10 Examples of Coating Failures

The various examples presented in this chapter have been selected to encompass not only a broad spectrum of coating failures, but also to demonstrate the utility of the various analytical techniques which have been described in the earlier chapters.

10.1 Urethane Topcoat Disbonding from Epoxy

The structural steel members for a new bridge were primed, coated with a two-component polyamide epoxy intermediate coat, and subsequently topcoated with a two-component aliphatic polyurethane. The specified mix ratio for the white epoxy intermediate coat was 1:1, by volume, with a required 20 min induction time. It was to be applied at a dry film thickness (*DFT*) of 4–6 mil. The blue urethane finish coat, which was relatively glossy, had a specified mix ratio of 4 parts of component 'A' (the pigmented portion which contained the acrylic polyol) to one part of component 'B' (a 'clear' containing the aliphatic isocyanate). It was to be applied at a *DFT* of 2–4 mil.

Approximately three months after the job was completed, it was found that there were areas where the urethane topcoat was peeling from the epoxy intermediate coat. A field investigation showed that while the actual amount of spontaneous peeling amounted to perhaps only 1 or 2 % of the painted surface, tape-adhesion testing indicated very poor inter-coat adhesion even in many visually intact areas. Although there were some exceptions, the bulk of the peeling and poor adhesion was on the horizontal and southern-facing exposures, with generally better adhesion in shaded or sheltered areas.

Several relatively large (up to 1 in^2) chips of delaminating topcoat were obtained. In addition, scrapings of the epoxy coating were obtained after the topcoat was peeled away. Shavings of non-failing, well-adhered topcoat were also obtained, as well as a few relatively thick chips from non-failing areas

consisting of the entire three-coat coating system. Although attempts were made at the job site to obtain 'clean' samples of epoxy intermediate coat from non-failing areas, this was very difficult due to the excellent adhesion in these areas.

Since the failure occurred months after the painting was completed, no quantities of liquid paint were left over, and batch retains from the coating supplier were not made available. However, fresh, off-the-shelf samples of coatings were provided.

As previously pointed out, the place to begin a failure investigation in the laboratory is at the microscope. Microscopic examination showed little difference in topcoat thickness between failing and non-failing samples. These ranged from a low of approximately 2 mil to a high of approximately 6 mil. Although the latter was over the recommended maximum of 4 mil, this was not felt to be high enough to be causative. Furthermore, non-failing samples were also found which were 6 mil thick.

At first glance, an examination of the back of the disbonded topcoat failed to reveal more than just a slight amount of dirt or debris, and certainly not enough to account for such poor adhesion. However, when viewed with oblique lighting, there appeared to be a faint, patchy haze on the back of the blue topcoat. Of course, the back of the non-failing topcoat was not available for examination, since it was firmly adhered to the epoxy intermediate coat.

In addition to the microscopic observations, infrared spectroscopy was also performed. Spectra were obtained of topcoat and epoxy from both good and bad areas, as well as on draw-downs of the fresh batches of coating material. Since, with multiple-component coatings, there is always the possibility of 'mis-mixing', draw-downs were prepared at both the specified mix ratios, and at mix ratios with a 50 % excess of each component.

Although the spectrum of an epoxy is usually not greatly influenced by cure times in excess of a day or so, the same is not true of urethanes. Therefore, the urethane draw-downs were cured at slightly elevated temperature (110 °F (43 °C), a temperature which much of the steel likely reached during the summer afternoons) for one week prior to obtaining the spectra.

The results of the infrared analysis indicated that 'mis-mixing' of the urethane finish coat was not an issue. The approximate mix ratio of the urethane was determined by using IR spectroscopy because of minor, predictable changes in the relative intensities of some of the silicate-extender pigment bands compared to the ester carbonyl vibration from the polyol component, as well as by variations in the amount of actual carbamate (urethane) formed.

However, the analysis of the epoxy produced mixed results. Infrared spectroscopy proved to be a viable technique for determining the relative amount of the polyamide component to the epoxy component. This was primarily because of variations in the relative intensity of the amide carbonyl band near 1640 cm^{-1} to that of a band near 1610 cm^{-1}, due to a C=C stretching vibration of the aromatic ring present in the epoxy resin. Some

mis-mixed coating was found in failing areas, with no mis-mixed epoxy in the three non-failing areas sampled. However, of the five samples of failing epoxy, three were properly mixed. Therefore, at this point the results seemed inconclusive.

