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Crosslink Density and the Development of Internal Stress in Organic Coatings

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SUMMARY: The corrosion test performance of organic coatings on certain substrates noted for relatively weak adhesion (unphosphatized steel and hot dipped galvanized steel) is dominated by internal stress in the coating. Internal stress develops due to a mismatch of the physical dimensions between a coating and a substrate to which it is bound1). This mismatch can be the result of temperature and humidity changes, chemical reactions and gain or loss of material. The magnitude of the stress is related to many factors, including: chemical and structural nature of the polymer, extent of crosslinking, temperature of the curing reaction, and the presence of plasticizers.

Of particular interest is the change in internal stress on cyclic exposure to corrosive aqueous media such as found in corrosion testing or the natural exposure environment. Unexpectedly large increases in internal stress are observed for some commercially important coating types with these increases correlated to corrosion failures. In some instances, water sensitivity of the coating as evidenced by high water permeability increase on exposure or loss of water extractable materials on exposure can explain the observed internal stress behavior, but anomalies exist. In these cases structural changes occurring as the polymer coils, uncoils, and coils again during cyclic water exposure may also play an important role.

Introduction

The development of a new generation of environmentally acceptable anti-corrosion metal primers has revealed the unusual behavior of coating films with increasing crosslink density providing weaker protection. This has been observed for coatings on cleaned-only, unphosphatized steel and other substrates which exhibit weak adhesion. Increased cure, which means a higher level of crosslink density, is associated with higher glass transition temperature, less free-volume, and better barrier properties1). These characteristics usually combine to provide better corrosion protection for metal substrates. However increased cure also leads to elevated levels of internal stress, which when combined with weak adhesion can act to reduce corrosion resistance.

Examples of the usual and reversed corrosion behaviors on changing crosslink density are exhibited by two coatings used as metal primers which are based on an epoxy backbone polymer and blocked isocyanate crosslinker. The details of the crosslinking between the two and the means of plasticizing the films were quite different however. Corrosion resistance as measured by salt spray testing on bare, cleaned-only steel and on a well phosphatized steel is given in the tables below as mm of scribe creep for various baking temperatures.

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Table 1. Scribe Creep in Salt Spray Testing for Phosphatized Steel Substrate

Coating Type	Bake Temperature		
	150°C	160°C	170°C
Highly Plasticized, low crosslink	1-2 mm	1 mm	<1 mm
No Plasticizer, high crosslink	1 mm	<1 mm	<1 mm

Table 2. Scribe Creep in Salt Spray Testing for Cleaned Only, Bare Steel Substrate

Coating Type	Bake Temperature		
	150°C	160°C	170°C
Highly Plasticized, low crosslink	3-4 mm	7 mm	5-6 mm
No Plasticizer, high crosslink	1-2 mm	10-12 mm	>20mm

The large difference in corrosion resistance for bare steel was unexpected considering the similarity of the corrosion resistance on phosphatized steel and the overall similarity of the coating formulations. In addition, measurements of the force of adhesion of these coatings to the substrate were not significantly different. There was, however, a large difference of adhesion between the coatings for the bare steel and the phosphatized steel. Values measured by the ASTM method D4541 "Pull Off Strength of Coatings" were approximately 3 MPa for bare steel and 18 MPa for phosphatized steel. The internal stress for these coatings is shown as a function of bake temperature in Figure 1.

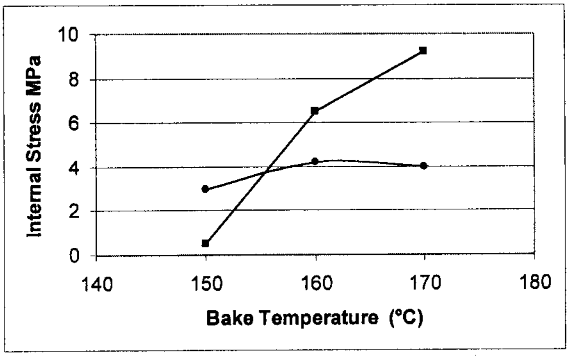

Figure 1. Comparison of internal stress for high crosslink ■ and low crosslink • systems.

The internal stress of the formulation with poor bare steel corrosion resistance is highly dependent on the extent of cure which correlates with progressively poorer corrosion resistance as the bake temperature is increased as noted in the table above.

