FAILRE ANALYSIS
PART: I

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It has been the objective of this series to review the mechanisms of paint film degeneration and coating failure from a non-mathematical yet relatively theoretical standpoint. This background is essential if we are to accurately interpret the cause or causes of any given failure. Such accuracy is essential if we are to rectify the problem and avoid repeating the mistake. This article discusses causes of paint failure, qualifications of a coating failure analyst, resources for identifying failures, and examples of patterns of failures. Types of failure common to particular generic types of coatings are also given.

FAILURE OR NOT?
Perhaps the most important thing to establish is whether an observed deterioration constitutes a failure. All paints deteriorate naturally with time. If the manifestation of that deterioration was predictable, and it occurred within the anticipated or guaranteed time frame, there is no failure. Deterioration that occurs prematurely, however, is clearly recognizable as a failure. As the exposure continues, the injury (severity of the damage) is lessened. However, it is often more difficult to establish the presence of actual failure. It is necessary to establish at the outset of the project what is and what is not expected of the coating system and within what time frame performance is expected to be preserved. These factors go a long way in establishing what is and what is not a failure.

PAINT FAILURE—THE BASIC CAUSES
It is not unusual to find several general deficiencies listed as causes for paint film failure. These causes include inadequate surface preparation, incomplete or inaccurate specification design, application flaws, poor inspection, and even inappropriately formulated coatings. This author thinks that such categorization is overly simplistic, except perhaps in the most egregious cases. There are probably as many potential causes of coating failure as there are coatings that fail. Fortunately, most applications are successful, but failures do and will continue to occur.

In this author’s experience, while there are many causes of coating failure, it ultimately may be traced to one of three basic causes: convenience, profit, or ignorance. Ignorance is sometimes more justifiable than the first two causes, especially where an honest attempt is made by all parties to do the right thing. But some unforeseen change or happenstance all too often confounds our best effort.

In other cases, particularly in a new application or when using a new product, the coating performs differently than expected. These occurrences will thwart our best design, and, in these cases, the ignorant are largely blameless. In some cases, a design engineer may “push the envelope” with a coating...
system. If successful, he will redefine the system’s limits; if unsuccessful, his action will be viewed as unwise.

In still other cases, the coating manufacturer, the specification writer, the applicator, or the inspector may have overlooked (or been unaware of) a well-defined limitation of the system. In this case, the problem was avoidable, and it is this that needs to be corrected. The best way to do this is by increased dissemination of information about failure.

**Who Is the Paint Failure Analyst?**

Equally important, especially in today’s increasingly litigious society, is the necessity of placing responsibility for the problem on the appropriate party. Interpretation of paint film failure has become quite a sizable business over the past 20 years. Today, there are numerous organizations specializing in the discipline, rectifying errors, rendering litigation support to lawyers, and providing testimony at trial and arbitration.

It should always be borne in mind that success in court, especially in jury trials, will very often boil down not so much to an accurate understanding of the failure, but to the relative believability, even intelligibility, of the opposing experts. Nonetheless, the problem must eventually be rectified, and if rectification starts from false assumptions, success here may be elusive.

What makes a good paint failure analyst? What set of criteria should we use to determine who is the best “expert”? Should the individual be an analytical chemist with expertise in modern instrumental techniques, a formulator, or a coatings system design engineer? Should the individual be a confident and believable witness in court? The answer is probably all of these and more. Competence in one category alone is, depending on the problem, likely to be insufficient, and competence in other areas, often having nothing to do with paint at all, can be important, sometimes essential.

It is important to differentiate a chemical analyst from the true expert in the understanding and interpretation of paint failure. The expert may use the services of the chemical analyst, much as a medical doctor will use the services of a medical laboratory. The expert often plays an increasingly vital role in uncovering the difficulty, but the chemical analyst is an expert in analysis. He may know little about either paint or paint film behavior and may serve several other disciplines (adhesives, plastics, forensics, etc.). Working alone, he may come up with an entirely inappropriate interpretation of the facts. However, working in tandem with the paint failure analyst, the two may make a formidable combination. The roles were once quite distinct, although today many of the larger firms specializing in the interpretation of paint failures use in-house analysts and much of their

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**Fig. 1: Tensile cracking of a thick-film composite as a result of exposure to sudden, intense cold. All photos courtesy of the author**
Coating Sensitivities to Specific Failure Modes

