The role of stress and topcoat properties in blistering of coil-coated materials

Tomas Prosek, Andrej Nazarov, Marie-Georges Olivier, Catherine Vandermiers, Dorothe Koberg, Dominique Thierry

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A bstract
The effect of topcoat properties on the tendency of painted materials to blistering was studied. Six topcoats were applied on identical panels of hot-dip galvanized steel painted with a polyester primer. The tendency to blistering was assessed under the conditions of permanent condensation in a Q-panel condensation test at 60 °C. Internal tensile stress and stress development in organic coatings during temperature and relative humidity cycling were investigated by the cantilever curvature method. Although blisters originated from the metal/polymer interface, the extent of blistering was strongly influenced by the topcoat. Available data suggest that it may increase with the coating thickness, glass transition temperature ($T_g$) and thermal expansion properties. Connection was found between the internal tensile stress formed in topcoats during the paint film preparation and the extent of blistering. A hypothesis that stress-assisted interfacial bond hydrolysis was responsible for blister initiation is proposed. Other experiments suggested that local paint buckling over non-adherent sites can be caused by plastic deformation of the paint due to relief of compressive stress generated at elevated temperature or by ingress of water.

1. Introduction

Coil-coated products comprise of a steel substrate, metallic coating, pretreatment layer, and complex organic coating are widely applied in the building and construction industry for architectural cladding and roofing. The organic coating usually consists of a primer providing optimal adhesion and containing leachable anticorrosive pigments, and a topcoat optimized for good UV and mechanical stability, showing appropriate barrier properties and fulfilling aesthetic aspects and functional requirements. Coil-coated materials provide numerous advantages to non-painted steel sheets. The costly and environmentally unfriendly on-site surface treatment and painting can be avoided. Because of a strict process control in production lines, quality and thus durability of coil-coated materials is generally superior. It allows producers to provide as long guarantees as tens of years, even for applications in aggressive conditions. Still, coil-coated materials are subjected to intense research and development in order to further improve their corrosion stability and durability.

Besides delamination, blistering is the most common form of a failure found in organic coatings. Blisters are local defects visible due to distortion of the coat that occurs along with a loss of adhesion at the metal/polymer interface [1–5] or between polymer layers [6]. Several mechanisms of the phenomenon were described [4,5,7,8]. It is believed to be primarily connected with either surface contamination or corrosion process and accumulation of aqueous solution or corrosion products at the interface. In both cases, blister formation is supposed to be promoted by the presence of water in the coating and interrelated with the local loss of adhesion [2,3].

The metal/paint interface properties, such as coating adhesion and surface contamination strongly affect the tendency of a paint system to form blisters. The stronger the interface bonding, the longer is the time needed for water clusters to occur at the interface [5]. However, the aim of this work was to study the effect of topcoat properties on blistering. It is often observed in practice that paint systems with supposedly similar metal/paint interfaces show different tendency to blistering. Thus, the thickness, chemical nature, and glass transition temperature ($T_g$) of topcoat paints were varied in model paint systems, while the substrate, metallic coating, pretreatment, and primer remained identical. This approach minimised the effect of interface properties, which are otherwise considered crucial for blister initiation.

It is well known that stress can significantly reduce the lifetime of adhesive joints and may lead to paint delamination [9–19]. During the fabrication of coil-coating products, paint films are polymerized at an elevated temperature followed by cooling to an ambient temperature. Polymer coatings and steel substrate have different coefficients of thermal expansion (CTE). Both cur-
ing and solvent evaporation during the coating preparation and cooling cause volume shrinkage of the coating. Since the substrate contracts only due to the latter process and the coating often displays higher CTE than the substrate, it gives rise to positive (tensile) internal stress, \(S\) [20]. The internal stress can be further built up by thermal, hygroscopic, or hygrothermal cycling [19]. The experiments have proven that the temperature and humidity cycling as well as outdoor weathering increased the internal tensile stress in polyester, alkyd and linseed oil coatings until the adhesion forces were exceeded, which resulted in coating delamination [13].

When coated substrates are exposed to variable temperature and humidity, dimensional changes are induced. Ingress of water and increase in temperature lead to a significant volume expansion of the coating [9,16] and hygroscopic, \(S_h\), and thermal, \(S_t\), stresses arise displayed as a negative value [13,16–19]. They relieve the internal tensile stress and compressive stress may develop.