Although the microscopic observations seemed to indicate that the delamination was a clean one between the urethane topcoat and the epoxy, there was still the issue of what appeared to be a faint haze on the back of the blue topcoat. In order to further investigate this, infrared spectra were obtained of both the front and back surfaces of failing paint chips by using attenuated total reflectance (ATR).

The ATR spectra obtained from the fronts of the topcoat samples were typical of urethanes (see Figure 10.1(a)). Not surprisingly, being reflectance spectra, they differed in several respects from the transmission spectra obtained by the potassium bromide pellet technique. More importantly, however, they differed somewhat from the ATR spectra obtained from the back of the samples. The spectra obtained from the back surfaces (see Figure 10.1(b)) contained additional bands near 1510, 1180 and 830 cm^{-1}, all of which are typical of epoxies.

Based on the above findings, it certainly appeared that the reason for the inter-coat delamination was degradation of the very upper surface of the epoxy intermediate coat prior to topcoating, thus resulting in an extremely thin, loose layer that acted as a 'bond breaker.' This mechanism was consistent with the observation that the bulk of the failure occurred in those areas receiving more sunshine, coupled with the known fact that epoxy coatings chalk upon exposure to sunlight. Two issues, however, seemed unresolved. First of all, inspection records showed that the bulk of the steel was topcoated within two weeks of when the epoxy was applied – a relatively short period for surface degradation to occur. Secondly, although not consistent, failing areas were found where the epoxy had been mis-mixed. How much of a factor did this mis-mixing play in the failure? Did it speed up the degradation of the epoxy? Would it, on its own, have accounted for inter-coat delamination?

One might be able to predict these answers, given an intimate knowledge of the formulas of the epoxy and urethane coatings, coupled with a detailed understanding of the chemistry of their cross-linking, the chemistry and physics explaining their adhesion to one another, and a thorough understanding of the degradation mechanism induced by weathering. However, in addition to the coating manufacturer not wishing to publicize his formulas for the world to see, such depth of knowledge into the behavior of coatings does not yet exist. Therefore, the best way to answer the questions posed above is by experiment, and not theory.

The epoxy intermediate coat was applied to steel test panels at both the correct mix ratio, and at the off-ratio found on some of the failing field samples (approximately 1.5:1 rather than 1:1). Three sets of panels were prepared, so that they could be cured in different fashions prior to topcoating. One set was