Internal Stress

Internal Stress in coatings develops due to a mismatch of physical dimensions between a coating and the substrate on which it is immobilized1). This mismatch is a result of physical and chemical changes of the coating that take place after solidification and adherence of the coating to the substrate. Examples of these changes may include continued cure reactions, temperature and humidity changes, and other reactions in response to environmental conditions of UV radiation, water, high temperature, or other exposures. High internal stress levels may be relieved in coatings by loss of adhesion to the substrate, cracking, or puckering of the film; all deleterious to coating performance.

Previous studies have related internal stress, in one case, to film cracking which could accelerate corrosion and, in another case, to the phenomenon of "flowering corrosion" which has been reported for some precoated galvanized building panels. High levels of stress were shown to accelerate the corrosion process by curling delaminated film away from the substrate thereby exposing fresh metal to corrosive attack4). The current study was undertaken to assess the influence of internal stress on corrosion protection particularly for heavy metal free primers such as electrodeposition primers for automotive applications and precoated metal used for building panels. This work is focused on internal stress changes on exposure to various environments.

Experimental

Internal stress was measured using the Braive Instruments Stressmeter. In this test, the coating under study is applied to one side of a thin steel sheet (273 x 12.7 x 0.127 mm). Internal stress in the coating applies a tensile force to the shim which, in response, assumes a circular deformation. The radius of this curvature, elastic modulus and Poisson's ratio for the shim, as well as geometric factors for the specimen allow a calculation of the internal stress1,2). An environmental chamber maintains temperature and humidity during measurement. Implicit in these measurements are the assumptions that: 1) there is perfect adhesion of the coating to the substrate, 2) the elastic properties of the coating and substrate are isotropic, 3) the elastic limits of the coating and substrate are not exceeded in the test, 4) internal stress is constant and uniform throughout the thickness of the coating. Particular attention must be paid to the first and the last of these assumptions as they are often not rigorously adhered to.

Internal stress is expressed in units of pressure and as such is independent of the dimensions of the coating film. The total force applied to a substrate, on the other hand, does depend on the film thickness. Total force in any direction is the product of internal stress (assumed, as above, to be isotropic) and cross sectional area perpendicular to the direction of the force. The magnitude of the total force is responsible for substrate deformation and potential delamination. Crosslink density of the coating film was measured using Dynamic Mechanical Analysis and the relationship between elastic modulus in the rubbery region and the number of elastically effective network links (crosslink density) by the equation$^{3)}$:

$\nu_e = E' / 3RT$

where: E' is the linear elastic modulus and ν_e is the volume density of network chains.

Results and Discussion

Internal Stress and Crosslink Density

A series of three metal primer formulations were prepared to have different levels of crosslink density at the equivalent cure conditions of 20 minutes at 170°C. The differences were achieved by changing both the concentration of hydroxyl crosslinking sites on the polymer backbone and the nature of the blocking group used with the diisocyanate. For comparison a commercial primer including lead silicate in the formulation was also tested. Lead is known to act as a cure catalyst and results in a high level of crosslink density, but also high levels of internal stress. The relationship between internal stress and crosslink density is demonstrated in Table 3 below.

Table 3. Relationship of Coating Crosslink Density to Internal Stress

Coating Type	Crosslink Density Mol / cm^3	Internal Stress MPa
Formulation "A"	0.0042	8
Formulation "B"	0.0065	12
Formulation "C"	0.0093	17
Formulation "C" with lead pigment	0.0111	23

Figure 2 below shows the results of salt spray testing on these coatings over bare steel substrate.

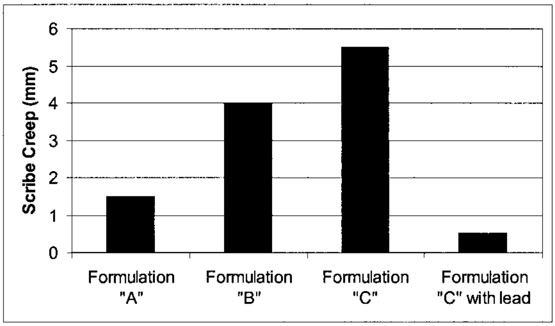

Figure 2. Scribe creep in mm for various metal primer formulations.

Although better barrier properties are expected for the coating exhibiting higher crosslink density, in this case, the increased stress levels combined with weak adhesion act to delaminate the coating leading to accelerated corrosion. Corrosion initiated along the scribe weakens the already poor adhesive bonding between substrate and coating allowing the high stress in the coating to delaminate the film exposing new metal surface for corrosive attack. The specimen containing lead behaves quite differently since lead acts as a corrosion inhibitor preventing the initial attack. In this case, even these high stress levels are unable to delaminate the coating film.