For the sake of simplicity, the term stress without an adjective refers in following text to internal, thermal and hygroscopic stresses arising in a paint regardless of the resulting stress being compressive or tensile.

2. Experimental

2.1. Materials

Panels of hot-dip galvanized steel with the zinc coating weight of 275 g/m², chromate-based pretreatment layer, and a film of 5–6 \(\mu\)m thick polyester primer were produced on a coil-coating line. Polyurethane (PUR), polyvinylidine difluoride (PVDF), and polyester (PES) topcoats from BASF Coatings AG designed for the building industry were applied in a laboratory using a bar coater. Two PES paints differing in \(T_g\) were used, PES-low and PES-high with the \(T_g\) of 31 and 45 °C, respectively. The polyurethane paint was applied at three dry film thicknesses of 20, 28, and 43 \(\mu\)m. The resulting paint systems are referred to as PUR-20, PUR-28, and PUR-43, respectively. The dry film thickness of other topcoats was applied at three dry film thicknesses of 20, 28, and 43 \(\mu\)m. The dry film thickness of other topcoats was 20 \(\mu\)m. The topcoats were cured in an oven at the peak metal temperature (PMT) of 240 °C. A list of the model paint systems is given in Table 1.

The glass transition temperature was measured on free films by the differential scanning calorimetry (DSC). The films were kept in air at 40–50% RH and at laboratory temperature for 24 h prior to the measurement. Two temperature cycles from −50 to 150 °C at the heating rate of 0.17 K/s were conducted. The cooling rate between the heating cycles was also 0.17 K/s. \(T_g\) values shown in Table 1 were identified from the second heating curve.

The internal stress was measured for the same topcoat paints applied on calibrated stainless steel beams of 282 mm × 12.6 mm × 0.1 mm without any pretreatment or primer. The coatings were applied manually using a bar coater. Before thermal curing in an oven, the coated substrates were dried overnight in air at ambient temperature to avoid holes shaping due to a rapid solvent evaporation. Three replicates of each system were prepared. The final film thicknesses were measured with a coating thickness gauge Elcometer 456 at 20 points. The dry thickness was 19, 16, 17, and 16 \(\mu\)m in average for PES-low, PES-high, PVDF, and PUR, respectively.

2.2. Accelerated testing

There is a number of standard test procedures used for rapid indication of the tendency of painted materials to blistering. Results of several accelerated tests were compared to the extent of blistering on 10 coil-coated materials exposed at a marine test site for 5 years [21]. It was shown that Q-panel condensation test at 60 °C (QCT60) provided the best correlation to the extent of blistering after the outdoor ageing. In the Q-panel condensation test described in e.g. ASTM D4585 and ISO 6270, painted samples face a chamber with air saturated with water vapour at 40 °C and the vapour condensates on the panel face. The vapour temperature was elevated to 60 °C in this work.

Two replicates of each paint system were tested. Panel dimension was 190 mm × 110 mm. The panels were aged in laboratory conditions for several weeks after the paint application. Edges were masked with tape. The panels were inspected after 500, 1000 and 1500 h of exposure to QCT60. The extent of blistering was evaluated according to ISO 4628-2. After 1500 h, the panels were examined with a microscope and the number and average size of blisters were evaluated. Blister density was calculated as a percentage of the panel surface covered with blisters.

2.3. Buckling test

To study the origin of visible blisters, blind holes were made from the backside of selected non-exposed panels forming areas with standing polymeric membranes. A hole with a diameter of 2 mm was pre-milled in the steel substrate from the back side. Two replicates of each paint system were tested. Panel dimension was 190 mm × 110 mm. The panels were aged in laboratory conditions for several weeks after the paint application. Edges were masked with tape. The panels were exposed to a climatic chamber at 95% relative humidity (RH) under the temperature cycling from 25 to 60 °C. Each cycle comprised of 1 h at 25 °C, 1 h of heating, 1 h at 60 °C, 1 h of cooling. In total, the panels were exposed for 152 h, i.e. 38 cycles. On completion of the test, the profilometry measurement was repeated.

A similar setup was used to measure the toughness of interface [22] and nucleation and propagation of delamination of oxide layers near interfacial defects [23].

