Adhesion of Coatings

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Outline:

• What is adhesion
• Factors affecting adhesion
• When and how does it happen
• How to test for adhesion
• How to improve adhesion

Adhesion Rules Coating Properties
A painted surface is viewed as a three-component system consisting of paint, substrate, and the paint/substrate interface.
Factors Affecting Adhesion

- Chemistry and physics of surface
- Chemistry and physics of coating materials
- Stresses in coating or substrate
- Application and service environment
Atmospheric Influences

Pollutants/O$_2$  hv/UV  Water

Coating
Before Aging

Coating
After Aging
ADHESION

Postulated coating film failure (Durability)

• Chemical reactions between the film and weather-borne reagents are driven by the energy of thermal and ultra-violet radiation.

• Reactions cause degradation, hydrolysis and polymer chain scission.

• Tensile strength and adhesion diminish, and the water solubility of film increases, leaving unbound pigment stranded on the surface.
Adhesion

The durability and performance of coatings depend on two basic properties:

**Cohesion and Adhesion**

*Cohesion* is associated with the strength of the bonds between the various molecules of the coating film.

*Adhesion* is viewed as the strength of the bonds between the coating material and the substrate.
The best procedure for measuring COHESION is the Tensile/Elongation test method, ASTM D638.
Adhesion Measurement

There are only ? adhesion test methods!
### ADHESION

#### PHYSICS OF ADHESION

#### BONDING FORCES AND BINDING ENERGIES

<table>
<thead>
<tr>
<th>FORCE</th>
<th>TYPE</th>
<th>EXAMPLE</th>
<th>E (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>Primary</td>
<td>Most Organics</td>
<td>15-175</td>
</tr>
<tr>
<td>Metallic</td>
<td>Primary</td>
<td>Metals</td>
<td>27-83</td>
</tr>
<tr>
<td>Hydrogen Bonding</td>
<td>Secondary</td>
<td>Water</td>
<td>&lt;12</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Secondary</td>
<td>Most Molecules</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dipole</td>
<td>Secondary</td>
<td>Polar Organics</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Induction</td>
<td>Secondary</td>
<td>Non-polar Organics</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>
Adhesion can be manifested in three different forms:

- Fundamental
- Thermodynamic
- Practical
Fundamental Adhesion is the sum of all interfacial intermolecular interactions between the contacting materials. Conversely, it represents the energy required to break the various interactions.
Thermodynamic Adhesion signifies change in free energy when an interface is formed (or separated).

\[ W_A = \gamma_{S1} + \gamma_{S2} - \gamma_{S1S2} \]

\( W_A \) = WORK OF ADHESION
\( \gamma_{S1}, \gamma_{S2} \) = SURFACE FREE ENERGIES
\( \gamma_{S1S2} \) = INTERFACIAL FREE ENERGY

\[ W_A = \gamma_{LV} (1 + \cos \theta) \]

\( \gamma_{LV} \) = SURFACE FREE ENERGY OF LIQUID
\( \theta \) = CONTACT ANGLE OF COATING/SUBSTRATE
Adhesion

**Practical Adhesion** is the force required to remove contacting materials (what is measured)

\[
\text{Practical Adhesion} = f \left( \text{fundamental adhesion} + \text{thermodynamic adhesion} + \text{other factors} \right).
\]
Adhesion is obtained when:

- Molecules achieve adsorption
- Diffuse or penetrate across the interface and form interfacial bonds
- Form chemical bonds with the interface molecules.
A durable coating will develop if and when the coating material comes in contact with the substrate surface and develops adhesion before curing or drying.
Wetting

Bond formation and adhesion begin with interfacial molecular contact by wetting.
Wetting

Wetting is the process by which a liquid interacts with a solid.
Wetting

• With paint, it involves bringing the paint into contact with a pigment, substrate, or even a contaminant, displacing air and moisture, and adsorbing onto the surface.

• A liquid will wet a surface if it has a surface tension that is lower than that of the surface.
ADHESION OF COATINGS

Surface Free Energy

Surface energy is the energy difference between an atom on the surface and an atom in the bulk.

For wetting to occur \( \gamma_s > \gamma_c \)

Epoxy-on-metal \( \gamma_s >>> \gamma_c \)

Epoxy-on-PTFE (Teflon) \( \gamma_s < \gamma_c \)
Theories of Adhesion

- Mechanical
- Electrostatic
- Chemical
- Weak boundary
- Wetting-contact
- Fracture
- Combination of phenomena
Adhesion will occur if the paint diffuses in the substrate and sets or cures while within the substrate.

- Electrolytically deposited metals
Mechanical Adhesion

Coating

Substrate
Surface Area and Adhesion

The cross section of actual interfacial contact area of coating
Dispersion, dipole and induction forces:

Adhesion is strongly affected by the interactions between the coating and substrate.
Electrostatic Attractions--Adhesion

ACTIVE SURFACE

ACTIVE COATING

H

N
The formation of covalent bonds between the resin molecules in the coating and on the surface of the substrate enhance adhesion.
Chemical Bonding--Adhesion

ACTIVE SURFACE

ACTIVE COATING

O\(=\)C\(=\)N
O\(=\)C\(=\)N

O\(\cdot\)H

O\(\cdot\)H

O

O

H

H
Adhesion to plastics can be enhanced if the resin molecules from the coating can penetrate into the surface layers of the plastic.
Mechanism of blister formation

Vapor transfer through a paint film with **good** adhesion

Vapor transfer through a paint film with **poor** adhesion

Pressure lifting paint in area of **poor** adhesion

Osmotic pressure 2,500-3000 kPa
Resistance to deformational forces 6-40 kPa
Adhesion Measurement

