# Performance Properties of Waterborne UV-Cured Coatings on Metal

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## Introduction

UV curable waterborne coatings based on acrylate functional polyurethane dispersions (UV PUDs) have found acceptance in the wood and resilient flooring markets[1], but the performance of waterborne UV technology may offer potential for other markets as well. The performance of waterborne coatings based on UV PUDs was evaluated by testing the properties of adhesion, impact resistance, flexibility, hardness, solvent resistance and corrosion resistance when applied to aluminum and steel substrates. For comparison, the performance of coatings based on selected 100% solids acrylate functional oligomers was also tested.

Coatings on metal can face a challenging combination of performance properties. These coatings are often required to protect the substrate from corrosion and provide solvent and scratch resistance. In 100% solids UV radical cured coatings, increased acrylate functionality imparts higher crosslinking of the cured coating. This results in harder coatings with increased solvent resistance and scratch resistance. Metal coatings also commonly require resistance to cracking under impact or bending, however, increased crosslinking will negatively impact these properties.

Adhesion to metal substrates can also be difficult for 100% solids UV cured coatings. The relatively high volumetric shrinkage of UV radical coatings on curing and the low potential for mechanical bonding with the substrate can result in poor adhesion unless coatings are properly formulated. This typically requires minimizing shrinkage by limiting the crosslinking of the coating and the incorporation of additives to create chemical bonding with the substrate. Such coatings can have excellent adhesion to metal but the reduced crosslinking will reduce properties such as solvent and scratch resistance, often to an unacceptable level of performance.

UV PUDs differ significantly from standard acrylate oligomers in both structure and physical properties. The resulting performance differences have demonstrated advantages in non-metal coating applications. UV PUDs might also provide a means to overcome some of the limitations of 100% solids UV coatings on metal.

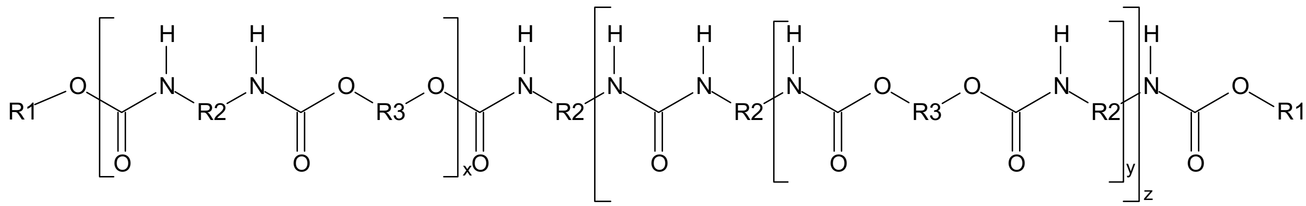
### Materials

The UV PUDs evaluated in this study offer properties unlike those of 100% solids acrylate oligomers. All exhibit viscosities less than 200 cP at 25°C and the use of low molecular weight acrylate monomers for viscosity control is not required. This makes them well suited to spray application, without the compromise in performance and irritancy potential that can occur by the need for high monomer levels in 100% solids spray applied coatings. They also have little (<1%) or no volatile content. After the evaporation of the water from a UV PUD coating the film can be tack-free. This can allow for processes such as the repair of coating defects or embossing to be performed prior to UV curing.

A significant disadvantage for UV PUDs compared to 100% solids UV systems is the necessity of removing the water from the film prior to UV curing. This step can increase the equipment and energy costs for a process using UV PUDs compared to 100% solids UV.

Figure 1 provides a model structure for a UV PUD.

**Figure 1 – UV PUD Structure**




x, y = 1-3
z = 0-1
R1 = capping acrylate
R2 = diisocyanate
R3 = diol

Similar to 100% solids urethane acrylates, UV PUDs are composed of isocyanates linked by polyols and capped with a hydroxyl functional acrylate. However, practical limitations exist on the molecular weight and component choice for 100% solids urethane acrylates due to the need to maintain a workable viscosity. For UV-PUDs, viscosity is largely independent of the polyurethane structure, allowing for greater variability in the components along with molecular weights that are several times higher than practical for 100% solids urethane acrylates.

Four UV PUDs were selected for testing in this study. While these UV PUDs were developed specifically to meet the needs of wood and resilient flooring applications, their structure and physical properties demonstrate potential utility for metal coatings. Table 1 lists the typical properties of these UV PUDs.