2.4. Measurement of internal stress in topcoat paints

The stress in organic coatings was measured by the cantilever (beam) curvature method introduced by Timoshenko [15] and developed by Perera [16,17]. The method is based on the fact that a coated substrate deflects in the direction that relieves the stress. The deflection is measured and if the elastic properties of the substrate are known, the stress can be calculated.

The mathematical equation proposed in the literature to calculate the stress is:

\[
S = \frac{4E_t d l^2}{3b t (t + c)} - \frac{4E_c (t + c)}{b l (1 - \nu_s)}
\]

where \(d\) is deflection in the middle of the substrate, \(E_t\) and \(E_c\) are elastic module of the substrate and coating, \(\nu_s\) and \(\nu_c\) are Poisson’s ratios of the substrate and coating, \(t\) and \(c\) are thicknesses of the substrate and coating, and \(l\) is distance between two knives edges. The equation assumes good adhesion between the coating

Table 1 Topcoat characteristics of model paint systems.

<table>
<thead>
<tr>
<th>Denomination</th>
<th>Composition</th>
<th>Dry thickness ((\mu)m)</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES-low</td>
<td>Polyester</td>
<td>20</td>
<td>31</td>
</tr>
<tr>
<td>PES-high</td>
<td>Polyester</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidine difluoride</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>PUR-20</td>
<td>Polyurethane</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>PUR-28</td>
<td>Polyurethane</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>PUR-43</td>
<td>Polyurethane</td>
<td>43</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 2: Extent of blistering according to ISO 4628-2 after 500, 1000 and 1500 h of exposure and number, diameter, and density of blisters after 1500 h of exposure to QCT60.

<table>
<thead>
<tr>
<th>System</th>
<th>ISO 4628-2</th>
<th>Blisters per panel</th>
<th>Average blister diameter (mm)</th>
<th>Blister density (% of surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 h</td>
<td>1000 h</td>
<td>1500 h</td>
<td></td>
</tr>
<tr>
<td>PES-low</td>
<td>4(S2)</td>
<td>4(S2)</td>
<td>4(S2)</td>
<td>12702± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.9± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES-high</td>
<td>5(S2)</td>
<td>5(S2)</td>
<td>79770± 0.6</td>
<td>4.0± 0.6</td>
</tr>
<tr>
<td>PVDF</td>
<td>&lt;2(S2)</td>
<td>2(S2)</td>
<td>4(S2)</td>
<td>35155± 0.6</td>
</tr>
<tr>
<td>PUR-20</td>
<td>&lt;2(S2)</td>
<td>0</td>
<td></td>
<td>2.3± 0.1</td>
</tr>
<tr>
<td>PUR-28</td>
<td>&lt;2(S2)</td>
<td>10</td>
<td>0.16</td>
<td>0.002± 0.001</td>
</tr>
<tr>
<td>PUR-43</td>
<td>&lt;2(S2)</td>
<td>2(S2)</td>
<td>20</td>
<td>0.006± 0.002</td>
</tr>
</tbody>
</table>

* Estimation from 10 evaluations in areas of 13 mm².

and substrate and isotropic elastic properties of the coating and substrate. It also assumes that the elastic limit of the substrate is not exceeded and that the stress is constant throughout the coating thickness. If $E_S \gg E_C$ and $t \gg c$, the second term in Eq. (1) can be neglected. For details, see reference [20].

Stainless steel beams painted with the studied topcoats were kept after the paint application at ambient temperature and at 50% RH for 1 week to allow stabilisation of the internal stress arising from the paint application. Commercial equipment CoRI-stressmeter was used to measure the metal beam deflection under controlled conditions. After measuring the initial value of internal stress, samples were submitted to hygrothermal cycles in a climatic chamber. One cycle consisted in two successive steps: 20 h at 55 °C and at 84% RH and 4 h at 23 °C and at 40% RH. On completion of 1st, 4th and 7th cycle, the internal stress was measured. The painted beam was placed to the stressmeter for 30 min prior to the deflection measurement. It was carried out at 23 °C and at 50% RH each 15 s for 10 min and the obtained data were finally averaged. Relative humidity in the testing chamber was maintained by saturated water solution of NaNO₃. The stress evolution of an uncoated substrate used as a reference was always subtracted from the data obtained for the coated sample.