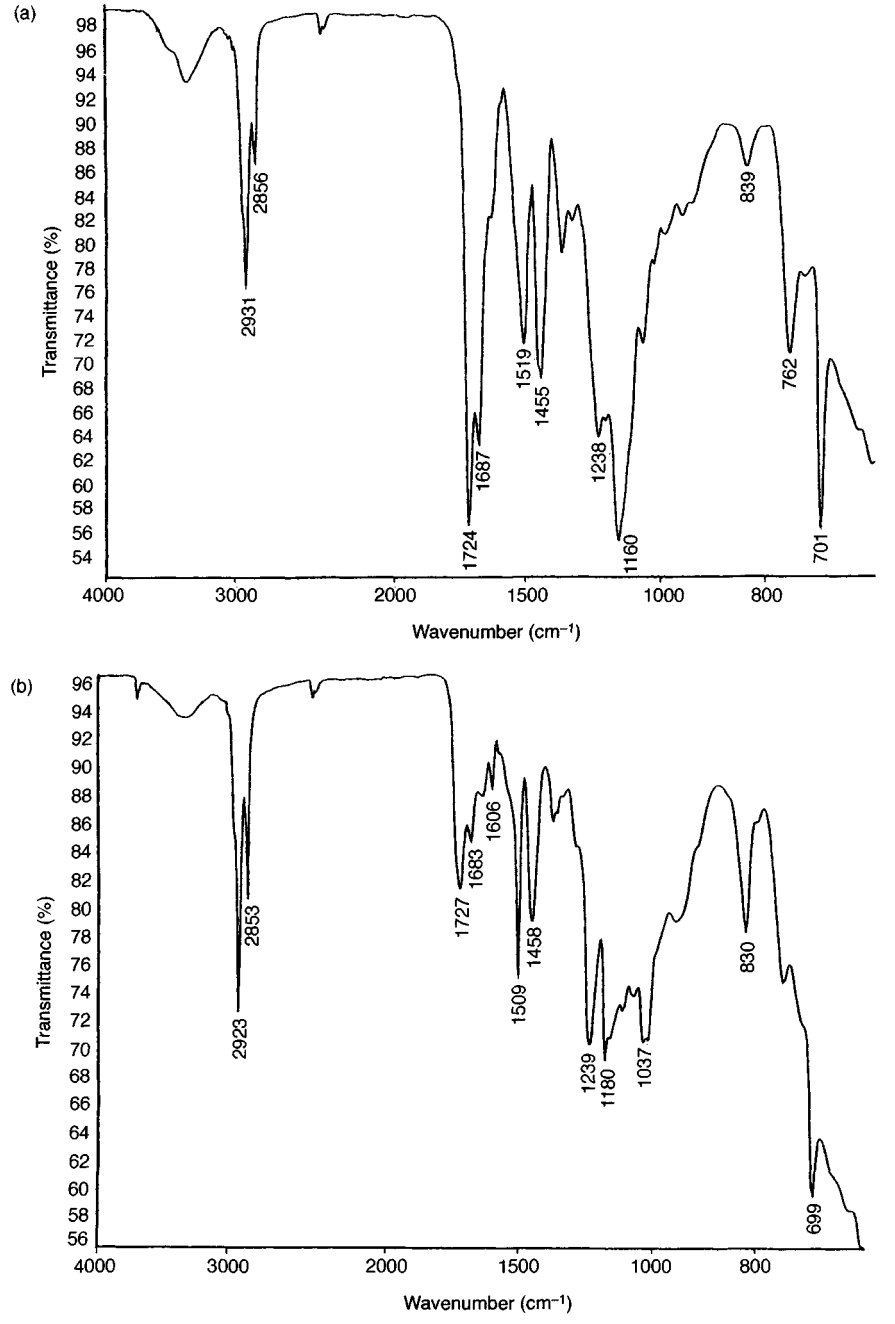


Figure 10.1 ATR spectra obtained from (a) the front (non-peeling) and (b) the back (peeling) surfaces of a urethrane topcoat

allowed to cure for two weeks at laboratory ambient conditions. A second set was cured for 11 days at laboratory ambient temperature and then for an additional three days in an ASTM G-53 accelerated weathering device equipped with UVA bulbs. The third set was cured overnight at laboratory ambient conditions, and then cured for an additional 13 days in the accelerated weathering device. Once topcoated with urethane, all of the panels were allowed to cure for an additional week at laboratory ambient conditions prior to being evaluated for adhesion.

Adhesion testing was carried out in accordance with the tape adhesion procedure previously discussed (ASTM D3359). This method involves using a knife or other cutting tool to scribe a cross-hatch pattern into the panel, followed by the application of a special pressure-sensitive adhesive tape. The tape is then rapidly removed, and the adhesion is assessed in accordance with the method's rating system. Ratings can range from a '5B', corresponding to no loss of adhesion, to a '0B', corresponding to 65 % or more delamination.

The adhesion testing on the laboratory panels produced some interesting results, as shown in Table 10.1.

The results indicate that mix ratio has no effect on inter-coat adhesion when there is no UV exposure, and only a slight effect when there is UV. However, even the properly mixed epoxy shows a serious drop-off in inter-coat adhesion after only three days of exposure to UV light, with more dramatic consequences being observed after 13 days.

Based on the field investigation and subsequent laboratory testing, the coating failure is due to the inability of even the properly mixed epoxy intermediate coat to withstand even a short exposure of heat, light and moisture. This weathering effect caused a visually undetectable deterioration in a very thin surface layer of epoxy. This loose, degraded epoxy resulted in peeling of the subsequently applied urethane topcoat.