Corrosion Testing Influence on Internal Stress

Internal stress is known to be influenced by the ambient relative humidity. The effects of relative humidity variation were expected to be reversible and were found to be so. Formulations “A”, “B”, “C”, and “D” were cycled four times through relative humidity conditions ranging from 15% to 70% with no permanent change in stress level. Of course the observed stress was dependent on the ambient humidity, for example, formulation “A” showed 20 Mpa at 15% RH and only about 10 Mpa at 70% RH. This result is in sharp contrast to the results reported below for films exposed to liquid water.

Exposure to liquid water followed by drying and re-equilibrating in the test chamber causes a permanent change in the state of stress. In all coatings studied the change observed was a significant increase in stress. This effect was first noted when examining test shims after they had been placed in salt spray testing. Later it was discovered that immersion in warm (40°C) water was sufficient to cause this permanent change in stress level. Figure 3 below shows the effect of one day of salt spray exposure for the three lead-free coatings studied above.

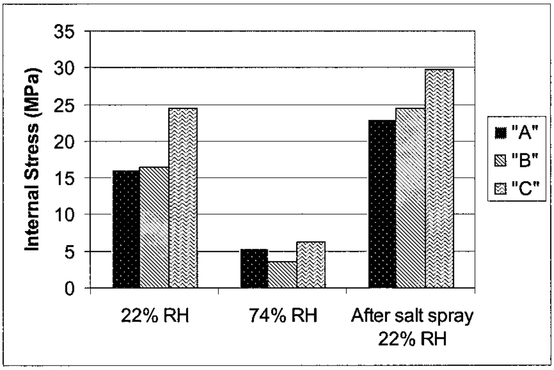

Figure 3. Effect of changing relative humidity and salt spray exposure for formulations with varied crosslink densities.

All three showed an irreversible increase in stress. Longer exposures were found to cause further increases in stress until adhesion to the substrate was lost. The process by which the stress increases suggests that extraction of some film components such as plasticizers or lower molecular weight fragments of polymerization may cause further shrinkage of the film on drying and therefore increased internal stress[4)]. Several experiments were conducted to determine if extraction could completely account for the observed stress changes.

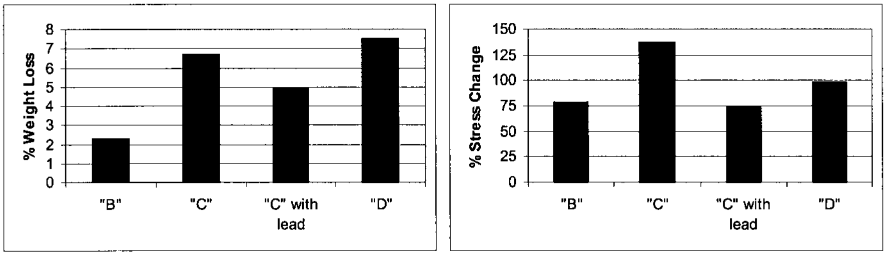

Figure 4. Comparisons of weight loss and stress change on extraction with water.

The pair of graphs in Figure 4 compare the amount of material extracted by water (as a percentage weight loss) from various films with the corresponding observed increase in stress. Because the coatings represent some differences in polymer structures, there is no reason to assume that there would be a simple, direct relationship between amount of extracted material and internal stress increase. The complete lack of correlation, however, is somewhat surprising as all of the coatings are of the same general type, isocyanate crosslinked, bisphenol A extended epoxies.

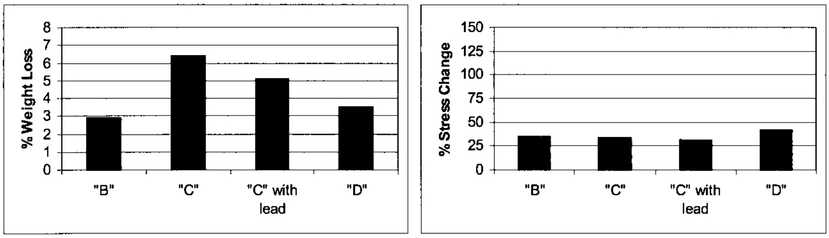

Figure 5. Comparisons of weight loss and stress change on extraction with MIBK.