3. Results and discussion

3.1. Accelerated testing

Results on the extent of blistering after QCT60 are in Table 2. Blisters on panels of PES-low, PES-high and PVDF were counted and measured in five randomly selected areas of 13 mm² per panel after 1500 h of exposure. For PUR-20, PUR-28 and PUR-43, the panel surface was inspected as a whole.

The PUR-20 system was free of blisters and a low number of blisters were found on PUR-28 and PUR-43. The other systems were heavily blistered. Photographs of 5 mm × 5 mm areas of PES-low, PES-high, PVDF, and PUR-43 are shown in Fig. 1. The diameter of the

![Fig. 1. Photographs of an area of 5 mm × 5 mm of blistered panels after 1500 h of QCT60.](image-url)
Fig. 2. Effect of polyurethane topcoat thickness on number of blisters after 1500 h in QCT60.

The number of blisters ranged from 0.05 to 0.3 mm with a mean value of 0.1 mm. The blisters on PUR-28 and PUR-43 were somewhat larger with a mean diameter of 0.16 and 0.22 mm, respectively. The blister density expressed as a percentage of a surface covered with defects increased in the following order:

$$\begin{align*}
\text{PUR-20}(0) & < \text{PUR-28}(0.002) \sim \text{PUR-43}(0.006) \ll \text{PES-low}(0.9) \\
& < \text{PVDF}(2.3) < \text{PES-high}(4.0)
\end{align*}$$

Thus, the blister density varied dramatically for paint systems with different topcoats. The experiment proved that not only the interface properties but also properties of the paint bulk play an important role in the blister formation.

The number of blisters and blister density increased from PUR-20 to PUR-43 with the coating thickness, see Fig. 2. The chemical nature of topcoats also affected the tendency to blistering. PUR-20 was intact whereas 0.9% and 2.3% of the surface of PES-low and PVDF at the same topcoat thickness of 20 μm were covered with blisters. The effect of $T_g$ can be assessed comparing polyester systems PES-low and PES-high with the $T_g$ of 31 and 45 °C. There were 6-times more blisters and 4-times higher blister density on panels of PES-high. In terms of the ISO classification, it was 4(S2) and 5(S2) for PES-low and PES-high. Nevertheless, this finding must be considered cautiously since $T_g$ reflects a complex array of paint properties rather than being an independent coating property.

Selected blisters on samples of PES-high and PVDF were opened and investigated by optical microscope and infrared spectroscopy (IR) in the microscope mode. The spectra were collected at 4 cm$^{-1}$ resolution in the range from 700 to 4000 cm$^{-1}$. The background spectrum was obtained from a gold-coated mirror. The blisters originated from the metal/paint interface. The metal under blisters was in all cases shining and no voluminous corrosion products were visible. This observation was confirmed by IR as none of typical zinc corrosion products containing carbonate or hydroxyl groups was detected under detached paints. Presence of a thin layer of zincite, ZnO cannot be excluded since it is not observable in the wavelength range.

3.2. Internal stress in topcoat paints

There is no technique known to the authors that would allow measuring the load at the metal/paint interface of studied coil-coated materials. However, it is possible to evaluate the stress in organic coatings applied on a thin metal beam using the cantilever curvature technique. Identical paints used as topcoats for PES-low, PES-high, PVDF, and PUR systems were applied on the calibrated beams and internal stress was measured before and after hydrothermal cycling for three replicates of each paint. Examples of obtained curves are plotted in Fig. 3. In all cases, the stress was of a positive value, i.e. tensile. It generally increased after the first hydrothermal cycle and kept almost constant after additional cycles. Although there was a scatter in results for three replicate samples caused mainly by differences in the actual coating thicknesses, both the initial internal stress and the internal stress after the hydrothermal cycling increased from PUR to PES-low to PVDF to PES-high and correlated to the extent of blistering after the accelerated blistering test, QCT60. This is shown in Fig. 4.

The experiment indicated that blistering was detrimentally affected by the internal tensile stress in topcoat paints. Indeed, there are limitations to the setup because the measurement cannot be carried out on complete paint systems corresponding to coil-coated materials yet. The substrate is different; zinc coating, the pretreatment layer, and the primer are missing. However, it can be expected that the topcoat will be the most important source of the stress because it is the thickest layer of the paint system and similar stress would be generated in these coatings, when a part of complex paint systems.

