

Automotive Coatings Defects Part I:

In-Plant and Field Defects



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This paper deals with field defects and problems in automotive coatings and how they are caused or affected by weathering. It begins with a brief discussion of defects that occur in the auto factory, such as craters, pops, sags, and foreign material (dirt), some of which can affect durability. Then, it moves on to field defects and problems, a number of which occur as part of the weathering process. Others become worse with weathering. Examples of defects caused by weathering include blistering, water spotting, acid etch, cracking and spalling, delamination, fading and other color changes, and corrosion. Examples of defects that are worsened by weather include mar and scratch, cracking and, sometimes, stone chipping. Each of these defects is discussed.

INTRODUCTION

Buyers of new automobiles demand excellent appearance and expect that their vehicles will retain this appearance. This requires attractive, defect-free coatings that protect themselves and underlying substrates from weathering and degradation. Unfortunately, coatings defects that hurt appearance and reduce protection can occur at almost any time in the life of the vehicle, including during painting and assembly in the auto factory. Factory defects usually are repaired, but field defects may not be, depending on cost and whether they are covered by warranty. Weathering is a major factor in the occurrence of field defects and may also affect areas of the finish repaired in the auto plant. Many field defects are directly due to weathering; others are made worse or more likely by weathering. Examples of the former include loss of gloss, blistering, water spotting, acid etch, most cracking and checking, delamination, fading and other color changes, and corrosion. Examples of the latter include mar and scratch, some cracking, and, sometimes, stone chipping. There is considerable interest in preventing these defects or reduc-

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ing their number and severity. To accomplish these goals, it is necessary to understand the defects and their place in the context of the coatings, the auto factory, and the weathering process. The combination of this paper and Part 2 to be published in the March issue, provides an introduction to these subjects.

DEFECTS IN THE AUTO PLANT

The painting of automobiles is a complicated process fraught with difficulties. Most cars and trucks are coated with a four-coat organic finish on top of zinc-coated steel and a phosphate pretreatment. The painting process consists of:

- electrodeposition dip primer plus bake,
- spray primer-surfacer (also called surfacer, filler, or antichip) plus bake,
- spray basecoat (also called color coat) without bake or with low temperature dehydration bake (waterborne basecoats), and
- spray clearcoat, followed by topcoat bake.

There also are plastic parts on most cars and many trucks, particularly bumpers and fascia, but, in some cases, also hoods, deck lids, and fenders. Plastic parts are spray painted, most of them with a relatively flexible three-coat paint system composed of:

- adhesion promoter or other primer (may be applied in the mold),
- basecoat, and
- clearcoat.

Plastic parts may be painted off-site or in the auto plant. The spray painting techniques for both metal and plastic are hand guns, robotic guns, and high-speed bell applicators. Often all three are used in a given factory, although there is a movement toward automated equipment to reduce cost and dirt.

A number of defects can occur during application of the paint layers.^{1,2} In terms of defects, spray painting probably is the worst possible method for painting auto bodies, but is the only one, so far, that provides the desired appearance. The most common defect is foreign material (dirt). Every auto plant must battle constantly to control dirt and application defects. Although application defects often look like dirt, they are the result of faults in the spray process such as spits, drops, and overspray. Other defects^{1,2} include craters, dewetting, telegraphing, picture framing, pinholes, solvent pops, air entrapment and bubbles, flooding and floating, Bénard cells, sags, and orange peel. Many of these only affect appearance, whereas others may affect the protective properties of the finish and/or the durability. In most plants, coatings are inspected after each bake and sanded as necessary to remove defects or to make them less noticeable. The next coat usually can

cover small defects. The critical layer is the basecoat/clearcoat combination since it is the final layer, the one that gives the appearance seen by the car owner and the ultimate protection of the layers below.

Dirt on the surface of the clearcoat, along with shallow craters, can be sanded and polished (finessed) so that the defects are no longer noticeable. Off-color areas, deep dirt, deep craters, pops, sags, and severe orange peel must be sanded more heavily and repainted. Small defects, if not repaired, will have little direct effect on protection, although pinholes and thin spots raise the rate and amount of water and electrolyte transport, which could lead to corrosion. Repairing defects can affect durability because of changes such as:

- film thickness reduction due to sanding,
- sanding through to metal or even through the zinc layer on the steel,
- multiple repair coats and bakes leading to embrittlement and stress build-up, and
- poor intercoat adhesion.