10.2 Blistering of an Epoxy Tank Coating

A shop in the northeast United States fabricated and coated the structural steel for an above-ground potable water tank. The specification called for a near-white

Table 10.1 Adhesion as a function of mix ratio and cure for an epoxy coating

Epoxy mix ratio	Epoxy cure treatment	Inter-coat adhesion rating[a]
1:1	ambient	4B
1.5:1	ambient	4B
1:1	ambient + 3 days UV	2B
1.5:1	ambient + 3 days UV	1B
1:1	ambient + 13 days UV	0B
1.5:1	ambient + 13 days UV	0B

[a]Measurements made by using ASTM D3359, Method B.

metal blast, followed by a two-component polyamide epoxy primer and a two-component polyamide epoxy topcoat. Both coats of epoxy were specified for 3–5 mil *DFT*, for a total coating thickness of 6–10 mil. The manufacturer's product data sheets for the epoxies listed 40 °F (4 °C) as the minimum application temperature. The work was done in the fabrication shop in the month of March, with air temperatures of approximately 50 °F (10 °C). The coated steel was shipped to the job site, where the tank was subsequently erected and put into service. The interior coating blistered within 6 months.

An investigation of the interior of the tank showed extensive blistering over the majority of the coated steel that was below the waterline. Most of the blisters were approximately 1/16″ in diameter, although some were as large as 1/4″. There was no exposed steel, and no visible corrosion. When the blisters were cut open, a clear, odorless liquid was contained inside, and the bare steel was exposed. When examined with a pocket microscope, no rust was present on the steel, and the blast cleaning profile was evident. Although the adhesion was obviously very poor immediately at a blister, the adhesion between blisters was very good, and the coating was still quite hard.

The coating thickness was surveyed by using a magnetic-dry-film thickness gauge. Although most of the steel exhibited blistering, there were some isolated areas of several square feet in size that were not blistered. The total coating thickness in the non-blistered areas ranged from 5–8 mil, while in the blistered areas, it ranged from 7–13 mil. Thus, the non-blistered coating fell within the specified thickness range, while the blistered coating was either within or above the specified thickness.

Samples of blistered, as well as tightly adherent, non-blistered, coatings were obtained. Furthermore, small quantities of the liquid inside the blisters were also obtained by using syringes. Note that when obtaining such samples, it is suggested that the surface of the coating be cleaned prior to puncturing it. Furthermore, some object other than the syringe being used to collect the sample should be used to puncture the blister. This could be a pin, or even the needle from another syringe. The reason is to prevent contaminating, clogging or breaking of the sampling syringe. Furthermore, in this case although no paint was left over, fresh samples of primer and topcoat were obtained.

As usual, the investigation began at the microscope. Measurements of coating thickness confirmed the field observation: the blistered coating was either within or above the specified thickness, while the non-blistered coating was always within the specified thickness range. Furthermore, the back of the blister caps had a rough texture, which was apparently the replica of the blast profile. Except for an occasional particle of 'blasting smut' (either minute particles of mill scale dust or broken-down blasting abrasive), the back of the blister caps appeared clean. There was very little cross-sectional porosity in the coating, and no evidence of microscopic pinholes in the tops of the blisters.

As with most two-component coatings, the possibility of mis-mixing usually needs to be investigated. Circumstantially, mis-mixing seemed an unlikely

possibility for two reasons. First of all, even in the space between blisters the coating was hard, tough, and well adherent, with all of the characteristics to be expected of a properly mixed, well-cured epoxy. Secondly, the vast majority of the steel was blistered. While it is certainly possible to mis-mix an occasional kit of coating, it is unlikely that nearly all of the paint needed to coat the entire tank could have been mis-mixed, especially in a shop environment with painters familiar with epoxy coatings.

Despite the circumstantial evidence against mixing errors, this possibility still needed to be investigated. Again, infrared spectroscopy proved to be a successful tool in determining the coating's mix ratio. Difficulties were encountered, however, in employing the polyamide region near $1650\,cm^{-1}$, since traces of moisture in some of the samples contributed to a water band near $1620\,cm^{-1}$, thus interfering with the analysis. Although thorough oven drying of the samples might have solved this problem, this was unnecessary because another pair of bands in the spectrum varied consistently with the mix ratio. These were the $1245\,cm^{-1}$ band originating from an aromatic carbon–oxygen stretching vibration of the epoxy resin, and the $1020\,cm^{-1}$ band coming from the talc extender pigment. As suspected, mis-mixing of the epoxy was not a problem.

The next logical step in the analysis seemed to be a characterization of the liquid contained within the blisters. This was almost certainly water, but additional minor components might explain the blistering mechanism. The liquid was analyzed for two components, i.e. salts and solvents.

