as they are going to get when the paint is manufactured, and the drying of the wet paint simply involves the evaporation of the solvent (which, in the case of a latex, is mostly water).

Thermoset coatings can also dry by solvent evaporation. Some people might even consider evaporation to be an initial step in the curing process, since the coating will usually become less tacky during the drying stage. However, unlike thermoplastic coatings, thermoset coatings continue to cure through a chemical reaction. This reaction is usually, but not always, between various ingredients formulated into the liquid paint, such as a polyamide curing agent reacting with an epoxy base component. One of the oldest of thermoset coatings is the air-dry alkyd. Here, a complicated process of oxidation and crosslinking at the carbon-carbon double bonds (unsaturation) of the alkyd resin allows the resin molecules to react very slowly with one another, such that the final molecular weight of the cured alkyd resin is very much higher than its initial molecular weight. A moisture-cured urethane is a more modern example of a thermoset coating that chemically reacts with some species that is not in the can of paint—atmospheric moisture—to crosslink and cure.

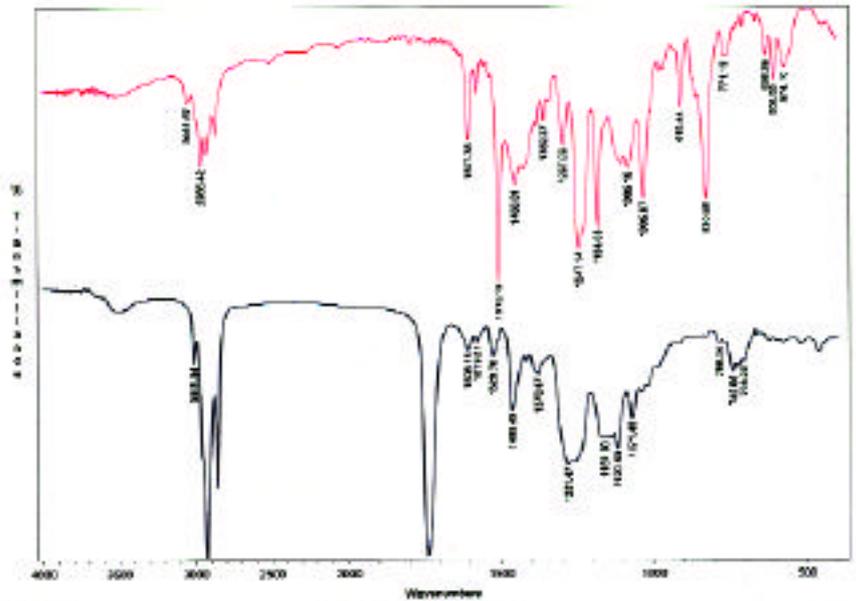As one might expect, the physical and chemical properties of a thermoset coating can depend greatly on

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

its degree of cure. When such a coating is initially mixed and applied, it consists of low molecular weight fragments or prepolymers. These prepolymers lack properties such as solvent resistance, chemical resistance, cohesive strength, impermeability, corrosion resistance, and tensile and flexural properties. Putting a coating into service before the prepolymers react to cure and develop the coating's properties would be somewhat like building a brick house without using any mortar. Over time, the house would fall apart. If a coating is put into service before it cures, or if something goes wrong and interferes with the normal curing process, premature failure can often result because the coating's properties will not have developed. An air-dry industrial maintenance coating might take several weeks to cure, and a plural-component sprayed polyurea might take sev-

eral seconds to cure. Regardless of the time the chemical reaction or curing process takes, the coating must not be put into service before it cures.

Failures Related to Incomplete Cure

There are several possible explanations for why a coating may not have cured properly. Possible reasons include a defective batch of coating, improper mixing on the part of the applicator (such as not observing the correct mix ratio, or adding the wrong thinner), unfavorable environmental conditions, and, for heat-cured coatings, improper baking conditions.