FIELD DEFECTS, CHANGES AND PROBLEMS

Many changes in the appearance of an automotive finish occur in the field, a number of which are results of the weathering process. Others are made worse by weathering. Most of these changes are considered defects or problems, but the reaction to them may depend on whether they take a long time to develop or happen early in the life of the vehicle. Field defects include loss of gloss, blistering, water spotting, cracking, checking, spalling, delamination, fading, yellowing and other color changes, corrosion, mar and scratch, and stone chipping.

Loss of Gloss

The gloss of an automotive finish decreases over time, although perception of this depends on the position of the viewer and the angle of viewing. Color plus clear coatings show improved gloss retention when compared to the old monocoats; but erosion, degradation, abrasion, and scratching still occur and lead to a decrease in gloss. The idea is to minimize the rate at which this occurs so as to keep the new car appearance as long as possible. Gloss retention varies with technology, with acrylic-melamines probably being the best at present due to a combination of scratch resistance, UV transparency, and general durability. Unfortunately, strategies to increase gloss and gloss retention by raising melamine levels and/or crosslink density often have led to other problems, such as chipping, cracking, or worse, etc. In addition, although UV-absorbers reduce photodegradation of any coating, they are much less effective at protecting the surface of a film than they are

Table 1—Change in Softening Point with 15-Day Water Soak

Coating	T_s before Water Soak, °C	T_s after Soak, °C	ΔT_s , C°	Water Spot Resistance
Clearcoat A	44	32	12	Fair
Clearcoat B	15	-9	24	Poor
Clearcoat C	37	9	28	Very Poor

the lower parts. This is because there is very little UVA at the surface, and therefore, little or no absorption by the additive. This leaves more UV to be absorbed by the polymer.

Blistering

Blisters (*Figure 1*) are dome-shaped defects that are most likely to occur when a coated object is immersed in water, but they can form when water lies on a horizontal coated surface or when the coating is exposed to high humidity. Blisters also can result from corrosion. In my experience, if non-corrosion blisters do occur on an auto finish, they do so early in the life of the coating. They need precipitation in order to occur, but it is not really accurate to blame them on weathering. Blisters can form whenever there is a water soluble material (salts, soluble impurities in pigments, or residual solvents) under the coating or in a lower layer. If water permeates the coating and dissolves the water soluble species (and that species is absent in the water outside of the coating), then an osmotic cell will be created.³ The cell consists of a semi-permeable membrane (the paint), separating a solution of relatively high concentration (the dissolved material) from a solution of low concentration (the water on the surface). This non-equilibrium situation provides a strong driving force to make the two concentrations equal. More water will pass through the coating in an attempt to dilute the concentrated solution, which results in a liquid-filled

blister. There also are indications that paint films that absorb water at elevated temperatures (such as in a rainstorm on a hot day) may exude or trap excess free water when the film is cooled.⁴ The water released by this process can cause blisters, microcavities, and even delamination.

Water Spotting, Acid Etch

Water spotting occurs when hard or dirty (rain) water residues settle down into the coating and react with it (hydrated carbonates hydrogen bond to the surface) to leave a permanent ring or spot.⁵ Polishing is not very effective in removing the blemishes and may actually cause damage. Water spotting can occur quite early in the life of a vehicle and is the reason why many manufacturers recommend wiping a vehicle dry after it is washed. *Table 1* indicates that coatings, which are softened more by water, are more likely to water spot. In this table, T_s is the softening point as determined with a Perkin Elmer TMS-2 thermal mechanical analyzer with a 10 g load.

Water spots tend to be rings with most of the material deposited at the boundaries (*Figure 2*). The dirty water droplets that form water spots are much like the evaporating coffee droplets described by Deegan et al.⁶ and reviewed by Ball.⁷ The edge of the droplet (the contact line) is pinned at points on the surface due to surface heterogeneities. Because of this, evaporation cannot simply shrink the droplet's lateral dimensions. Instead there must be a net flow towards the edge to replenish liquid lost by evaporation, while keeping the contact line in place. Suspended material is carried along by this flow.

