Enhancing Adhesion and Film Formation in UV Coatings

Abstract

Adhesion of radiation curable (RC) coatings on polyolefinic substrates such as packaging films or automotive trim is often very challenging. Reasons include instantaneous curing with significant shrinking, the combination of chemical inertness and low surface tension of the substrates and the rheology and surface tension of the acrylate coating.

Chlorinated polyolefins have been used successfully to adhere RC coatings to such substrates. These materials have limited use as additives in RC formulations, but are very effective when used as separately applied primer coats. Five different generic acrylate formations applied over thermoplastic polyolefin automotive test panels not only showed excellent adhesion as tested with the normal ASTM D3359 cross hatch adhesion test, but showed excellent gasoline resistance and Cleveland Humidity resistance as well.

Cellulose esters have been used as additives in solvent borne coatings for decades to promote quick drying and flow and leveling over a variety of substrates. In RC coatings they have been used at low levels, typically 1-3%, to provide a rheology that allows acrylate coatings to flow and level over challenging substrates, and reduce shrinkage thereby improving adhesion. One of the main difficulties with cellulose esters in UV coatings is their impact on viscosity.

In 2006 Eastman introduced Eastman ™ 2100 performance additive (PA), which provides the benefits similar to cellulose esters, but at a greatly reduced viscosity. It has excellent solublity in most commonly used monomers and also has excellent compatibility. The benefits of Eastman Solus™ 2100 PA on film formation has been examined by evaluating surface tension, drop spread, and using time-lapse photography.

Improving Adhesion

Low molecular weight polyolefins that have been chemically modified by chlorination and maleation have been used as adhesion promoters for coatings, inks, and adhesives that are applied to polyolefin-based substrates. These adhesion promoters are used in both primer and additive applications and must meet a variety of performance specifications, particularly in coating applications. This study shows the compatibility and adhesion performance characteristics of a variety of adhesion promoters evaluated with five UV-curable coating systems.

Experimental

In the table below five generic starting formulations (all 100% solids) are shown. These exhibit a range of performance, from hard and more brittle coatings for highly functionalized (highly crosslinked) to softer coatings consisting of oligomers and monomers with lower functionality. All the components were supplied by UCB Chemicals (now Cytec Surface Specialties), except where indicated.

Table 1. Compositions of Acrylate Plastics Coatings

	A	B	C	D	E
Ebecryl® 3720-HD20	40	28	0	0	0
Ebecryl 810	0	20	0	0	0
Ebecryl 284	0	0	38	0	0
Ebecryl 264	0	0	0	38	0
Ebecryl 1290	7	0	0	0	36
HDODA	36	0	40	45	22
TRPGDA	0	26	0	0	0
TMPTA-N	10	0	15	10	10
OTA-480	0	19	0	0	0
DPHPA	0	0	0	0	25
Ebecryl P 115	4	4	4	4	4
Irgacure® 500	3	3	3	3	3
Viscosity (cPs)	106	186	140	106	500

- Ebecryl 3720-HD20 is a bisphenol A epoxy acrylate diluted with 20% HDODA.
- Ebecryl 810 is a trifunctional polyester acrylate.
- Ebecryl 284 is a difunctional aliphatic urethane acrylate.
- Ebecryl 264 is a trifunctional aliphatic urethane acrylate.
- Ebecryl 1290 is a hexa-functional aliphatic urethane acrylate.
- HDODA is hexane diol diacrylate monomer.
- TRPGDA is tripropylene glycol diacrylate monomer.
- TMPTA-N is trimethylolpropane triacrylate.
- OTA-480 is propoxylated glycerol triacrylate.
- DPHPA is dipentaerythritol hydroxy penta-acrylate.
- Ebecryl P 115 is an amine synergist.
- Irgacure 500 is a photoinitiator available from Ciba.

Application and Cure of the Acrylate Coatings

The coatings were applied using an RK automated draw down machine (Print-Coat Instruments, Ltd., England). Wire-wound rod #6, (orange; 2.5 mil wet film deposit) was used for this work. The speed was set at "4" (middle of the range). The coating thickness was measured on steel panels with a magnetic thickness gauge, which indicated this resulted in an approximately 1-3-mil thick cured coating. All panels were coated in the same manner regardless of CPO pretreatment.