A very common example of a coating failure due to lack of cure is the splitting, or cohesive failure, of an inorganic zinc-rich primer topcoated with an epoxy intermediate/urethane topcoat (the so-called "Cadillac" of bridge coatings). When these failures
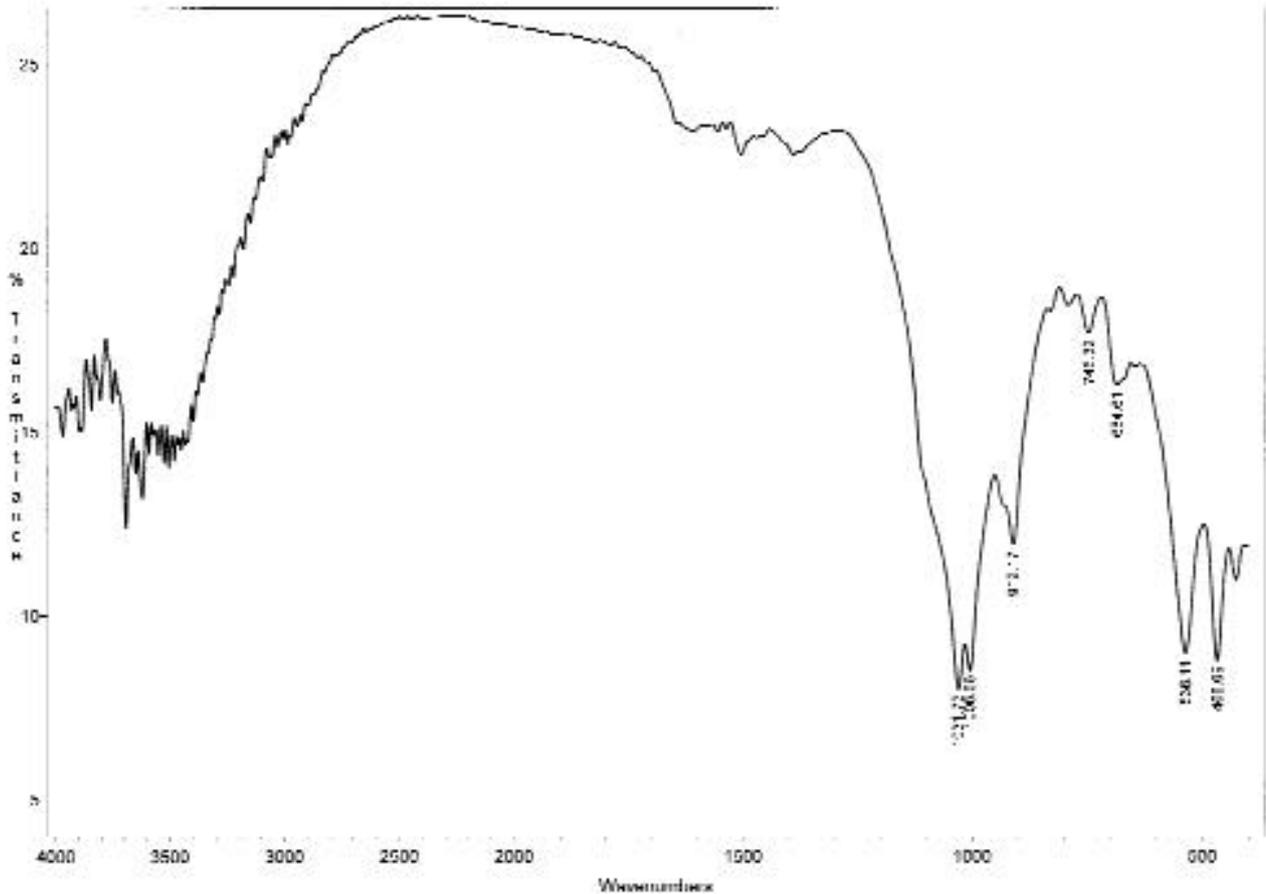
Fig. 3: Infrared spectrum of an inorganic zinc-rich primer. Note that there are practically no carbon-hydrogen absorption bands near 2900 cm^{-1}, a feature typical of a fully cured coating.

happen, they can often be catastrophic (Fig. 1). The undercured zinc-rich primer not only has poor solvent resistance, but also has low cohesive strength. It can be softened and weakened by the strong solvents in the epoxy intermediate coat.