3.3. The effect of topcoat properties on internal stress and load at the metal/polymer interface

The internal stress after paint film formation corresponds to the volume shrinkage due to solvent evaporation and curing and con-
traction or expansion of the paint relative to the substrate due to a
difference in CTEs of the coating and substrate. The latter contri-
bution can be expressed as

$$S_T = \int_{T_1}^{T_2} \frac{E_c}{1 - \nu_c} \left( \alpha^{\text{CTE}}_c - \alpha^{\text{CTE}}_S \right) \, dT$$

(2)

where $\alpha^{\text{CTE}}_c$ and $\alpha^{\text{CTE}}_S$ are CTEs of the coating and substrate, respec-
tively [20]. Polymers expand and contract usually more than
metals. Linear CTE at 20 °C is about 12, 31, 20, and 40–70 μm/mK
for steel, zinc, polyurethane coating, and polyester coating, respec-
tively [24]. The range found for PVDF was too wide to enable any
reasonable comparison. The thermal stress according to Eq. (2)
that developed during cooling after the paint application and con-
tributes to the internal stress can be supposed to be higher for
polyester coatings than for polyurethane coatings. It may explain
the fact that PES-low showed a higher internal stress than PUR-20,
see Fig. 3.

Thermal expansion coefficients of particular paint formulations
differ substantially with the amount and type of plasticizers,
additives and pigments, and as a function of temperature. Water also has a plasticizing effect. Moreover, other paint prop-
erties, such as the elastic modulus and pigmentation, affect the
stress [13,17,19]. Thus, a more careful paint characterization will
be required to allow a clear conclusion.

The stress depends on the temperature range relative to $T_S$ of the
polymer [13,17–19,23]. The coating polymer is in a rubbery state
above the $T_S$ and internal stress relaxation can occur in theory. If
the service temperature range is below $T_S$, only slow relaxation of the
stress is allowed. It can be supposed that for materials with similar
mechanical properties, the internal stress will tend to be higher in
systems with higher $T_S$ during their service life [19]. Indeed, the
internal stress measured in the PES-high topcoat with $T_S$ of 45 °C
was 3–4-fold higher than for the PES-low topcoat with $T_S$ of
31 °C.

The coating disbonding initiates when the strain energy release rate $G$ is larger than the fracture toughness. For long and wide
bonds, $G$ can be expressed as follows:

$$G = \frac{S^2 c (1 - \nu_c)}{2E_c}$$

(3)

According to Eq. (3) [19], the load at the metal/polymer interface
is a function of the coating thickness, $c$, and the stability of the
metal/paint joint would be better for coatings with lower thickness.
In this study, paint systems with identical polyurethane topcoats
with the thickness varying from 20 to 43 μm were tested. As seen
in Fig. 2, topcoats with higher thicknesses induced more profound
blistering. It is supposed to be so due to higher mechanical load at
the metal/polymer interface for the systems with thicker coatings,
see Eq. (3). These data are in agreement with the results of O’Brien
and Ward who showed that nearly 20 thermal cycles in water were
needed to cause failure to a 50-μm coating and only four cycles were
sufficient when the thickness was 150 μm [9].

3.4. Buckling test

Behaviour of unsupported paint films was studied in the buck-
ling test. Panels of PES-low, PES-high, PVDF and PUR-20 with blind
holes from backside were exposed to temperature cycling. PES-
low optical profiles taken before and after the exposure are plotted
in Fig. 5. They revealed irreversible paint distortion of about 50 μm.
The paint of PES-high cracked. No change in the paint shape was
found for PVDF and PUR-20.

3.5. The role of stress in the mechanism of blistering

In accelerated or laboratory tests, blisters can appear very
quickly in few days or even hours. Taking into account that
coil-coated systems are generally highly advanced materials with
powerful corrosion inhibitors, showing good dry and wet adhe-
sion properties, and containing no salts and corrosion activators
at the metal/paint interface, the origin of blistering cannot be the
electrochemical corrosion or osmotic pressure in these cases. Nei-
ther voluminous corrosion products nor aqueous solution were
found beneath the delaminated paint on samples investigated in
this study. Panels of a similar coil-coated system that were exposed
to cyclic temperature and humidity conditions and rapidly blistered
were investigated by the scanning Kelvin probe and no corrosion
activity was detected [25]. When exposed to water at laboratory
temperature, coil-coated systems have often stable EIS parameters
for months [26]. It also evidences good paint adhesion and a low
substrate corrosion rate. These systems are stable even at elevated
temperatures when stored in dry air. Blistering often appears when
both humidity and temperature increase. It proves the generally
accepted view that the process of blister formation is connected to
local hydrolysis of adhesion bonds at the substrate/polymer inter-
face [1,3]. The elevated temperature not only kinetically accelerates
hydrolysis of the adhesion bonds, but it also increases water solu-
ability in organic coatings.