The coated substrates were cured with a UV cure machine made by American Ultraviolet, using a belt speed of 20 ft/min and irradiation with a 300 watts-per-inch medium-pressure mercury lamp, resulting in exposure of approximately 650 mJ/cm^2.

Use of CPOs as Additive in Acrylate Coatings

Compatibility

The compatibility of a variety of adhesion promoters with the UV monomers was determined by adding 20 weight percent of a range of adhesion promoters (on a solids basis) to each monomer in table one and styrene. This was done by adding 5 gram of the monomer in an 8-dram vial. After this, 2 grams of 50% (solids), 2.5 grams of 40%, 4 grams of 25% or 5 grams of 20% adhesion promoter in solvent was added to each of the monomers and mixed well. Eastman™ CP 343-3, which is high in chlorine content (30 weight %), is the only adhesion promoter found to be compatible with the acrylate monomers. Unfortunately, Eastman™ CP 343-3 did not significantly improve the adhesion properties of the coatings when used as an additive at this level, with only slight improvement in adhesion of coatings A and B applied to TPO.

Use of CPOs as an Adhesion-Promoting Tie-Coat

The second part of this work was to determine if a tie coat (or primer coat) of adhesion promoter applied to the substrate would improve the adhesion of acrylate coatings to TPO substrates. The adhesion promoters were applied to the TPO as described below, with Eastman™ CP 730-1 chosen for the first screening tests. After the adhesion promoters were applied, these were air-dried and then the RC coatings were applied as described earlier. As shown in Table 2, the radiation-cured coatings showed very poor adhesion to the TPO substrate without the use of an adhesion promoter. When Eastman™ CP 730-1 was used as an adhesion promoter marked improvements were obtained, and only coating B had some adhesion loss. Interestingly, all of the adhesion promoters provided adequate adhesion of coating E to the TPO substrate. Coating E is the hardest coating tested and it exhibited hairline cracks upon cure. Despite this cracking, the adhesion promoters provided adequate adhesion of the coating to the substrate.

Application of the Adhesion Promoters on TPO

All TPO panels were wiped with isopropyl alcohol before coating. All coatings were applied using a Devilbiss Model JCV-570 spray gun. All adhesion promoter primers were spray applied at 5% solids in xylene, using 35-40 lbs. of air pressure at the gun. Two coats of adhesion promoter were applied to each panel, giving an approximate adhesion promoter film thickness of 0.1-0.3 mils.

Substrates- The substrates used in this study were provided by Standard Plaque, Inc. The lot # for the Sequel 1440 TPO used was 880545 Code # 55042AA.

Table 2. Adhesion of Various Radiation Cured Acrylate Coatings*

Coating	Untreated TPO	TPO w 730-1
A	0%, 0%	100%, 100%
B	0%, 0%	60%, 80%
C	0%, 0%	100%, 100%
D	0%, 0%	100%, 100%
E	0%, 0%	100%, 100%

* Results are shown from duplicate panels

Separate panels of the adhesion-promoter/RC coated substrates were prepared for gasoline and humidity resistance testing. Gasoline resistance testing was determined using a Ford modified test method (Ford Modified Juntunen). One TPO sample was tested for each primer/topcoat/substrate system. The panels were scribed with a sharp knife to give approximately 100 squares, each square being approximately 3 mm in width and height. The scribed panels were immersed in the gasoline mixture and were checked for adhesion and lifting of the coating every 15 minutes for up to 60 minutes. After 60 minutes the panels were removed from the gasoline mixture, dried, and rated for performance. Ford Gasoline Resistance Mixture is a blend, by weight, of Toluene (45%), isooctane (45%), and ethanol (10%). Table 3 shows that the gasoline resistance properties of the coated TPO substrates are very good overall, with only minor amounts of lifting, but 100% of the coating remained on the substrate.