Furthermore, when coatings cure, they shrink, resulting in a stress known as shrinkage stress. Since the undercured zinc-rich primer has already been weakened by the solvents in the epoxy intermediate coat, when the epoxy itself cures and shrinks, the resulting stress is sufficient to tear apart the underlying primer, sometimes resulting in large sheets of disbonded coating.[1,2]

Even the simple oil-based alkyd coatings mentioned above are not immune to failure because of lack of cure. Such coatings cure by reaction as the carbon-carbon double bonds with oxygen in the atmosphere. The process has been studied extensively but is still not completely understood. However, it is clear that it can be sped up by the use of certain catalysts, or "driers," which are often organometallic compounds such as cobalt naphthenate. Although failures involving alkyds that do not dry properly are rarely as catastrophic as the inorganic zinc-rich primer failures discussed above, it can be very frustrating to paint a bridge, or a house for that matter, and not have the paint dry. Not only can it be messy, but the soft, sticky alkyd will retain excessive amounts of dirt, turning an otherwise beautiful paint job into an unsightly problem. The lack of cure could be due to the wrong type or amount of catalyst formulated into the coating, to the use of the wrong type of alkyd resin, or perhaps to excessive coating thickness.

Urethanes are another type of thermoset coating whose properties, and hence serviceability, can be dramati-

cally decreased by lack of cure. Types of failures related to lack of cure include poor chemical resistance, poor adhesion, blistering, inferior weathering properties such as chalking or color fading, and, for the flexible variety, decreased tensile and flexural properties.

Lack of cure is not restricted to air-dry coatings. Some coatings will not react or cure properly unless heated to a certain temperature for a certain period of time. The elevated temperature speeds up the chemical crosslinking reaction, which would occur slowly or not at all, at room temperature. Therefore, the underbaking of coatings such as fusion-bonded epoxy powder coatings or polyester-melamine coil coatings can result in the coatings being undercured. Undercured epoxy powder coatings on buried underground pipe can result in poor adhesion, increased permeability, and a tendency to blister. An occasional, isolated blister is probably not a problem, particularly if the pipeline is also under cathodic protection. However, excessive blistering of hundreds of feet of pipeline—or even miles in the worst case scenario—can result in the draw of very large amounts of current. This may exceed the capacity of the cathodic protection system, or become very expensive as greater and greater amounts of electricity are required to protect the exposed steel.

Undercured coil coatings can suffer from excessive dirt retention, and significantly undercured or even over-cured ones can show inferior tensile and flexural problems, resulting in cracking upon forming. Furthermore, lack of cure of coil coatings applied to galvanized sheet results in a coating
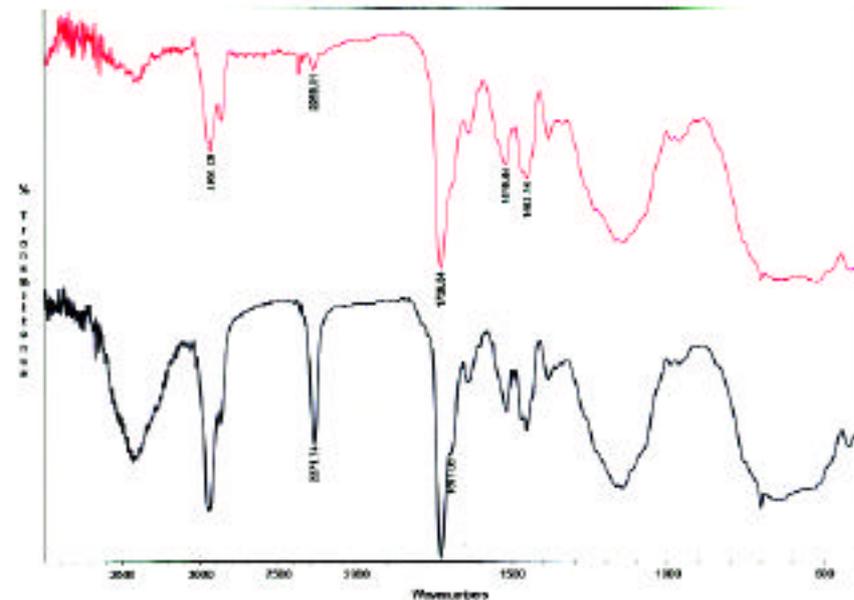

Fig. 4: Infrared spectra of a two-component urethane coating cured for 24 hours (bottom) and 2 weeks (top). Note that as the coating cures, the isocyanate band near 2270 cm^{-1} becomes dramatically weaker.

that is more permeable to water. The author is familiar with at least one instance where this led to blistering of the coating as a result of excessive white rust which formed under the permeable coating during storage (the "storage stain" familiar to many users of coil-coated galvanized stock).

Detecting Curing Problems
There is more than one way to investigate the possibility that a failing coating has not cured properly.