**Table 1 – UV PUD Properties**

| | UV PUD-1 | UV PUD-2 | UV PUD-3 | UV PUD-4 |
|---|---|---|---|---|
| Type | Aliphatic urethane acrylate | Aromatic acrylic urethane acrylate | Aliphatic urethane acrylate | Aliphatic urethane acrylate |
| % solids | 35 | 38 | 35 | 40 |
| Viscosity, 25°C, cP | <200 | <200 | <200 | <200 |
| Tensile strength, psi | 9900 | 5000 | - | 7500 |
| Elongation, % | 7 | 13 | - | 7 |
| Tg, °C | 112 | 116 | - | 86 |
| Tack-free before UV cure | Yes | Yes | Yes | No |

Four acrylate functional oligomers were selected for preparing 100% solids formulation. Table 2 provides the typical properties for these oligomers.

**Table 2 – Standard Oligomer Properties**

| | EA | PEA | M-EA | UA |
|---|---|---|---|---|
| Type | Epoxy acrylate | Acid functional polyester acrylate | Modified epoxy acrylate | Aliphatic urethane acrylate |
| Viscosity, 25°C, cP | 800,000 | 60,000 | 20,000 | 20,000 |
| Diluent | None | hexanediol diacrylate | 2-phenoxyethyl acrylate | isobornyl acrylate |
| Tensile strength, psi | 12000 | 1000 | 400 | 4000 |
| Elongation, % | 5 | 30 | 75 | 186 |
| Tg, °C | 65 | 30 | 11 | 46 |

The EA (epoxy acrylate) oligomer is the widely used diacrylate ester of bisphenol-A diglycidyl ether. The PEA (polyester acrylate) oligomer was selected for its generally good adhesion properties and is an acid functional polyester resin in a reactive diluent. The M-EA (modified epoxy acrylate) oligomer is an epoxy diacrylate modified to have much higher elongation and flexibility than the bisphenol-A diglycidyl ether diacrylate. The UA (urethane acrylate oligomer) is an aliphatic urethane diacrylate specifically designed for high elongation and flexibility.

**Formulations**

Table 3 provides the coating formulation used for the UV PUDs.

**Table 3 – UV PUD Formulations**

| Component | % |
|---|---|
| UV PUD | 95.0 |
| wetting aid | 3.0 |
| photoinitiator | 2.0 |

The wetting aid is a polyacrylic type (50% active). The photoinitiator is a 1/1 mixture of benzophenone and 1-hydroxy-cyclohexylphenyl-ketone.

Table 4 provides the two coating formulations used for the standard oligomers.

**Table 4 – Standard Oligomer Formulations**

| Component | % | |
|---|---|---|
| EA | 50.0 | - |
| PEA; M-EA; UA | - | 50.0 |
| 2-phenoxyethyl acrylate | - | 20.0 |
| 1,6-hexanediol diacrylate | 20.0 | - |
| neopentyl glycol propoxylate(2) diacrylate | - | 20.0 |
| trimethylolpropane triacrylate | 20.0 | - |
| adhesion promoter | 5.5 | 5.5 |
| wetting aid | 0.5 | 0.5 |
| photoinitiator | 4.0 | 4.0 |

The adhesion promoter is an acid functional phosphate methacrylate ester. The wetting aid is a fluorocarbon acrylate. The photoinitiator is 2-hydroxy-2-methyl-1-phenyl-propanone.

The EA formulation was designed to impart scratch and chemical resistance to the cured coatings through higher crosslinking. The PEA, M-EA and UA formulations have significantly less crosslinking and were designed to provide the cured coatings with high flexibility and impact resistance.

### Procedures

Three different standard metal test panels were used as substrates: bare aluminum[2], bare polished steel[3], and polished iron phosphate coated steel[4]. The substrates were wiped with a dry paper cloth to remove dust and particles prior to coating. No other cleaning or treatment of the substrates was performed.

The coating formulations were applied to the substrates using wire wound applicators to provide the desired dry coating thickness (~8-13μ).

All UV PUD coatings were dried prior to UV curing. Coated substrate samples were placed in an oven set at 60°C for 5 minutes. All UV PUD coatings were UV cured immediately upon removal from the drying oven.

All coatings were UV cured using two 600 watt/inch electrode-less H type lamps set to 100% output, to give a total UV energy exposure of ~1000 mJ/cm$^2$.