Acid etch involves surface damage by acid rain, fog, or dew. It is often compounded by particulate fallout (fly ash, soot, dirt, etc.). The acid usually is sulfurous, H_2SO_3 , but the possibility of nitric acid has been con-

Figure 1—Blisters

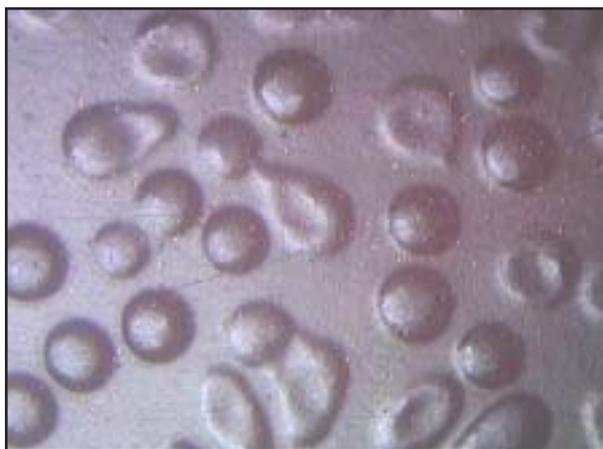


Figure 2—Waterspotting

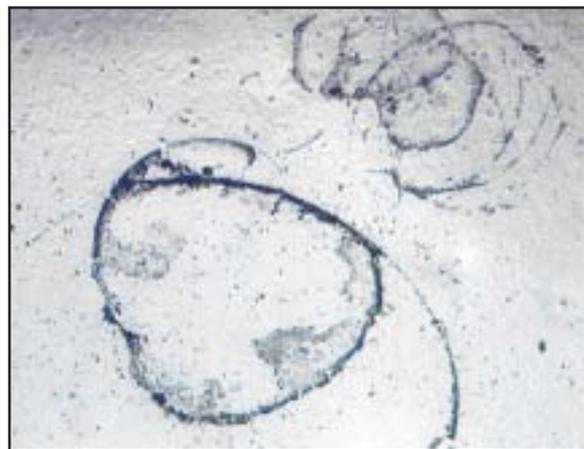


Figure 3—Acid etch

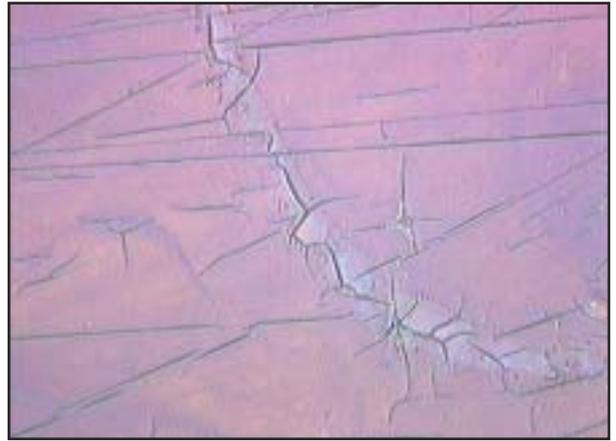


sidered.⁸ The acid catalyzes hydrolysis that acts in concert with photo-oxidation to cause bond breaking and embrittlement.^{8,9} The result usually is a series of small, but very obvious rough-floored, low-gloss depressions on the clearcoat (*Figure 3*). Unfortunately, acrylic-melamine clearcoats, which have so many excellent properties, are very prone to this defect. It was first thought that acid etch was initiated by water spotting and that etching was a slow process. Now, it is known that there are two separate defects, and cases have been seen where etch literally occurred overnight as the result of fallout from pollution or a severe thunderstorm. All of the paint suppliers to the automotive industry have developed acid-resistant clearcoats to combat this defect.