Field Investigation
Perhaps the most common procedure, and certainly the least expensive, is to perform some type of solvent resistance test. Since thermoset coatings cure by a chemical reaction, which transforms very low molecular weight starting material into very high molecular weight coatings, the ability of the coating to resist solvent improves as the coating cures. One

simple way to evaluate this is described in ASTM D5402 (Standard Practice for Assessing the Solvent Resistance of Organic Coatings Using Solvent Rubs). The Significance and Use section of this practice states that "Coatings which chemically change during the curing process, such as epoxies, vinyl esters, polyesters, alkyds, and urethanes, become more resistant to solvents as they cure. These coatings should reach specific levels of solvent resistance before being topcoated and before placing in service."

Briefly, ASTM D5402 is performed by saturating cheesecloth with methyl ethyl ketone (MEK), or another specified solvent, and rubbing the cloth back and forth (one back and forth stroke is referred to as a "double rub") on the coating, for at least 25 double rubs. The test area is then evaluated for such things as changes in appearance, hardness, or thickness, and the
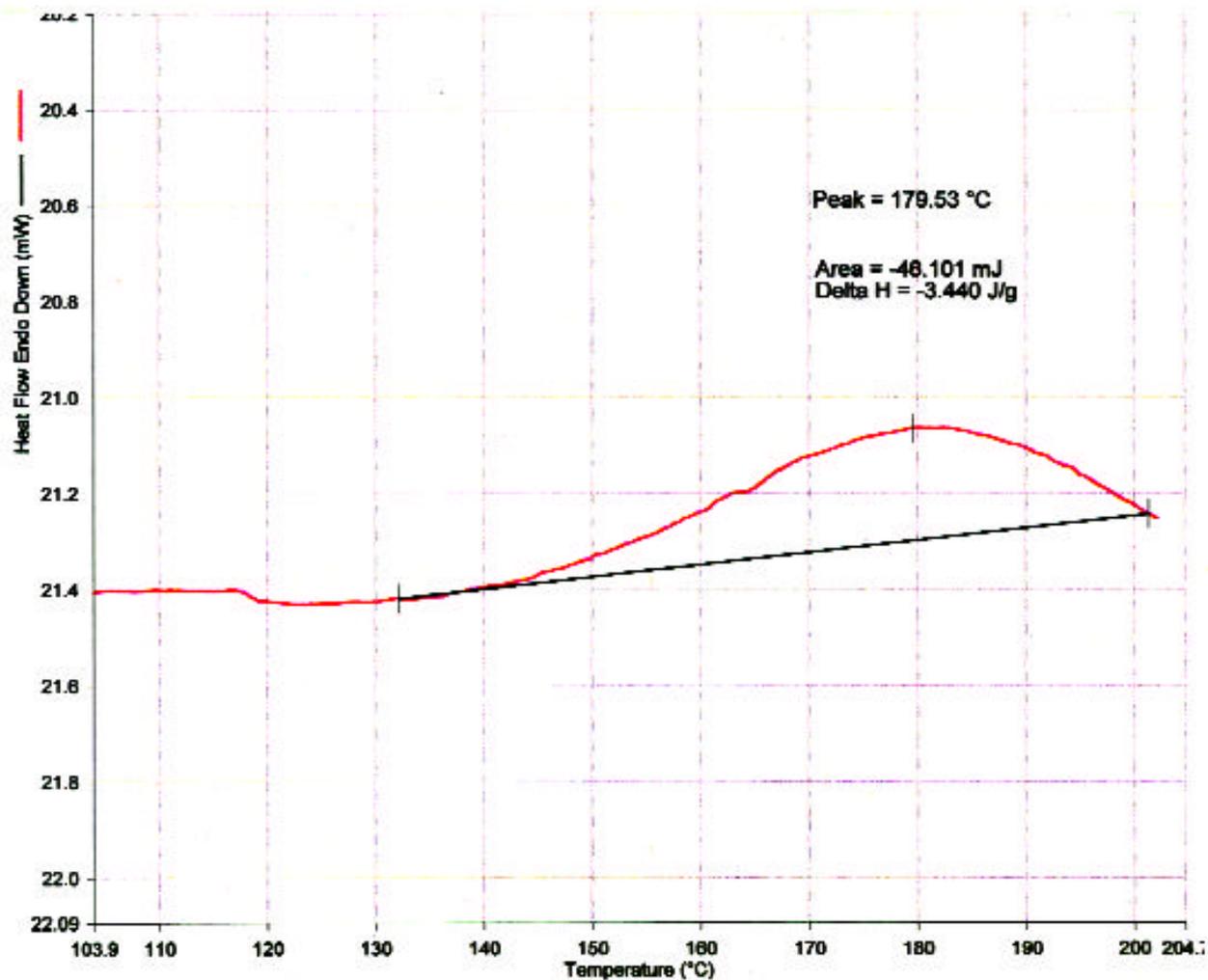
Fig. 5: A DSC heating curve of an uncured powder coating, displaying a strong exothermic peak from 145 to 205 C