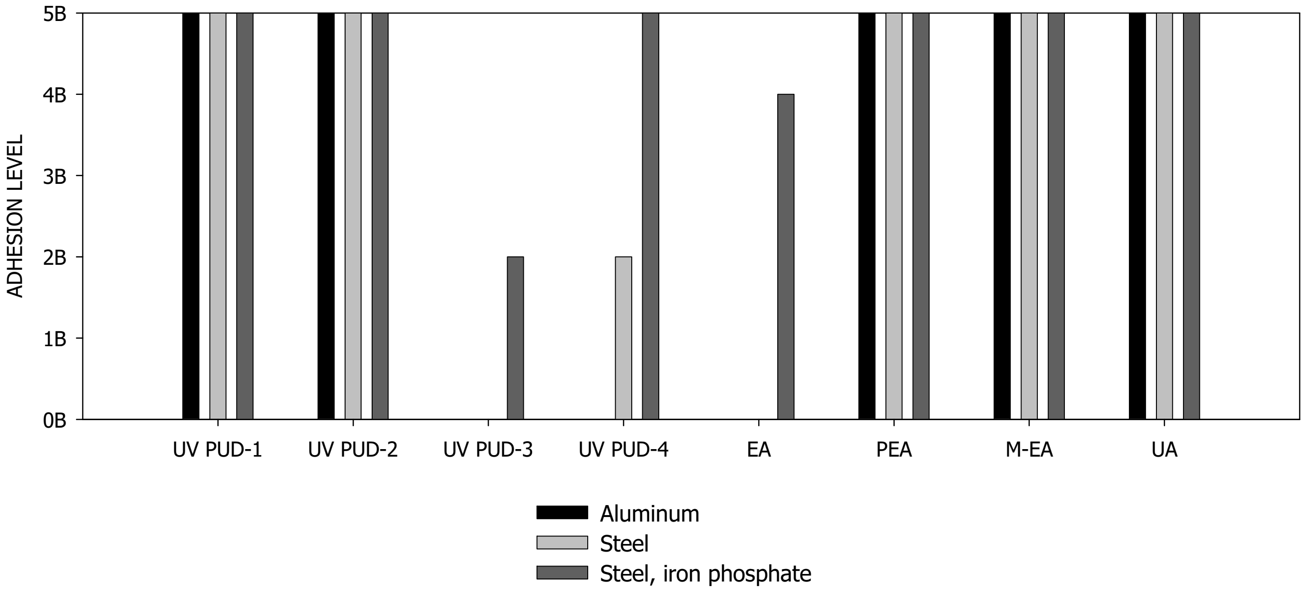
## Performance

### Adhesion

Adhesion of the coating formulations to the test substrates was evaluated by crosshatch tape test in accordance with ASTM D 3359. The adhesion for each coating/substrate combination was tested using two different tapes[5]. One tape consistently demonstrated more aggressive adhesion to the coatings and subsequently gave lower adhesion levels for the coatings to the substrate. Adhesion levels using this tape are those reported and discussed.

Graph 1 presents the adhesion results for each coating formulation/substrate combination.

**Graph 1 – Adhesion (tape 1)**




UV PUD-1 and UV PUD-2 exhibited no coating adhesion loss on any of the three substrates, UV PUD-3 demonstrated low adhesion to all three substrates as did UV PUD-4, with the exception of iron phosphate coated steel.