The next pair of graphs in Figure 5 also compare extractables to stress increase, but in this case the extracting solvent is methyl isobutyl ketone (MIBK). Although the absolute amounts of material extracted differ from the water extraction, the trend for coatings “A”, “B”, and “C” are the same for MIBK as for water. For coating “D” water is apparently much more effective in extracting some components than MIBK.

Interestingly, exposure to MIBK and extraction of similar amounts of material from the film results in significantly less internal stress increase than does exposure to water. Spectroscopic analysis of the extracted material did not show that significantly different material was extracted in each case. A possible explanation of the differing effects on internal stress may depend on some specific chemical interaction, but none has been determined to this time by spectroscopic or other analysis.

Bake Temperature Effect on Extractables and Internal Stress

Experiments were conducted to examine the influence of crosslink density on both the amount of extractables and internal stress development. A series of six shims were coated with coating “A” and baked for 20 minutes each at bake temperatures of 138, 149, 160, 171, 182, 193 °C. Initial stress measurements were made followed by soaking in water at 40°C for two days. The weight loss of these shims was determined as well as the new stress value after equilibration to the conditions of the original measurements. The weight loss due to extractables was as expected with the poorly cured film, baked at 138°C, showing the highest weight loss. From the 149°C bake through the 182°C bake the weight loss was essentially constant, while there was a small increase in weight loss for the 193°F bake. See Figure 6.

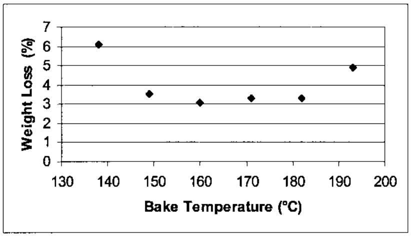

Figure. 6. Water extraction of coating "B".

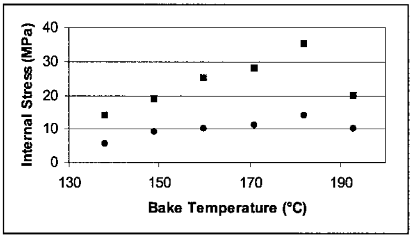

Figure 7. Stress vs bake for coating "B".

Unlike the data for the amount extracted, the internal stress values continue to rise steadily through the bake temperature region of 149°C through 182°C and finally fall significantly for the 193°C bake. These results are shown in Figure 7. For each bake temperature the phenomenon of stress increase on exposure to water is observed. It is interesting that as the extent of cure increases with increasing bake the effect of extraction on the internal stress level is larger.

These results are consistent with the model that there is insufficient crosslinking for the case of the 138°C bake for even one functional group of each crosslinking moiety to be connected into the forming network. This results in some loss of these materials in the extraction. In the bake temperature range from 149°C through 182°C there is sufficient crosslinking so that at least one functional group of every crosslinking moiety has been reacted, connecting it to the network, and preventing loss due to extraction. Therefore, through this region the extractable amount is constant, consisting only of low molecular weight uncrosslinkable material. However, through this region the crosslink density continues to rise as additional functionality continues to react. Thermomechanical analysis (TMA) of these specimens confirm the increasing crosslink density by showing increasing softening point temperatures as the bake temperature is increased. The increasing stress levels correlate with the increasing crosslink density. These data are shown in the graph below. For the bake at 193°C, polymer degradation gives rise to higher levels of extractable, a less stressed film, and the appearance of a second lower temperature transition in the TMA.

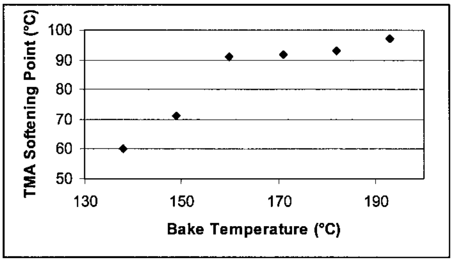

Figure 8. Softening point determined by TMA for coating "B".

Conclusions

- For substrate/coating systems exhibiting poor adhesion, the internal stress of the coating can have a significant influence on the rate of corrosion in standard corrosion testing procedures, especially where cyclic conditions are used in the test.
- Cycling of coatings through corrosion tests which include some exposure to water in the liquid state, especially at elevated temperature, will lead to increasing levels of internal stress with each cycle.
- Highly crosslinked films generally are highly stressed and increase stress more rapidly through cyclic corrosion testing
- Film shrinkage due to removal of extractables may cause some increase in internal stress, but other factors such as specific reactions also probably play a role.

References

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