The theory behind osmotic blistering has already been discussed previously in this text. Briefly, such blistering can occur if there is a solution of high concentration behind a coating, and a solution of low concentration on the other side of the coating. Since water can eventually permeate any coating, it can dissolve water-soluble contaminants either in the coating or on the substrate. This results in a solution of high concentration, which is separated from the solution of low concentration (the potable water in the tank) by a semi-permeable membrane (the coating). In such situations, the water-soluble material is usually a hydrophillic solvent, or a salt.

Salt levels in the blister liquid were evaluated by using ion chromatography, which is very sensitive and which requires very small samples. Only chloride and sulfate were detected, at concentrations of approximately 15 and 5 parts per million (ppm), respectively. This was somewhat less than the concentrations in the tank water, and it was unlikely that they were responsible for the massive blistering failure.

The presence of solvents in the blister liquid was evaluated by gas chromatography (GC). This showed that, although the blister liquid was almost entirely water, it also contained a small amount (approximately 200 ppm) of a glycol ether solvent. This same solvent was detected in large quantity (several %) in the liquid sample of the epoxy primer, and was therefore not an adulterant. Such solvents typically show substantial water solubility, and can

clearly cause osmotic blistering. Therefore, the cause of the failure was the use of a coating that was not formulated properly for its intended service.

Although a relatively straightforward failure analysis, the above example brings out several interesting factors, one of which is thickness. Although a blistered coating was observed above the maximum recommended thickness, it was also encountered in thinner areas. The non-failing areas were always near the low end of the acceptable range. Therefore, as might be expected, thickness certainly contributed to the coating failure, but it (and therefore the applicator) could not be held as the primary factor in the failure. It simply illustrates that at a low enough thickness, enough of the solvent could escape so as not to cause osmotic blistering.

Secondly, it must be remembered that the steel was painted in the shop, and then shipped in early spring to the job site for subsequent erection. Hence, the coated steel had weeks to cure in an outdoor setting with excellent ventilation, and yet enough solvent still remained to cause blistering. This illustrates the fact that, unless solvent escapes during or shortly after application, small quantities can remain trapped in coatings for a very long time (sometimes years). Whether this causes a problem depends largely on the type of solvent and the service environment.

Another interesting aspect of this failure is the fact that the microscopic examination of the blistered coating failed to detect any pinholes in the blister caps. Some people believe that such pinholes play a major role in blister formation since they allow water easy ingress to the coating. However, this is usually not the case.

For a liquid-filled blister to form, there must be a pressure (in this case, osmotic pressure) pushing against the back of the coating and forcing it off of the steel. If water has easy ingress through a pinhole, it also has an easy route back out, and it would be difficult to develop enough pressure to delaminate the coating. This might happen, however, if for some reason the coating had poor initial adhesion, or if the ingress of water resulted in corrosion of the substrate. In the latter case, the formation of corrosion product might undercut and physically push the coating off of the steel.

10.3 Cracking and Delamination of Epoxy Coating Systems on Masonry Walls

A new wing housing a testing and quality control laboratory was added to an existing food processing facility. Because of the sterile condition required in such a facility, the masonry block walls had to be effectively sealed with a glossy, hard coating system resistant to rigorous daily cleaning. The system chosen was a two-component polyamide epoxy block filler and a two-component amine-cured epoxy topcoat. The amine-cured epoxy was selected because it cures to a hard, chemically resistant, glaze-like finish. It also had the

advantage of high volume solids (95 %), thus emitting minimal odor. The mix ratio of the primer was 1:1 by volume, while that of the topcoat was 4:1 by volume. The primer was to have been applied by airless spray, and then back-rolled to fill in the voids and porosity in the concrete block. It was then topcoated within two or three days.

Unfortunately, within six months large areas of coating several square inches in size began delaminating from the walls. During the field inspection, it was noticed that invariably the delamination initiated at the mortar joints, and then proceeded over the face of the block. Delamination occurred on the inside of exterior walls, and on the single interior wall which divided the laboratory area from an adjoining office area.

At the time of the investigation, approximately 5 % of the coated surface area had already failed. Subjective probing with a utility knife in visually intact areas showed that poor adhesion was much more widespread. When an 'x' cut was made and the coating probed at the intersection, it was not unusual to be able to 'pop' off chips as large as one square inch in size. In every case, a continuous coat of block filler was on the back of the disbonded coating. Some block filler also remained on the walls. The amount of remaining block filler varied from a thin residue, to what was estimated as a mil or two in thickness.