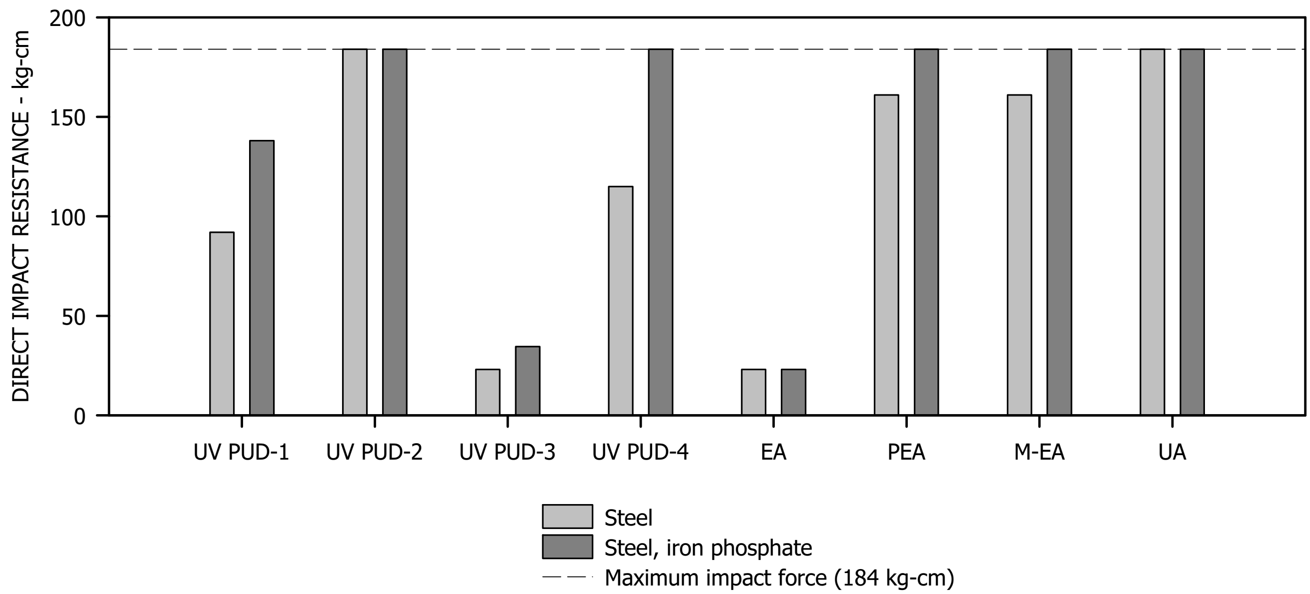
Of the standard oligomer formulations, only the EA based formulation demonstrated any adhesion loss. The low adhesion of the EA-based formulation can be attributed to its higher crosslinking, while the reduced crosslinking of the PEA, M-EA and UA formulations contributes to their excellent adhesion.

Of the three test substrates, the aluminum test panels proved the most difficult for adhesion. Not surprisingly, the iron phosphate coated panels, which are intended to provide better anchorage for organic coatings, were the least difficult for adhesion.

**Impact Resistance**

Impact resistance of the coatings was tested in accordance with ASTM D 2794. Intrusion (direct impact) of the indenter into the coated surface was used to assess the impact resistance, which is reported in Graph 2. The limited ductility of the aluminum test panels made them unsuitable for use, and the impact testing was conducted with only the bare and iron phosphate coated steel test panels.

**Graph 2 – Direct Impact Resistance**




The UV PUD coatings, with the exception of UV PUD-3, demonstrated moderate to excellent impact resistance. The impact resistance of the UV PUD-3 coating was significantly lower and is indicative of a relatively brittle coating.

As designed, the less crosslinked PEA, M-EA and UA-based formulations demonstrated high impact resistance. The higher crosslinked EA-based formulation exhibited low impact resistance.

Where differences in impact resistance varied with the substrate, the impact resistance was consistently higher on the iron phosphate treated steel. This can be attributed to the greater coating adhesion to this substrate, providing the coating with increased resistance to the force of impact.

**Flexibility**

Coating flexibility was assessed by conical mandrel testing in accordance with ASTM D 522. This testing was conducted only on the coated aluminum test panels. The results are reported in Table 4 as the measured distance (mm) of any observed cracking of the coating.