cloth can be examined for color transfer of the coating. The author often uses a slightly modified version of this procedure, substituting cotton swabs for cheesecloth. ASTM D4752 (Standard Test Method for Measuring MEK Resistance of Ethyl Silicate (Inorganic) Zinc-Rich Primers by Solvent Rub) is similar to D 5402, but as the title suggests, was developed specifically for inorganic zinc-rich primers.

Solvent rub testing is a fairly rough way of measuring degree of cure. It is quite capable of detecting moderate to large differences in cure, but not small differences. It should also be kept in mind that not every properly cured coating has the same degree of solvent resistance. Thus, it would not be fair to assume that an alkyd coating would have the same degree of solvent resistance as an epoxy-phenolic. Therefore, it is useful for the person doing the testing to have a control sample of the coating in question, or at least a non-failing sample, in order to establish what the "normal" degree of solvent resistance is for the particular coating.

Laboratory Investigation

In the laboratory, infrared spectroscopy is often a very useful technique for investigating degree of cure. In some instances it can be much more sensitive than a solvent rub test.

Very briefly, infrared spectroscopy relies upon the fact that molecules are in a constant state of motion, or vibration. Indeed, it is convenient to think of a molecule as a collection of balls

(atoms) connected by springs (the chemical bonds holding the molecule together). Depending on the type of atoms and the type of chemical bonds holding them together (springs), portions of the molecule will vibrate at different frequencies, often measured in units of cm^{-1} (reciprocal centimeters). The frequency of vibration is very dependent on the structure of the molecule. Therefore, a carbon atom single bonded to a hydrogen atom will always show a stretching type of vibration near 2,800–2,950 cm^{-1}.

Likewise, a carbon atom double bonded to an oxygen atom will typically vibrate at about 1,650 to 1,750 cm^{-1}. The significance of this is that when infrared light is focused on or through a sample, if the frequency of the infrared light matches one of the vibrations in the molecules making up the sample, the sample will absorb some of that particular light. Since there are many different structural features in a typical organic molecule (or, in our cases, polymer), which are often referred to as "functional groups," the sample will absorb infrared light at numerous frequencies and to differing degrees. The result is an infrared spectrum, which is very characteristic of the sample being analyzed. Fig. 2 shows the infrared spectrum of both an alkyd and an epoxy, and clearly illustrates that the two spectra differ substantially in appearance.

Not only are the positions of the bands in an infrared spectrum indicative of the chemical structure, or functional groups, of the sample, but also the intensity of the bands is proportional to the concentration of that particular functional group. It is this quantitative aspect of infrared spectroscopy that makes it a useful tool in

measuring degree of cure.

The catastrophic failure of an undercured inorganic zinc-rich primer topcoated with an epoxy intermediate coat has been previously discussed. While solvent rub testing might be able to show that the primer was undercured, infrared spectroscopy can detect smaller variations in degree of cure. A detailed discussion of this procedure has been previously presented.[3] Briefly, when ethyl sili-

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cate zinc-rich primers cure, they do so by reaction with atmospheric moisture. This results in a cleavage of the ethoxy groups (CH_3CH_2O-) in the silicate prepolymer and their evaporation from the coating in the form of ethyl alcohol. Since the ethoxy groups are rich in carbon-hydrogen bonds, the absorption bands in the infrared spectrum due to carbon-hydrogen vibrations in the 2,800–2,950 cm^{-1} region decrease upon curing (Fig. 3). This decrease can be measured quantitatively by infrared spectroscopy, allowing one to determine the primer's degree of cure.