Peel Adhesion Testing
ASTM D3359-02

• Organic coatings on metals

Method A

Method B
Adhesion Measurement

### Classification of Adhesion Test Results

<table>
<thead>
<tr>
<th>Classification</th>
<th>% Area Removed</th>
<th>Surface of Cross-Cut Area From Which Flaking Has Occurred for Six Parallel Cuts and Adhesion Range by Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B</td>
<td>0% None</td>
<td><img src="image" alt="Illustration of 0% area removed" /></td>
</tr>
<tr>
<td>4B</td>
<td>Less than 5%</td>
<td><img src="image" alt="Illustration of less than 5% area removed" /></td>
</tr>
<tr>
<td>3B</td>
<td>5 - 15%</td>
<td><img src="image" alt="Illustration of 5-15% area removed" /></td>
</tr>
<tr>
<td>2B</td>
<td>15 - 35%</td>
<td><img src="image" alt="Illustration of 15-35% area removed" /></td>
</tr>
<tr>
<td>1B</td>
<td>35 - 65%</td>
<td><img src="image" alt="Illustration of 35-65% area removed" /></td>
</tr>
<tr>
<td>0B</td>
<td>Greater than 65%</td>
<td><img src="image" alt="Illustration of greater than 65% area removed" /></td>
</tr>
</tbody>
</table>

ASTM D 3359 Method B

- Up to 2.0 mils (50µm), 11 cuts 1 mm apart,
- 2-5 mils (125 µm), 6 cuts 2 mm apart.
Adhesion Measurement

Pneumatic Adhesion Tester (PATTI)
ASTM D4541
Adhesion Measurement

Pull-Off Adhesion Tester
ASTM D4541
Adhesion Measurement

Balanced Beam Scrape Adhesion and Mar Tester
ASTM D2197, D2248, D2454, D5178
Enhancing Adhesion
Enhancing Adhesion

- By formulation
- By application
Enhancing Adhesion

- By formulation
  - Base polymer
  - Additive

- Reduction of internal stresses
- Reduction of surface tension
- Incorporation of surface reactive groups
The forces or stresses that oppose adhesion and cohesion are diverse. They depend on:

* the service conditions,
* the chemistry of coating - composition,
* film formation mechanisms and conditions,
* film thickness,
* age
Stressed Films

Stresses can produce either adhesive (delamination) or cohesive (cracking) failure in the coating system.

A poor adhesion actually means that the adhesive strength is not sufficient to maintain adhesion under the stress conditions that act upon the film.

If the magnitude of the stress is reduced, then the same adhesive strength may be quite adequate to sustain system integrity.
Enhancing Adhesion

- Monomer line up
- Functional groups
- Particle size (in latex)
- Molecular weight distribution
- Polymer morphology
- Surface tension
Adhesion Promoters

General formula for silane coupling agents

\[ \text{R-} \left( \text{CH}_2 \right)_n \text{Si-} X_3 \]

- \( X = \text{alkoxy, acyloxy, halogen} \)
- \( R = \text{amine, epoxy, acrylate} \)

Following hydrolysis, silanol groups can form bonds with each other and other surfaces such as Al, Fe, Ti, siliceous fillers, etc.
Enhancing Adhesion

Wet Adhesion Acrylic Monomers

Sipomer WAM II

Sipomer WAM

$n = 1, 2$
Aminosilane

Epoxysilane

Cardura E

$R^1 + R^2 = 7$ carbon atoms
Enhancing Adhesion

-----[-ACRYLIC RESIN-]_n-----

[ C ]_m

m = 4-5

OH
Improving Adhesion

COATING COMPOSITION AND ADHESION

In general:
Latex resins with smaller average particles provide better adhesion than larger particles. 85 nm vs. 1050 nm

Latex resins containing sulfate type surfactants adhere better than ethoxylated phenol containing latexes

Combination of very small particle and large particle provide stronger adhesion than one latex with a broad particle distribution.
Figure 1— Adhesion trends (Drying temperature: 28 °C, surfactant Conc.: 0.3wt% solid).
Interface between the plastic and film of the latex resin (85 nm) after peeling off test. A large quantity of latex resin embedded in the micro-holes of the plastic, indicating a good diffusion of latexes into the plastic substrate.
Scanning electron micrograph

Interface between the plastic and film of the latex resin (1050nm) after peeling off test.
In general:

Adhesion of thermosetting coatings to plastics can be enhanced by incorporating low levels of chlorinated polyolefin resin.

Adhesion and dispersion of large particle pigments (aluminum, mica, etc) can be improved by treating the pigments with a variety of alkoxy silanes prior to incorporation.
Enhancing Adhesion

- Resins with small--sub-micron or nano-particles tend to improve adhesion
- Alcohol solvents in a resin containing hydrocarbon or ester solvents enhance adhesion
- Incorporation of a small amount of non-polar resin in the formulation can help adhesion
Enhancing adhesion

- Incorporate co-resins with low surface tensions and low Tg.
- Consider acid-base properties when selecting additives, pigments, and fillers.
- Use resins in which the hard segments are separated from the soft segments with at least 4 carbon units.
- Blend high and low molecular weight resins instead of using one narrow molecular weight resin.
In summary:

- Adhesion is a surface phenomenon. It is related to physical forces and chemical reactions / interactions in the interface.
- Adsorption and wetting aided by the low surface tension of coating material and high surface free energy of the substrate are central to adhesion.
- Adhesion of coatings may be enhanced by incorporating low surface energy lower Tg co-resins and by removing weak-boundary layer from the surface of substrate.
Thank You!