The data obtained in this work indicate that the internal tensile
stress arising during film formation and hygrothermal cycling may
mechanically load metal-polymer bonds and contribute thus to the
chemical process of their hydrolysis, which can lead to a local loss
of adhesion. This mechanism can be called stress-assisted interfacial
bond hydrolysis. It is particularly important when the mechanical
load is strong or the interface stability weak. In other cases and
particularly during long-term exposure to natural environments,
the corrosion process influences the system more significantly.
Cathodic and anodic blistering as well as cathodic delamination
from defects have the electrochemical origin. However, the stress is
supposed to affect the blister initiation even under these conditions.

Based on the proposed mechanism, three conditions must be
met to initiate this mode of blistering: presence of a site with lower
adhesion at the interface, presence of water in the coating needed
for the bond hydrolysis, and internal tensile stress at a certain level.
It was shown that both liquid water and water vapour penetrate
organic coatings of coil-coated materials rapidly, i.e. the coatings
cannot prevent water from reaching the interface [2,21]. Thus, it is
mainly the quality of the interface and the internal tensile stress that
govern the tendency of a given paint system to blistering.

The former factor can be affected by the pretreatment technology,
primer composition and properties, curing conditions, quality of
the production control and other parameters. The latter factor was
studied in this work. The results suggest that topcoats generating
higher levels of stress are prone to more serious blistering.

Besides damaging the metal-polymer bonds and assisting in the
interfacial loss of adhesion, stress can also promote blister growth.
It is generally believed that visible blisters are formed due to accu-
mulation of aqueous solution or corrosion products at the interface,
creating thus pressure leading to paint bulging [3,5,7,8]. However,
empty blisters are found on materials exposed to accelerated tests
or even outdoors. The metal under blisters formed in QC150 was
shiny and no voluminous corrosion products were detected. The
experiment described in Section 3.4 proved that the paint can dis-
tort and form a blister-like shape even over a hole in the metal
substrate, i.e. the pressure originating from accumulation of for-
eign species and corrosion products is not necessary for blister
growth. Therefore, it is proposed that blisters can grow over non-
adherent locations due to the release of compressive stress by
plastic deformation of the paint. The compressive stress can arise
as a consequence of organic coating expansion due to ingress of water (paint swelling) and/or an increase in temperature.

Although results of this work must be seen as preliminary and need to be approved, they indicate that tailoring of certain topcoat parameters can increase the lifetime of coil-coated products. Elastic and relatively thin coatings with lower $T_g$ and thermal expansion coefficient close to that of the substrate are supposed to generate less internal stress and provide thus better resistance to blister formation. Indeed, there are many, often antagonistic, requirements on coating properties based on expected mechanical, corrosion, aesthetic, functional and other application characteristics and a sensible blend must be reached to formulate a successful product.

4. Conclusions

Topcoat properties affected the tendency to blistering. Six paint systems with the identical interface showed blistering performance from full resistance to heavy blistering. More profound degradation may be due to increasing topcoat thickness, $T_g$ and thermal expansion coefficient. Connection between the internal tensile stress in topcoat paints and the blister density on full paint systems was shown.

It was proposed that the internal tensile stress formed in the topcoats mainly during the paint application mechanically loads the metal/paint interface at weak points and affects the interface stability in presence of water. According to the proposed stress-assisted interfacial bond hydrolysis mechanism, the mechanical load may cause damage of the metal-polymer adhesion bonds and lead to their replacement with metal-water bonds. The hydrolyzed sites can serve as precursors for blister formation. Blister growth, i.e. visible local buckling of organic coating over non-adherent sites can result from the relief of compressive stress by plastic deformation of the paint. The compressive stress arises due to water ingress and/or an increase in temperature.

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