**Table 4 – Conical Mandrel Flexibility**

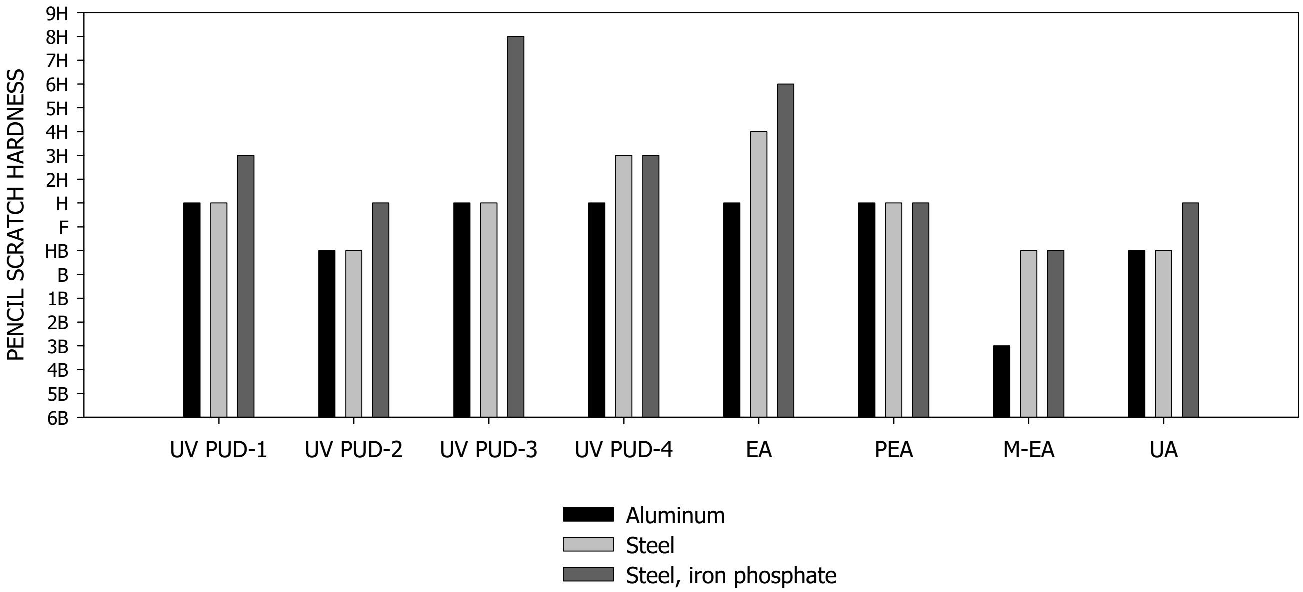
| | UV PUD-1 | UV PUD-2 | UV PUD-3 | UV PUD-4 | EA | PEA | M-EA | UA |
|---|---|---|---|---|---|---|---|---|
| Crack length, mm | 0 | 0 | >100 | 0 | 35 | 0 | 0 | 0 |

The same trends observed in the impact resistance test were apparent in the conical mandrel testing. Only the UV PUD-3 and the EA-based formulations, which demonstrated low impact resistance, exhibited any cracking in the conical mandrel testing.

**Pencil Hardness**

The hardness of the coatings was measured using the pencil hardness test in accordance with ASTM D 3363. Scratch hardness, the hardest pencil that will not rupture or scratch the film, is reported in Graph 3.