When the chips were examined in the laboratory, two coats were visible, namely a highly filled white block filler that ranged from 2 mil up to approximately 12 mil, and a white topcoat at roughly 4–6 mil. The recommended topcoat thickness was 6–8 mil. The block filler did not really have a recommended dry film thickness, but rather a recommended coverage rate. This is because the purpose of the block filler is principally to fill the voids and smooth out the roughness of the masonry block. Its actual thickness over the 'surface' of the block is usually only a few mils, since most of the coating is used in filling the surface roughness. Specifying a dry-film or even a wet-film thickness for masonry block fillers is usually an academic exercise, since there is no practical way for a contractor to actually measure it.

Even the microscopic measurement of masonry block filler thickness in the laboratory can be misleading, and sometimes difficult to accurately communicate. With any heavily textured, porous, masonry surface coated with a block filler, huge variations in 'thickness' can occur simply because pits or 'bug holes' in the masonry might be 10 or 20 mil deep. In fact, even the reporting of an 'average' thickness, if it could be readily obtained, can be misleading.

When probing the back of the failing paint chips with a scalpel, it was observed that the block filler was rather soft, especially in the thicker areas. In the thinner areas, the block filler had a very unusual appearance in that it had somewhat of a honeycombed appearance, almost like it had melted and subsequently reformed.

Partly because of these observations, the solvent resistance of the block filler was evaluated. This was carried out in a rather subjective fashion by rubbing

with a cotton Q-tip dipped in methyl ethyl ketone (MEK) while observing under the microscope. The block filler, unlike a typical polyamide epoxy, had very poor solvent resistance, with dramatic softening and rapid color transfer to the Q-tip. The same test performed on the front, or topcoat side, had little effect.

An analysis of the block filler on the back of the failed coating by using infrared spectroscopy quickly explained the reason for the poor solvent resistance. Rather than being a polyamide epoxy, the block filler was actually a vinyl acrylic. Such acrylics (sometimes referred to as acrylic-modified vinyls) are thermoplastic water-borne coatings with poor solvent resistance. They are much less expensive, and of lower performance, than the specified polyamide epoxy block filler.

In addition to the poor solvent resistance of vinyl acrylic block fillers, because they are water-borne coatings formulated with considerable amounts of surfactants, they have only a moderate resistance to moisture. When used in a dry, benign environment such as corridors in a school, they are entirely adequate. However, they will tend to soften in moist or humid environments, such as shower areas or areas subjected to repeated daily washings, such as a food laboratory.

In one respect, the failure analysis did not need to go any further. After all, the contractor had substituted a less expensive, inferior product for that which was specified. There was, however, one curious aspect of the microscopic observations that seemed less than satisfactorily explained. This was the honeycombed, melted appearance of the block filler in the thin areas.

Sometimes, when solvent-based thermoset coatings are applied over thermoplastic coatings such as vinyl acrylics, the solvents will partially solubilize, or 'melt', the surface layers of the thermoplastic. When the solvent-borne topcoat subsequently cures, the shrinkage stress can pull the weakened, underlying coating apart, and when the partially redissolved upper layer eventually dries out, the melted, honeycombed pattern is created.

The problem with the above theory in this case is that the amine-cured epoxy topcoat was a 95 % solids material. It only contained 5 % solvent, to meet both stringent VOC requirements and also to produce low odor. It did not seem like such a material could induce the effects in the block filler that were observed microscopically.

One possibility was that, in addition to using a substitute block filler, the contractor had also used a substitute topcoat. However, infrared spectroscopic analysis of the failing topcoat and a control sample obtained from the manufacturer quickly ruled out this possibility. 'Mis-mixing' of the topcoat seemed an unlikely explanation, since neither component contained much solvent.

The investigation then shifted to an analysis of the topcoat for residual solvents. This was carried out by using headspace gas chromatography (GC).

Headspace GC has been previously discussed (see Section 8.3.4.1). Basically, this technique involves placing samples in a closed septum vial and then heating the vial. Any solvents that remain in the sample will partially evaporate. A gas-tight sampling syringe is then used to remove some of the air (headspace) from the vial, which is rapidly injected into the chromatograph. The technique is not quantitative, but can usually quickly determine if a coating was thinned with an unauthorized solvent prior to application. In this case, not only were material safety data sheets available which listed the solvents in the coating, but liquid control samples were also available for analysis.