Infrared spectroscopy is also ideally suited to monitoring the degree of cure of urethane coatings. Urethane coatings consist of a component A, which is typically a hydroxyl (-OH) functional polyester or acrylic resin, and a component B, which contains an isocyanate (an isocyanate contains the -NCO functional group). When mixed together, these two ingredients react to form the actual urethane. Fortunately for the analytical chemist, the isocyanate group has a very strong and very characteristic band in the infrared spectrum near 2,270 cm^{-1}. There is very little else that absorbs in this region of the spectrum. Since the isocyanate group is consumed during the curing reaction, resulting in the production of the urethane polymer, the intensity of the 2,270 cm^{-1} isocyanate band decreases, as shown in Fig. 4. Therefore, the degree of cure of a urethane can be monitored by measuring the decrease in the intensity of this band, usually relative to some other band in the spectrum.

It should be pointed out that when doing failure analysis, alternative possibilities should be considered. Thus, it is entirely possible that the spectrum of a failing urethane could have no trace of any unreacted isocyanate, and yet the coating could be completely uncured. This could happen if the contractor neglected to add any of the isocyanate curing agent to the component A. Fortunately, an experienced investigator would normally recognize this by other clues in both the physical nature of the sample and the features of the infrared spectrum.

Although infrared spectroscopy can theoretically be used to monitor the degree of cure of epoxy coatings,[4,5] the author has found it to be of very
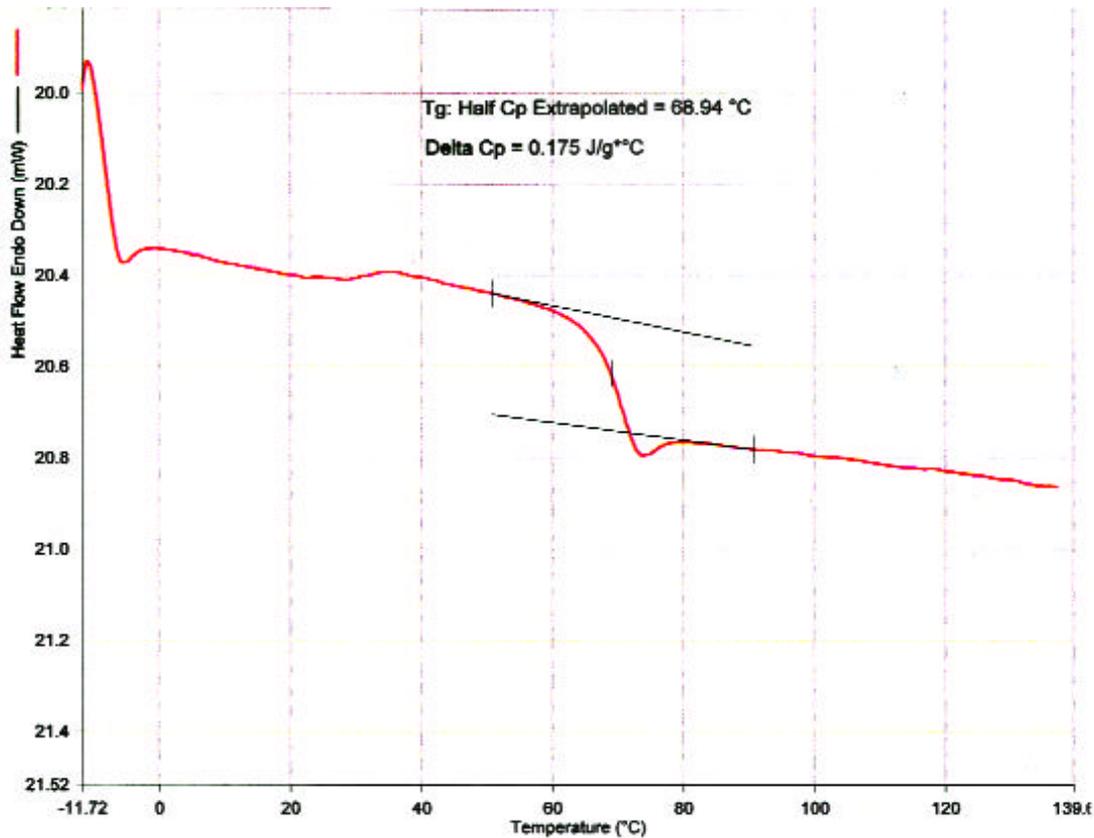
Fig. 6: A DSC heating curve of an epoxy coating. Note the sudden change in the position of the baseline in the 60-80 C region due to its glass transition (measured at 68.9 C).

in a small aluminum pan, which is typically crimped shut. Inside the sample compartment of the furnace there are two small platforms, one for the sample and one for the reference. (The reference is often just an empty aluminum pan.) Attached to the undersides of the sample and reference platforms are temperature sensors, or thermocouples. The furnace is programmed to heat up over a certain range, at a certain rate (for instance, from 20 to 200 C at 10 C/minute).