**Graph 3 – Pencil Scratch Hardness**

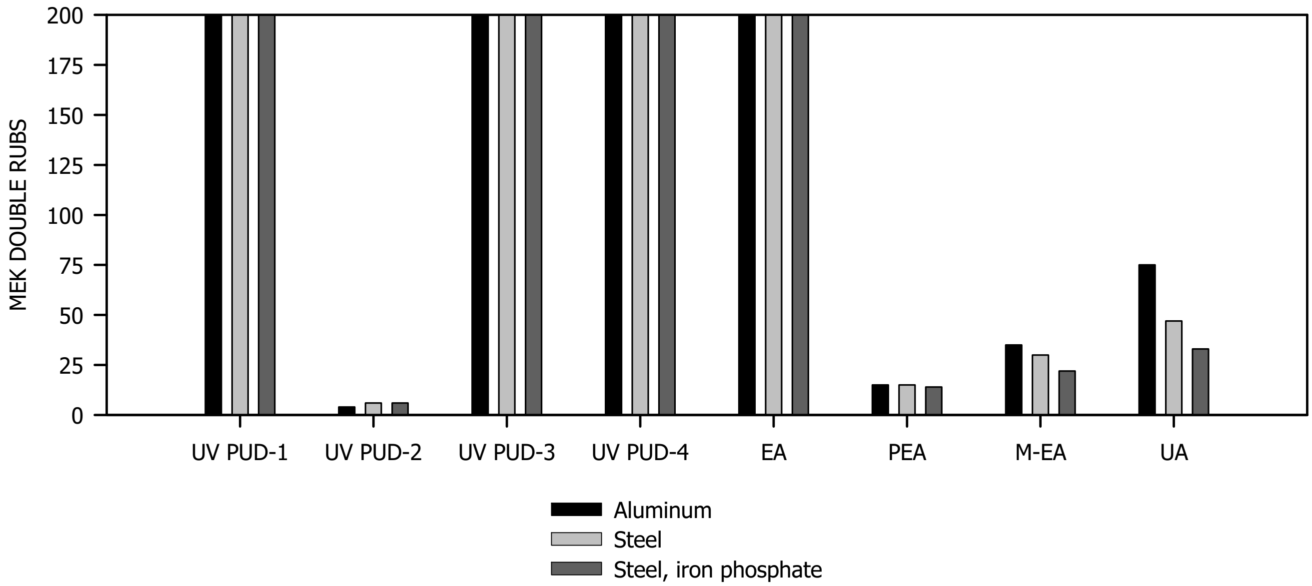



Pencil hardness of the coatings follows the trends observed in impact resistance. Those coatings with the lowest impact resistance and flexibility, UV PUD-3 and EA, also demonstrated the highest overall hardness. Pencil hardness decreased for those coatings with greater impact resistance and flexibility, with those coatings having the highest impact resistance and flexibility exhibiting the lowest pencil hardness. The UV PUD-1 and PEA-based formulations are notable in demonstrating moderate pencil hardness while also having high levels of adhesion, impact resistance and flexibility.

**Solvent Resistance**

The solvent (MEK) resistance of the cured coatings was determined using an internal test procedure. In this test, cloth covering the curved face of a 32-ounce ball-peen hammer is saturated with methyl ethyl ketone. Holding the hammer's handle and exerting no downward force other than the hammer weight, the cloth-covered face is then rubbed back and forth across the surface of the coating. One back and forth motion is one double rub. The double rubs are counted and the test is concluded when the first break in the coating to the substrate is detected, or when 200 double rubs are reached. These results are shown in Graph 4.

**Graph 4 – MEK Resistance**




Three of the four UV-PUD coatings exhibited excellent solvent resistance. One, UV PUD-1, had previously demonstrated excellent adhesion to each substrate and good-to-excellent impact resistance, flexibility and impact resistance. UV PUD-2, with similar performance to UV PUD-1 in other properties, exhibited minimal solvent resistance.

Of the standard oligomer based coatings, only the more highly crosslinked EA based coating exhibited superior solvent resistance. The lower crosslinking of the other standard oligomer-based coatings correlated with significantly lower solvent resistance.

**Corrosion Resistance**

Coatings were subjected to salt fog testing in accordance with ASTM B 117 to assess corrosion resistance. Coatings were applied at 20-25µ dry film thickness to iron phosphate coated steel panels. Protective tape was applied to the uncoated sections of the test panels. The corrosion resistance of the coatings was classified according to the rating scale in ASTM D 610. This scale is numeric, with a rating of 10 indicating less than or equal to 0.01 percent surface rusting and 0 indicating greater than 50 percent surface rusting. The nature of the rusting is also taken into consideration by indicating if the rusting is spot (S), general (G) or pinpoint (P). Test panels were removed from the salt fog chamber when the corrosion resistance was judged to be significantly less than the remaining coated panels. Table 5 shows the results of the salt fog testing.