The GC analysis showed easily detectable levels of toluene and methyl isobutyl ketone (MIBK) in samples of failed coating from the job site. These solvents were not listed on the material safety data sheets, and nor were they detected in the liquid control samples. It is extremely likely that the contractor added some unauthorized thinner to the epoxy topcoat, perhaps as a means of extending its short (20 min) pot life. This might also explain why the topcoat was consistently somewhat thinner than its recommended thickness of 6–8 mil. If the contractor applied a thinned coating at the wet-film thickness specified for an unthinned coating, the dry-film thickness will be less than expected.

10.4 Discoloration of Coil Coated Aluminum Siding

Within a period of nine months, a manufacturer of coil coated aluminum siding had received numerous complaints about discoloration of the siding. Although records were incomplete, it appeared that the bulk of the siding in question had been coated the previous year, within a period of approximately a month. The complaints came through several contractors who had used the material on houses scattered in several states along the east coast of the USA. Nearly all of the problems were with white, off-white or beige colors.

The process used in the coil coating facility involved a simple pre-cleaning of the aluminum coil, followed by detergent washing and rinsing. A proprietary chromate conversion coating was then applied, rinsed, and sealed via a chromic acid rinse. After the coil went through a dry-off oven, the coating was finally applied and baked. The topcoat was a polyester cross-linked with a melamine–formaldehyde resin. The dwell time in the oven was approximately 50 s, and the coating supplier had specified a peak metal temperature of 400 °F (204 °C). Although there was a temperature probe located near the center of the oven, it was not calibrated on a regular basis, and nor were there any measurements made of the peak metal temperature.

Samples that were furnished included five pieces of either white or off-white siding taken from different houses in two different states (New Jersey and North Carolina). In one case, the homeowners had actually saved some of the leftover siding, so that a piece of uninstalled, unexposed siding was also

furnished. Although it was difficult to know exactly which coil had been used on which house, the manufacturer did provide three small coil coated retains from runs during the general time period in question, along with a pint of a recent batch of paint.

When the various samples were examined, it was seen that the discoloration was in the form of uneven gray or dark gray splotches, rather than a uniform discoloration. When examined with a stereo zoom microscope, the discoloration appeared to be due to fine particles of embedded dirt or debris. Closer observations with a scanning electron microscope, equipped with an X-ray spectrometer, confirmed that fine silicon-rich particles were indeed embedded in the surface of the coating. The discoloration appeared to be a simple physical effect, and not some type of chemical- or light-induced form of deterioration.

During the course of the observation, attempts were made to remove the discoloration by cleaning. Water, along with common household cleaner (including bleach), had little effect. A strong, industrial-strength cleaner performed reasonably well. It was also observed that methyl ethyl ketone (MEK) on a Q-tip rapidly removed the discoloration. Closer observations, however, actually showed that the MEK was not so much removing the discoloration as it was the paint. This seemed unusual behavior for a baked polyester–melamine coating. Similar solvent sensitivity was observed on the unexposed, leftover piece of siding, as well as on the coil retains.

The solvent sensitivity of the various samples suggested two possibilities. Either the coating was not a polyester–melamine, or it had been under-baked. A third possibility, i.e. that the poor solvent resistance was a consequence of chemical- or sunlight-induced deterioration, was ruled out since unexposed samples were also solvent-sensitive.

Infrared spectroscopy easily confirmed that the coating was a polyester–melamine. In fact, the spectra of the field and retain samples matched the spectrum of the recent batch of coating.

There are certain types of coatings whose degree of cure can be approximated by using infrared spectroscopy. However, pigmented polyester–melamine coatings are not one of these. Therefore, differential scanning calorimetry (DSC) was employed in the further analysis.

As previously discussed (see Section 8.7.4), there are two possible approaches to measuring the degree of cure by using DSC, i.e. investigating the glass transition temperature (T_g), or the residual curing exotherm. On coatings that are close to being fully cured, the residual exotherm can often be rather small and sometimes difficult to accurately measure. In such cases, the T_g is often a more sensitive and accurate measure of a coating's degree of cure.

One problem with this line of testing was establishing the correct T_g for this particular coating. The only coated samples available were either 'failing' ones, or unexposed samples that were suspect by virtue of displaying the same

solvent sensitivity as the discolored ones. The alternative was to produce a control sample from the quart sample of a currently used batch of coating.