Cracking, Checking, and Spalling

Cracking is the formation of fissures in the surface when the coating pulls apart to release stress (*Figure 4*). High tensile strength enables a coating to resist cracking, but extremely high stresses may exceed the strength of the coating. A coating with a high tensile strength may fail if there are defects (pinholes, etch spots) in the surface that allow the concentration of stress. Also, fatigue-inducing cyclic stresses or chemical degradation caused by weathering may lead to failure at lower-than-expected stress. Some stress comes from the cure process, but most comes from external effects such as temperature and humidity¹⁰⁻¹² and/or from densification due to physical aging.^{12,13} Coatings undergo thermal stress on cooling and heating due to thermal expansion coefficient mismatches between coatings, and between the coatings and the substrate. Heating above the softening point (as in summer sunlight) releases stresses, but cooling restresses the film and freezes in the stress. Coatings also expand and contract as they

Figure 4—Cracking



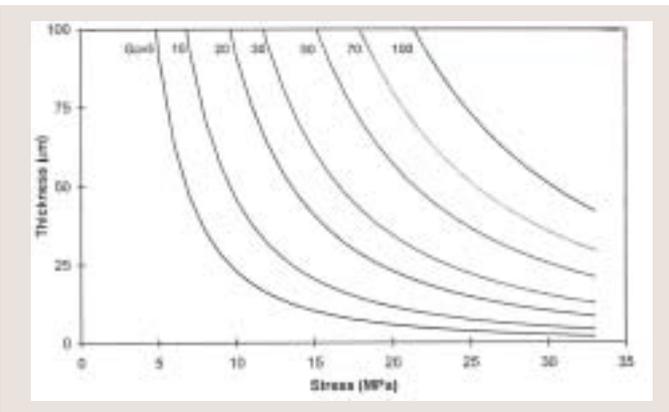
absorb and lose water, and stress is caused by humidity expansion coefficient mismatches. Low humidity causes increased stress. Multiple coating layers and multiple bakes lead to higher stresses if they produce an increase in T_g and/or in crosslink density. Nichols has shown that cracking is dependent upon stress and film thickness as indicated in *Figure 5*.^{14,15} Based on these curves, for a coating of fracture energy 50 J/m^2 facing stresses up to 25 MPa, the maximum film thickness that can be applied without the occurrence of cracking is $36 \mu\text{m}$. If a range of materials is being considered, the curves show that a coating of film thickness $50 \mu\text{m}$ and stresses up to 25 MPa must have a fracture energy of at least 70 J/m^2 to avoid cracking.

The term checking describes cracking that occurs in a regular, often checkerboard pattern (*Figure 6*). These cracks tend to be shallow. Spalling occurs when the surface of a cracked or poorly adhering coating breaks up (often crumbling and powdering) and falls off under stress similar to the surface of a concrete walk or driveway that has undergone multiple freeze-thaw cycles.

Delamination

Delamination is loss of adhesion such that large pieces or strips of the paint film flake off or can be pulled off. There have been several serious outbreaks of delamination of automotive paints in the last 15 years. Some have been failures between the clear and basecoat, but most have involved three-layer paint systems that failed at the interface between the basecoat and the E.D. primer. Failure occurred because of transmission of UV through the base/clear layer and subsequent degradation of the surface of the epoxy E.D. primer. Because of the delamination outbreaks, nearly all vehicles now have primer-surfacers over the e-coat to protect the surface of the e-coat from UV degradation.

Figure 5—A family of curves showing the dependence of critical film thickness (maximum thickness without cracking) on the applied stress in a coating. Each curve represents a material of a given fracture energy, G_c , whose value is shown at the top of each curve.



The primer-surfacer itself must be resistant to UV. In addition, much more attention is being paid to UV packages (UV absorber/hindered amine light stabilizer or UVA/HALS) in basecoats and clearcoats, and what happens to them on cure and on exposure.

Fading, Yellowing, and Other Color Changes

Weathering, particularly UV exposure, can lead to color changes. Certain pigments undergo changes in chemical structure, either to a colorless form (many organic reds, yellows and oranges) or to a different shade. If the pigment changes to a colorless form, the color will slowly fade, for example, from red to pink. Yellowing occurs in clearcoats and is most noticeable over whites and silvers. Yellowing can occur during the bake, before any exposure, and is more likely with overbakes. Contaminants in resins and solvents may change to colored forms on exposure giving the coatings a noticeable yellow or pink cast. Occasionally, the

Figure 6—Checking



color will appear immediately on baking. I once arrived at a plant that manufactured large, brawny pickup trucks to find that nominally white trucks were coming out pink to the point that they looked like they were being built for a certain well-known cosmetics firm. As one of my colleagues said, "Pink is not macho." Fortunately, fading came to the rescue and the trucks regained their white color after a few hours in the sun.