Oxidizing Systems
- Poor film formation, slow drying (sagging, wrinkling, poor through-dry, early water sensitivity, flashing, early contamination) due to slow drying aggravated by effect of low temperature, oil length, and barrier pigmentation on cure
- Drier absorption (especially blacks) and drier imbalance
- Solvent sensitivity, recoating difficulties
- Susceptibility to saponification, cathodic alkali attack at breaks
- Instability of mechanical properties, embrittlement on aging
- Skinning, livering, and gelation in high acid number systems
- Reactivity of high acid number systems with basic pigments. Phase separation
- Poor adhesion to zinc surfaces

Latex Systems
- Early water sensitivity
- Reduced coalescence—negative effects of humidity, low temperature, porous surfaces, and high winds
- Flash rusting over active steel because of humidity
- Softening at high temperature, dirt pick-up, and blocking due to thermoplastic nature
- Wet paint subject to freezing
- Poor adhesion to dirt, chalk, rust, grease, and oil
- Crawling and wetting problems due to high surface energy of water-borne system
- Coagulation due to sensitivity to reactive pigments and soluble ions

Zinc-Rich Coating Systems
- Adhesive and cohesive difficulties due to high pigment volume concentration/critical pigment volume concentration (PVC/CPVC) ratio. Initial strength may be low especially when recoated.
- Surface preparation critical to performance.
- Surface preparation critical to adhesion with inorganic zincons.
- Film thickness critical—corrosion (as pinpoint rusting) when low; mud-cracking, splitting, and poor through-cure when high.
- Rapid drying (especially inorganics—reduced cohesion); overreaching difficulties, dry spray, especially on high structures or in wind
- Porous films, contaminated easily, inducing bubbling in finishes
- Reactive film sensitive to pH extremes (<6 and >10)
- Cure of ethyl silicates (inorganic zinc-rich) and moisture-curing urethanes (zinc-rich) sensitive to humidity and temperature. Under-cured primers can result in early recoating problems and zinc splitting after recoating.
- De-adhesion of oxidizing recoats due to saponification of esters in polyurea with oxides and hydroxides of zinc
- Incompletely homogenized product may result in diminished properties, especially with organics. Necessity of in-pot mixers during application.
- Recoating diminishes anode: cathode area ratio—will reduce cathodic protection at breaks and holidays.
- Two- and three-package systems sensitive to mixing errors
- Single-pack systems may gas, resulting in distortion of cans.

Vinyls, Chlorinated Rubbers, and Other Lacquers
- Chlorinated systems subject to dehydrochlorination, gelling, embrittlement, can and substrate corrosion, gassing, osmotic blistering of recoats, heat and light sensitivity, critical stabilization. Single-pack metallics may gel and gas.
- Surface preparation critical for optimum performance
- Correct co-polymer critical to adhesion to metals and other substrates
- Carboxylated vinyl systems react with metals and basic pigmentation. Gelation and gassing
- Controlled pigmentation necessary to ensure optimum weathering.
- Conventional lacquers are fast drying, subject to cobwebbing, and dry spray, especially in high winds.
- Evaporation cooling of fast drying systems. Blushing in humid air. Water pickup by hygroscopic solvents, osmotic problems
- Some modified (e.g., high-solids lacquers) are slower drying systems subject to solvent entrapment, bubbling, vacuoles, and osmotic blistering from entrapment of water-miscible solvents.
- Powerful solvents in recoats may disrupt primer film.
- Films remain solvent sensitive after full cure.
- Vinyl wash primers have critical mixing ratio. Film thickness control and recoat interval control are critical. Pot life is critical but not indicated by noticeable increase in viscosity.