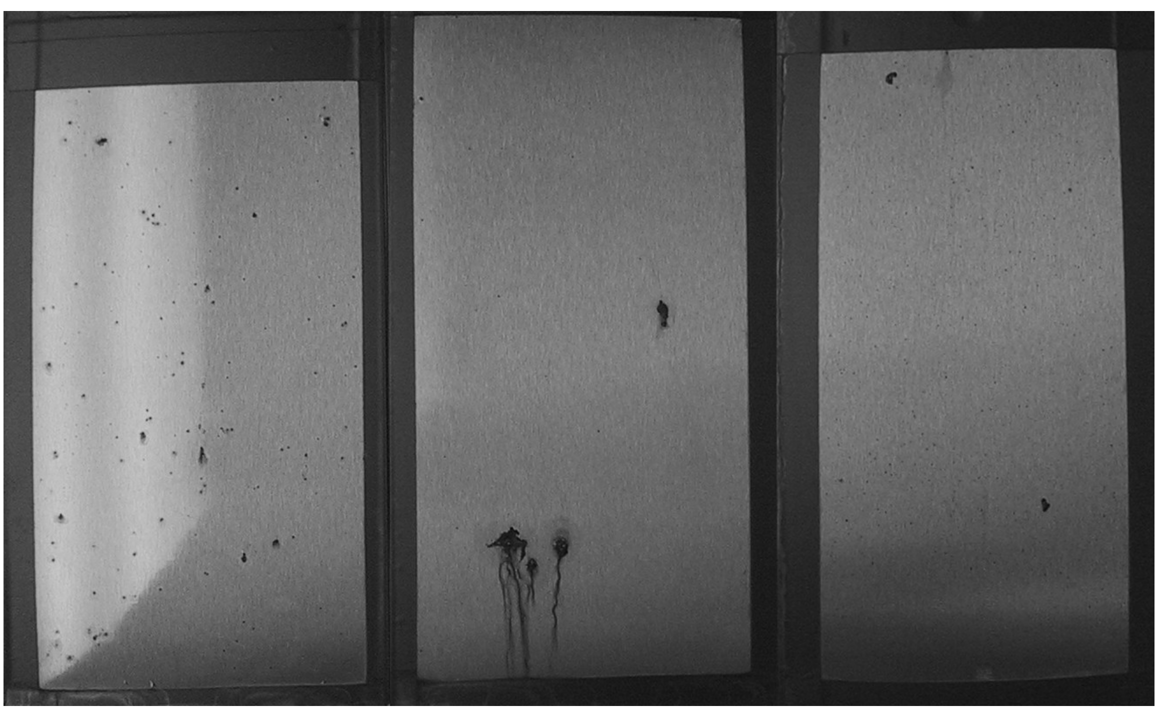
**Table 5 – Degree of Rusting**

| Hours Exposure | Rust Type | Coating | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | UV PUD-1 | UV PUD-2 | UV PUD-3 | UV PUD-4 | EA | PEA | M-EA | UA |
| 24 | Spot Rusting | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| | General Rusting | 10 | 3-G | 10 | 10 | 10 | 10 | 10 | 10 |
| | Pinpoint Rusting | 10 | 10 | 10 | 2-P | 10 | 10 | 10 | 10 |
| 96 | Spot Rusting | 9-S | | 9-S | | 10 | 10 | 10 | 9-S |
| | General Rusting | 10 | | 10 | | 9-G | 10 | 10 | 10 |
| | Pinpoint Rusting | 10 | | 10 | | 10 | 9-P | 6-P | 6-P |
| 240 | Spot Rusting | 8-S | | 9-S | | 10 | 10 | | |
| | General Rusting | 10 | | 10 | | 6-G | 10 | | |
| | Pinpoint Rusting | 10 | | 8-P | | 10 | 7-P | | |
| 312 | Spot Rusting | 7-S | | 9-S | | | 10 | | |
| | General Rusting | 10 | | 10 | | | 8-G | | |
| | Pinpoint Rusting | 10 | | 8-P | | | 10 | | |

The panels coated with UV PUD-2 and UV PUD-4 exhibited significant rusting after 24 hours exposure and were removed. Test panels with UV PUD-1 and UV PUD-3 exhibited relatively low levels of rusting after 312 hours of salt fog exposure.

Among the standard oligomers, the PEA-based coatings demonstrated the best corrosion resistance. Figure 2 provides a visual comparison of the degree of rusting exhibited by the UV PUD-1, UV PUD-3 and PEA-based coated test panels after 312 hours of salt fog exposure.

**Figure 2 – Corrosion Resistance at 312 Hours Salt Fog Exposure**



PEA UV PUD-1 UV PUD-3

## Conclusion

The data from this study demonstrate that metal coatings based on UV PUD exhibit a superior balance of performance properties compared to coatings based on standard oligomers in conventional 100% solids UV systems. UV PUD-based coatings demonstrated excellent adhesion when applied directly to aluminum and steel substrates. In addition to adhesion, UV PUD-based coatings exhibited excellent resistance to solvent attack combined with superior flexibility and good impact resistance and pencil hardness.

In salt fog testing, UV PUD-based coatings also demonstrated corrosion resistance on the same level of performance as the best standard oligomer based coatings.

While standard oligomer-based coatings could provide equivalent performance to the UV PUD based coatings for any single coating property, none was able to achieve the combination of performance properties demonstrated in the best UV PUD-based coatings. Standard oligomer-based coatings that exhibited excellent adhesion and impact resistance suffered poor solvent resistance, while those standard oligomer-based coatings having superior solvent resistance and hardness demonstrated low adhesion and impact resistance.

The performance of the best UV PUD coatings in this study demonstrates the potential utility for UV PUDs in metal coating applications. The development of UV PUDs targeted specifically for the metal coatings market offers the possibility of even higher levels of performance.