If nothing happens to the sample, one essentially gets a straight line, although possibly sloping in either the positive or negative direction, in a plot of heat flow versus temperature. However, if a thermal "event" occurs, there will be a deviation from this baseline. If the thermal event is curing of the sample due to reaction between residual unreacted components, the sample will liberate heat. (The curing reactions of paints and coatings are exothermic, meaning that they evolve heat.) The evolution of heat by the sample will be detected by the thermocouple attached to the underside of the sample platform, and the heating curve will show a peak in the exothermic direction. An example of such an

limited practical use. However, one of the main reasons why epoxy coatings do not cure properly is because they have not been mixed properly. For instance, many polyamide epoxy coatings are to be mixed in the ratio of 1.0 parts of the A component to 1.0 parts of the B component, by volume. One of these components contains the epoxy resin and the other contains the polyamide curing agent, or hardener. For instance, if only half of the curing agent is used, the coating will not cure properly and will likely fail prematurely. Solvent rub testing may indicate lack of cure, and infrared spectroscopy can often

determine the approximate mix ratio.

Mention was made previously of blistering failures of fusion-bonded epoxy pipeline coatings, and failures of oven-cured coil coatings that have not been properly cured. While solvent rub testing might reveal deficiencies in the cure of such coatings, and while there is a possibility that infrared spectroscopy might also prove useful, differential scanning calorimetry (DSC) is the technique of choice for these types of coatings.

A differential scanning calorimeter is, in essence, a very expensive and precisely controlled furnace. The sample (usually a few milligrams) is placed

exotherm is shown in Fig. 5.

The presence of an exotherm in a DSC curve of a suspect coating sample clearly means that the sample has not been fully cured and that residual functional groups remain for continued reaction. However, it is also quite possible that the coating might show no exotherm, yet still be undercured. This could happen, for instance, in the case of a two component epoxy if it had not been mixed correctly. There might very well be unreacted epoxy resin present, but there will be no chemical reaction, and hence no exotherm, if there is no curing agent left to complete the cure. Or perhaps the wrong curing agent was used, either during the factory production of the coating or by the applicator at the jobsite.

Fortunately, a DSC curve usually gives an additional piece of information besides a curing exotherm: the glass transition temperature. There are various definitions for the glass transition temperature (often abbreviated Tg). The most common, and perhaps most practical definition, is that the glass transition temperature is that temperature below which a polymer is in a hard, glassy state, and above which it is in a flexible or rubbery state. The glass transition temperature can vary from one type of polymer to another. However, for any specific thermosetting polymer type, the glass transition temperature is proportional to the coating's crosslink density, or degree of cure.[6,7] In other words, the greater the degree of cure, the higher the coating's glass transition temperature. This is a very important concept, since it allows one to measure a coating's relative degree of cure independent of whether or not there also happens to be an exotherm in the DSC curve. As we have seen above, the absence of an exotherm does not necessarily mean that a coating is fully cured. However, a low Tg, compared to either a reference sample or a non-failing sample, is a clear indication of lack of cure.

The glass transition is neither an exothermic nor an endothermic process, and hence there are no actual peaks associated with it in a DSC curve. Instead, when a coating goes through its glass transition, there is a relatively sudden shift in the position of the baseline, as shown in Fig. 6. Sometimes this shift is rather strong and distinct, and sometimes it is more gradual. In either case, it can be easily measured by the software which operates all modern scanning calorimeters.

Summary

In summary, the lack of cure of a protective coating can be caused by many factors, including a defective batch of coating, application errors such as mismixing or inadequate baking, or unfavorable environmental conditions. Lack of cure, for whatever the reason, can often lead to a premature coating failure. Solvent resistance testing can often detect moderate or large differences in degree of cure, and is an inexpensive technique that can often be performed on-site. Infrared spectroscopy and differential scanning calorimetry are two laboratory techniques that can detect more subtle differences in degree of cure. Both techniques can sometimes shed light on why the sample is undercured.

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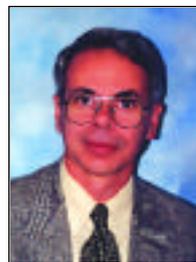
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