Corrosion

Corrosion of auto bodies is no longer the early occurring, life-threatening disaster that it was years ago. Although it still can be a problem, particularly along the seacoast and in areas where the roads are salted in the winter. Cosmetic corrosion is common, especially around stone chips, deep scratches, and other damage where topcoats have been removed, but it usually is not a danger to the vehicle. Perforation (inside-out) corrosion is now rare and vehicles should go at least 10 years without experiencing this kind of failure. The improvement is the result of better vehicle design, galvanized steel, improved pretreatments, and widespread use of cationic E.D. primers. Isolated cases of severe corrosion still occur and must be investigated on an individual basis to determine the root cause. Examples of causes include parts made of cold rolled steel instead of galvanized steel, poor quality phosphate, and the removal of e-coat, phosphate, and zinc coating by sanding during the repair of paint defects.

Mar and Scratch

The terms mar and scratch refer to surface damage caused by contact with sharp or rough objects. There is disagreement over definitions, but there is no doubt that consumers are demanding better abrasion and scratch resistance, especially resistance to carwash damage and to polishing swirls. I think of mar as meaning

Figure 7—Mar and scratch



abraded or discolored spots or other small blemishes, in contrast to scratches which are relatively long, thin groove- or furrow-like marks (Figure 7). Many scratches involve tearing (fracture) of the coating. However, scratches can occur in groups to give low-gloss patches that could be called mars. Surface damage can arise from a number of stresses, including the trim process in the car factory, keys and fingernails, dragging objects (even protective covers) across painted surfaces, air-borne sand and grit, and branches and shrubs, as well as car washing and polishing. A particularly destructive practice is the wiping of dust from a vehicle with a cloth (dry wiping) rather than by washing. The dirt and dust particles on the coating are highly abrasive and rubbing a cloth across them has much the same effect as rubbing with sandpaper. Over time, a vehicle will experience surface damage from many sources. The result is reduced gloss, and often, unsightly marks.

For many years, auto companies specified mar tests on freshly painted panels. However, paint suppliers noticed that mar resistance decreased with weathering and suggested that retained mar resistance was a more meaningful test of a coating system. The auto companies are now beginning to accept this. Acrylic-melamine clearcoats have excellent initial mar resistance, but lose this fairly rapidly with outdoor or accelerated weathering. A few technologies such as epoxy-acids and certain polyurethanes have lower initial mar resistance than acrylics, but improve in early weathering (the first six months or so), and then after a year, drop off again to levels similar to or slightly better than acrylics. Certain newer technologies, such as modified epoxy-acids, silane-modified acrylics, and fluorocarbons, have high initial mar resistance and retain that resistance for a year or more.

Stone Chipping

Motor vehicles are often bombarded with stones thrown up by their own tires and those of vehicles in front of them or passing them. Occasionally, stones and grit fall from trucks or their loads and strike other vehicles. The defect produced by this type of damage to the coating is called stone chipping. The damage is worse with repairs and overbakes, but can occur with first run paint jobs. Depending on the size and shape of the stone, its velocity and the angle at which it hits, the damage can be crushing/smashing or slicing of the coating, failure at an interface below the surface (often accompanied by lifting), or just abrasion. Videotaping of stones striking rocker panels and rear portions of fenders has shown that failure may not occur until the second or third stone hits a spot.

There is considerable interest in reducing the size of chips and making sure that they only penetrate to the primer or basecoat, not to the e-coat or metal. Color-

key primers (for example, a red primer under a red basecoat) make chip to primer much less noticeable. Resistance to stone chipping and the locus of failure depend on the mechanical properties of the coatings, the adhesion between them, their adhesion to the pre-treated zinc layer and its adhesion to the base steel.

CONCLUSIONS

Automotive finishes occasionally develop surface defects during paint application and baking, but these usually are repaired in the auto plant. More problematic are field defects, many of which are related to weathering. There is much interest in preventing or delaying the occurrence of these defects. **CT**

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Coming in March COATINGS TECH . . .

*Automotive Coatings Defects Part 2:
Weathering Processes and Their Effects on Coatings Properties*