## Acknowledgements

The author expresses appreciation to Ms. Angela Carmack, Cytec Senior Laboratory Technician, for assisting in the preparation and evaluation of the formulations tested in this study.

1. Tielemans, M., Bleus, J-P., Vasconi, M., “Braving the Weather”, European Coatings Journal, March 2007, p. 38-42
2. Stock No. A-48, 0.6 x 102 x 203 mm, Q-Panel Lab Products
3. Stock No. S-48, 0.8 x 102 x 203 mm, Q-Panel Lab Products
4. Cold rolled steel, B1000, P60, DIW, Polish, 0.8 x 102 x 203 mm, ACT Test Panels, Inc.
5. Tape 1 is 3M Scotch brand Tape 600; tape 2 is Permacel brand P-99, Permacel Co.

# Appendix: Coating Formulations and Properties

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| UV PUD-1 | 95.0 | | | | | | | |
| UV PUD-2 | | 95.0 | | | | | | |
| UV PUD-3 | | | 95.0 | | | | | |
| UV PUD-4 | | | | 95.0 | | | | |
| EA | | | | | 50.0 | | | |
| PEA | | | | | | 50.0 | | |
| M-EA | | | | | | | 50.0 | |
| UA | | | | | | | | 50.0 |
| 2-phenoxyethyl acrylate | | | | | | 20.0 | 20.0 | 20.0 |
| 1,6-hexanediol diacrylate | | | | | 20.0 | | | |
| neopentyl glycol propxylate(2) diacrylate | | | | | | 20.0 | 20.0 | 20.0 |
| trimethylolpropane triacrylate | | | | | 20.0 | | | |
| adhesion promoter(1) | | | | | 5.5 | 5.5 | 5.5 | 5.5 |
| wetting aid(2) | | | | | 0.5 | 0.5 | 0.5 | 0.5 |
| wetting aid(3) | 3.0 | 3.0 | 3.0 | 3.0 | | | | |
| photoinitiator 1(4) | 2.0 | 2.0 | 2.0 | 2.0 | | | | |
| photoinitiator 2(5) | | | | | 4.0 | 4.0 | 4.0 | 4.0 |
| | | | | | | | | |
| Viscosity, cP, 25°C | <200 | <200 | <200 | <200 | 1000 | 510 | 850 | 550 |
| | | | | | | | | |
| **Aluminum, bare, type A**; adhesion, tape 1(6) | 5B | 5B | 0B | 0B | 0B | 5B | 5B | 5B |
| adhesion, tape 2(7) | 5B | 5B | 0B | 4B | 2B | 5B | 5B | 5B |
| MEK double rubs | >200 | 4 | >200 | >200 | >200 | 15 | 35 | 75 |
| conical mandrel bend, crack length, mm | 0 | 0 | >100 | 0 | 35 | 0 | 0 | 0 |
| pencil scratch hardness | H | HB | H | H | H | H | 3B | HB |
| | | | | | | | | |
| **Steel, polished, type S**; adhesion, tape 1 | 5B | 5B | 0B | 2B | 0B | 5B | 5B | 5B |
| adhesion, tape 2 | 5B | 5B | 1B | 4B | 3B | 5B | 5B | 5B |
| MEK double rubs | >200 | 6 | >200 | >200 | >200 | 15 | 30 | 47 |
| direct impact, in-lbs | 80 | 160 | 20 | 100 | 20 | 140 | 140 | 160 |
| pencil scratch hardness | H | HB | H | 3H | 4H | H | HB | HB |
| | | | | | | | | |
| **Steel, iron phosphate, type S**; adhesion, tape 1 | 5B | 5B | 2B | 5B | 4B | 5B | 5B | 5B |
| adhesion, tape 2 | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B |
| MEK double rubs | >200 | 6 | >200 | >200 | >200 | 14 | 22 | 33 |
| direct impact, in-lbs | 120 | 160 | 30 | 160 | 20 | 160 | 160 | 160 |
| pencil scratch hardness | 3H | H | 8H | 3H | 6H | H | HB | H |

(1) acid functional phosphate methacrylate ester
(2) fluorocarbon acrylate
(3) polyacrylic, 50% active
(4) benzophenone/1-hydroxy-cyclohexylphenyl-ketone 1/1
(5) 2-hydroxy-2-methyl-1-phenyl-propanone
(6) Scotch® 600 tape
(7) Permacel® P-99 tape