Epoxies
- Diverse family of coatings with many curing agents complicates analysis. Wide-ranging property profile and divergent application and performance characteristics
- Two-pack systems are sensitive to mixing ratio (especially aliphatic amines and Mannich bases). Polyamides less sensitive to mixing ratio
- Poor cure at low-temperature (50°F [10°C]) except Mannich bases and cycloaliphatic amines. Amine reactivity with atmosphere, carbamate formation, recoat, and color problems

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• Amine blush (especially at low temperature) with amidoamines and polyamides. Recoating may be problematic.
• Induction is often required, especially with polyamides, which are initially poorly compatible.
• Limited pot life after mixing, especially with aliphatic amines and Mannich bases
• Limited recoat window.
• High crosslink density systems (low molecular weight epoxies with amine curers) are very brittle, with high internal stress. Need excellent surface preparation. May induce adhesive or cohesive failure in old films. Polyamides and amidoamines more flexible, more forgiving of marginal surfaces.
• Recoating difficult due to solvent resistance. Scarification may be necessary.
• Epoxies chalk and discolor on exposure to UV, giving poor exterior aesthetics; recoating requires chalk removal.
• May degrade beneath light-stable clears, which delaminate from degradation product (acting as interference materials)
• Solvents may catalyze (alcohols) or retard (ketones) cure. This will affect pot life.
• Water-borne epoxy may have indistinct pot life termination, which is not indicated by increase in viscosity.

Polyurethanes and Polyureas
These are a diverse family of coatings with many co-reactants that can complicate analysis. They have wide ranging property profiles and divergent application and performance characteristics. Different cure types can range from two-pack systems to lacquers and oxidizing films to moisture cures and latex dispersions.
• Two-pack systems require care to ensure stoichiometry. Mixing ratios are reasonably critical.
• Reactivities of polyureas may be fast with short pot life. Polyureas often applied by plural spray techniques.
• Catalyst response is extreme. Small amounts of metallics and tertiary amines will greatly reduce pot life and decrease cure time.
• Two-pack and moisture-cures are water sensitive. Water-contaminated solvent and damp surfaces cause CO2 bubbling in films, giving reduced aesthetics and performance. Spraying in humid air may result in bubbling, pinholing, and gloss loss.
• Water contamination will affect stoichiometry of two-packs.
• Bubbling in moisture-cure urethanes (MCU) restricts film thickness and pigmentation type.
• MCUs are sensitive to humidity and temperature. Requirements for good cure are between 30% and 85% relative humidity.
• Aromatic urethanes yellow, chalk, and degrade outside, whereas aliphatic urethanes are very light stable.
• Recoating may be problematic. Even oil-modified oxidizing polyurethane systems require intercoat scarification after 24 hours.
• Solvent system of finishes may attack solvent-sensitive primers.
• Two-pack, water-borne urethanes require careful mixing with controlled mixing rates. Non-equalized component viscosities may lead to reduced gloss and grainy films.

Polyesters and Vinyl Esters
These systems are usually two-pack systems with mixing ratios that are not whole numbers.
• High shrinkage on polymerization leaves high residual strain. This shrinkage lends to the system’s vulnerability to delaminate over smooth substrates and crack in non-reinforced composites.
• Reinforced systems require deep gritcut anchor patterns (>3 mils [>75 micrometers]) and reinforcement with mats, chopped fibers, or platy pigments (glass flake, mica, etc.).
• Application of polyester and vinyl ester may induce cohesive failure in weak substrates. Substrate tensile strength 300 psi [2.1 MPa] minimum
• Residual strain increases with film thickness.
• Highly impermeable floor systems may lift in areas of high water table.
• High modulus systems are subject to crack propagation from substrate (concrete cracking after lining installation).
• Sensitive to deformation and local strain in steel substrates (floor/wall tank junctions, etc.)
• High chemical resistance, especially the novolacs, but some systems sensitive to alkalis and low molecular weight solvents (acetone, methylene chloride)
• Wax that is used to prevent oxygen inhibition of surface cure may need removal.
• Barrier films may have pinholes and other discontinuities requiring quality control with high voltage holiday detectors.

Formaldehyde-Cured (Baking Systems)
• Insufficient temperature and time of cure, and insufficient or inappropriate selection of crosslinker or catalyst can result in incomplete cure.
• Heat sink effects of substrate and oven placement can result in inadequate cure.
• Overbaking has an effect on aesthetics (color and gloss loss) and performance (embrittlement).
• Reduced flexibility due to self-condensation of crosslinker, or an excess of catalyst or crosslinker.
• Catalyst deactivation by pigmentation, etc. Catalyst absorbed and neutralized
• Incorrect solvent selection, and oven conditions (i.e., temperature control) can result in solvent popping.
• Flocculation of pigmentation by catalyst
• The type and level of catalyst can increase viscosity.
• Catalyst sensitivity to substrate can result in de-adhesion.
• Poor solvent resistance due to insufficient crosslinker or catalyst.
• Poor humidity and detergent resistance due to hydrophilic catalyst.
instrumentation. This practice has blurred the distinction somewhat.