The control sample was made by drawing-down a film of this coating, of approximately 2 mil 'wet', on a 3″ × 5″ thin-gauge aluminum panel. A small thermocouple was attached to the panel, and it was then placed in a laboratory oven at 520 °F (271 °C) until the thermocouple measured a temperature of 400 °F (204 °C) (the recommended peak metal temperature). This does not reproduce the conditions inside a coil coating oven, where air temperatures can be well over 600 °F (316 °C) and dwell times can be very short, but it should provide a reasonably representative control sample.

The DSC measurements of the various samples produced interesting results. Although exotherms were small, broad, and difficult to accurately measure, the glass transition temperatures were relatively distinct in all cases. The results obtained are shown in Table 10.2.

The results clearly showed a trend, in that most of the failing samples and associated retains had glass transition temperatures ranging anywhere from 13 to 8 °C below that of the laboratory-prepared control sample. Most of the glass transition temperatures were below 27 °C (81 °F).

The fact that most of the failing samples had significantly lower T_gs than the control sample was a clear indication that they were either under-baked, or perhaps that they simply represented defective batches of coating that would not cure properly even if baked correctly. In either case, not only would the lower cross-link density of these coatings result in inferior chemical and physical properties, but the fact that their T_gs were only in the 22–27 °C range means that they will soften during hot summer weather. A softer coating is more likely to pick up and retain wind-blown dust and dirt than a harder

Table 10.2 Glass transition temperatures of the various coil coating samples

Sample	T_g[a] (°C)
Failing 1	22
Failing 2	24
Failing 3	34
Failing 4	22
Failing 5	25
Homeowner 'retain'	26
Coil retain 1	25
Coil retain 2	27
Coil retain 3	36
Laboratory 'control'	35

[a]Measured at onset.

coating, thus accounting for the splotchy surface discoloration. The examination is also consistent with additional SEM-EDS results, which showed fine silicon-rich particles (dirt) embedded in the coating surface.

The above example points out some interesting aspects of practical failure analysis. It would have been desirable to conclusively establish whether the lack of cure was due to defective batches of paint or inadequate baking. Although the lack of reliable temperature monitoring at the coating facility is certainly cause for suspicion, it is not proof of under-baking. If liquid retain samples of the various batches in question were available, either their composition or, more easily, their curing characteristics could have been evaluated against the current batch of coating. Unfortunately, the coil coater did not keep any retains, and nor were records kept of the batch numbers of the paint used. An important question could not be answered because of the lack of certain samples. Unfortunately, this is not a rare occurrence.

A second interesting aspect of the above study is that the data is not entirely consistent. One of the discolored samples had a T_g of 34 °C, essentially equal to the control T_g of 35 °C, and one of the coil retain samples from the time frame in question had a T_g of 36 °C, actually a degree higher than the control.

One possible explanation for this is the experimental error of the analytical technique. If, for example, the T_g results are only accurate to ± 2 °C, then it is still possible that the true T_g of the control could be as high as 37 °C, and the true T_gs of the failing sample and the coil retain could be as low as 32 and 34 °C, respectively. In this case, all of the suspect samples have T_gs below that of the control. Although the precision of the analytical method can be established by carrying out a large number of replicate analysis, in many cases this extra cost burden cannot be justified to the client. In addition, there are times when there is insufficient sample to perform such exhaustive testing.

A second possibility to explain the above data is that the 'control' is not really a true control. The type of oven used in the laboratory was much different to the type used on the coil line. It is possible that the T_g of a true control may have been several degrees higher than the laboratory-prepared version. It is also possible that coil retain 3, with a T_g of 36 °C, did not actually represent a 'failing' batch of coil. Retains were simply selected by the coil coater from runs produced in the general time frame of the reported failure. This particular retain may actually have represented a run of coil that was satisfactory.

Another thing to consider is that coating failures are really statistical in nature. Things have a certain probability of failing, and this probability can be increased or decreased due to certain variables (paint thickness, bake, % of catalyst, etc.), some of which may be totally unknown (a brief wind storm, for instance, or some chemical excursion). To use an analogy, while it is well known that cigarette smoking greatly increases the risk of lung cancer, not everyone who smokes develops cancer. Therefore, in failure analysis as well as in medical studies, these will always be exceptions to the general rule.