Also confused with the paint failure expert are the paint formulator and the engineer who designs the coating system. In truth, a number of the more respected experts are somewhat multidisciplinary in these regards. However, an individual who knows how to formulate coatings or knows how to write a specification that may provide cost-effective performance to a particular structure may not necessarily be an expert in the interpretation of a coating failure.

Nor will a familiarity with coatings technology in itself be sufficient. It is not unusual for failures to have as much to do with some peculiarity of the substrate, the application, or the service environment as they do with the coating materials. Where coating failure occurs on metal, some

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appreciation of corrosion science is often necessary for a complete understanding. Failures on wood will require knowledge of the physics of the substrate behavior under a variety of marginal conditions such as differential absorptivities of grain structures and their mechanical response to changes in moisture content, for example. On concrete, alkalinity, porosity, the presence of water, and the presence of loose or impregnated contaminants may play a role in the failure of an applied coating.

Experience is a principal qualification of a potential expert in paint film failure. The individual who has seen many different failure types and is familiar with the most likely pitfalls (given the use, application, and service) of a particular coating system under a specific set of circumstances can most likely and readily identify causes.

Certain coating systems have a unique vulnerability to specific types of failure. If this vulnerability is known, the analysis may (though not always) be easier. The sidebar on pp. 69–70 reviews the inherent sensitivity of several of the more common classes of coating systems that the failure analyst will most likely encounter.

**Needed and Existing Resources for Failure Analysis**

There are fundamental deficiencies in our resources for analyzing coating failures, but there also are useful texts available. What we need and a sampling of what we have are described below.

**The Lack of a Schematic Methodology**

Questions are sure to arise regarding how the job is done, what procedures are involved, and how the analyst

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begins, proceeds, and concludes the practice of uncovering the cause and mechanism of distress.

Unfortunately, the scientific organization of the process appears elusive. There is most certainly a lack of a good resource on this subject. This may be partly related to the diversity of possible causes, and to the fact that paint failure is rarely a product of any single happenstance. It is usually a result of the concomitant interplay of two or more unrelated factors. Many failures are unique and defy categorization. Other failures may go without complete explanation.

Little attempt seems to have been made to bring any semblance of schematic order to the discipline of the analysis itself. With very few exceptions, each account of failure or certainly each type of failure is described as a special case, with no attempt to explore its relationship to other failures.

**Texts on Instrumentation**

There are many texts that describe the instrumentation that may be used in failure analysis. These instruments include microscopy and surface analysis, by ESCA (Electron Spectroscopy for Chemical Analysis), Auger, infrared spectroscopy, gas chromatography, atomic absorption, and other instrumental techniques. Volumes on instrumental techniques are available in both general scientific literature and in publications of the manufacturers of such instrumentation.

**Texts on Procedures**

While there is little published in the way of a schematic methodology on

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*Fig. 4: Localized coating failure due to non-uniform, inadequate surface preparation. Mill scale was still present at corroding sites.*
the actual practice of determining why a coating system failed, there are texts that bring some limited order to the practice of identifying applied coatings in both field\(^9\) and laboratory.\(^{10}\) Possibly the most complete exposition on paint failure is to be found in Hess’s *Paint Film Defects* by Hamburg and Morgans.\(^{11}\) Here, again, while the problems themselves are categorized in terms of when and where they occur, including notes on rectification, there is no instruction on the failure analysis procedure. A chapter in Munger’s book\(^{12}\) again subdivides the problems in terms of formulation, coating selection, system design, surface preparation, and application. There is, however, little guidance as to how one systematically approaches the analysis itself. In *The Paint and Coatings Testing Manual*,\(^{13}\) Mills lists many of the vulnerabilities of different coating binder types, pigmentations, etc. The same chapter provides discussions on system selection and specification error as well as on surface preparation and application. He also proposes a limited outline of the analysis procedure (e.g., gathering background information, conducting field and laboratory investigations, establishing and testing a hypothesis, and, finally, reporting). Perhaps still more valuable from the standpoint of methodology is the newly released volume by Weldon,\(^{4}\) which deals more centrally with the methodologies of failure analysis. Weldon discusses many of the techniques typically used in the field and in the laboratory.

In fact, it seems that most analysts proceed unsystematically, observing, sampling, and testing until they come up with what is the most plausible, if not the definitive, cause of the problem. All that can be done in some cases is to present several possible scenarios that fit the facts, and opine on the most likely cause. There are, of course, things to look for that will lead to understanding and that will narrow the choices for a potential cause. There
are well-defined vulnerabilities in all coatings, and their behavior in the presence of different reagents or in a given environment may in some cases be entirely predictable.

**Other Literature**

Without getting too specific, it is fair to say that there may be a history of failure patterns in similar application and service under a given set of circumstances. Many such anomalies will be well covered in the literature, and it helps to be aware of these. Many of the previous units in this series should provide valuable background for the analysis in this regard. Information may also be found in reviewing many of the texts described above together with their references as well as others not specifically mentioned.\(^{14-19}\) *The American Painting Contractor*, for example, has published many valuable case histories on coating failures (reference 17, for example).

**Finding Patterns in Coating Failures: Two Examples**

**Effects of Climate**

Some failures may be specific to a given climate. Broadly appreciated are the effects of the Florida sun on the rate of UV-induced degradation, as are thermal effects on heat-sensitive vinyls and chlorinated rubbers. Less appreciated are the negative effects of exceptionally cold winters of the midwest and northeast areas of the U.S. on the buildup of stress in coating systems. These effects occur especially when a deep and sudden drop in temperature occurs (Fig. 1 on p. 67). Neither is there a good appreciation of the dangers of incurring similar stresses of the same
A tensile stress on top of an existing tensile stress is an accumulating and worsening condition, whereas a compressive stress applied to a system under tensile stress will result in some stress relaxation. Thus, a film applied and, therefore, undergoing a tensile shrinkage stress in spring will have that stress dissipated during the hot summer months. On the other hand, the same system applied in the fall may still be under tensile stress when the cold weather hits, compounding the stress model. Local environments may also develop and cause coating breakdown (Fig. 2 on p. 73).

Contractors and specifiers have sought to extend the painting season in the northern U.S. in the fall in spite of low temperatures and damp conditions. These factors have increased the frequency of amine blush, discoloration, and recoat delamination problems during recoating that will often arise with some epoxy systems. The effects of thermal stress and cold, wet conditions during application are probably as likely to cause coating problems in the north as is high incident sunlight in the southeast and desert southwest of the U.S.

In other cases, the coating system may be vulnerable to both low temperature and low humidity. Examples are alkyl silicate zinics and moisture-curing urethanes, both of which have different disadvantages that result from extending the painting season. In winter, for example, solvent-borne inorganic zinc coatings will require much more time to cure than in summer because of low humidity. In shop application, early recoating with moisture-impermeable intermediates and finishes is influenced by limited storage facilities. Shops have limited facilities for storing inorganic zinc-coated steel to allow it to properly cure.
Therefore, the steel is frequently recoated too rapidly. This practice has resulted in many stress-induced splitting failures of the improperly cured zinc beneath strong intermediates and finishes after shipment to the field. On the other hand, latex finishes may suffer from application under cold, wet conditions, especially over excessively porous substrates. Here the result may be loss of cohesion and microcracking.

**Effect of Substrate**

Failure may also be specific to a given substrate (Figs. 3 and 4 on pp. 73 and 75). Friable plaster surfaces and concrete may have weak surface layers such as laitance or an existing weak undercoat (Fig. 5 on p. 77). These systems will be subject to the shedding of the coating system by cohesive failure of the weak surface layer. Galvanized steel is often sensitive, especially to oil and alkyd coatings (Fig. 6 on p. 78).

Wood is not only sensitive to UV-induced degradation prior to painting, but also to differential mechanical effects between spring and summer wood bands in response to humidity. Steel, of course, corrodes, and this proclivity may lead to underfilm attack. Attempts to suppress such corrosion (e.g., with soluble corrosion inhibitors) may lead to other problems such as osmotic blistering in immersion. (The use of inhibitors of high solubility may stop the corrosion but will cause blistering in humid environments.)

**Conclusion**

In the next unit of our series, we will attempt to organize a schematic approach to the analysis of coating failure.

**References**

2. K.B. Tator, “Can Failure Still Occur Continued