Table 3. Gasoline Resistance of TPO Panels Coated with CP-730-1 and Radiation Cured Acrylates

	15 min.		30 min.		45 min.		60 min.	
Coating	Adhesion	Lift	Adhesion	Lift	Adhesion	Lift	Adhesion	Lift
A	100	0	100	0	100	0	100	0
B	100	0	100	0	100	0	100	100
C	100	0	100	Edge	100	100	100	100
D	100	0	100	Edge	100	100	100	100
E	100	Edge	100	Edge	100	Edge	100	Edge

Humidity resistance was determined using ASTM test method D4585 in conjunction with ASTM D3359B and ASTM D714, which is described below. After the panels were checked for initial adhesion (ASTM D3359B), the panels were placed in a QCT Cleveland condensation tester/chamber (supplied by Q-Panel) that was maintained with a continuous water supply and at a temperature of 120^{o}F. All cracks between test specimens were closed through the use of aluminum panels supplied by Q-Panel. After 4 and 11 days respectively, the panels were removed from the chamber, wiped dry, and were then tested for blistering and adhesion. The panels were tested less than 2-3 minutes after removal from the chamber and were returned to the chamber as soon as testing was complete, which is estimated to be less than 5 minutes after removal from the chamber. The percent-retained adhesion of the coating was determined in accordance with ASTM D3359B and was reported as percent of coating remaining/adhering to the substrate in the crosshatch area. The tape used for determining adhesion in this study was Permacel 99. The degree of blistering of the coating was determined in accordance with ASTM D714. In our study, 0 represents no observable blistering and 8, 6, 4 and 2 would represent progressively larger blister sizes. A blister size of 8 represents the smallest size blister easily seen by the unaided eye. The frequency of blisters is reported as F (few), M (medium), MD (medium dense), and D (dense).

Table 4 shows the humidity resistance of the coated TPO substrates. Coating A passed both 4 and 11-day humidity with CP 730-1, but coatings B, C and D showed poor adhesion. Coating E showed good adhesion after both 4 and 11 days humidity exposure. Most of the coating systems showed blistering and anything that had blister ratings of 6 or 4 were very large sized blisters. Overall, the humidity resistance results can be rated as shown in Table 4:

Table 4. Cleveland Humidity Results of TPO Panels Coated with CP-730-1

Sample	4 days Adhesion/Blisters	11 days Adhesion/Blisters
A	100 / 6M	100/ 6M
B	0 / 6F	—
C	0 / 6F	—
D	96 / 6F	0/ 6F
E	100 / 8F	100/ 8M

In summary, excellent adhesion of UV coatings on polyolefinic substrates can be obtained when a tie or primer coat of adhesion promoter is applied first. In this work the primer coat had been spray applied, but in other industrial settings such as printing presses, such primer coats can also be roll applied.

Improving Film Formation using Eastman Solus™ 2100 Performance Additive

Achieving appropriate rheological performance and flow and leveling is among the more difficult challenges faced by formulators of RC coatings, while maintaining the required application viscosity. In RC over-print- varnishes (OPV) especially, where the printed substrates exhibit large variability in chemical inertness and surface tension, surface defects can become an issue. This has become more pronounced with the continual introduction of new and modified packaging films to which these RC systems must be applied. Many of these, for example polyolefinics, can present a significant challenge.

In 2006 Eastman introduced a new additive called Eastman Solus™ 2100 performance additive into the automotive coatings market for high solids applications. Eastman Solus™ 2100 PA has been shown in solvent borne automotive coatings to provide rheology control, quick drying, color consistency, and flow and leveling, with minimal impact on coating viscosity. It was desired to determine if the benefits of Eastman Solus™ 2100 PA observed in solvent borne systems would translate into RC coatings as well. In this work we examined the behavior of a generic RC OPV formula, with and without Eastman Solus™ 2100 performance additive (OPV+), as shown in Table 5 below.

Table 5. Formulation of over-print-varnishes

Ingredient	OPV	OPV+ Eastman Solus™ 2100 PA
Ebecryl 3720TP25	35.0	35.0
HDODA	48.0	15.0
Additol BP	6.0	6.0
MDEA	6.0	6.0
Additol HDMAP	5.0	5.0
Eastman Solus™ 2100, 15% in HDODA	0	33.0
Viscosity cPs	62	113
Liquid Surface tension dynes/cm	34.8	33.5
Cured film dynes/cm	49.3	33.0

Viscosity has been determined by Brookfield. The liquid surface tension was measured with a Cahn Dynamic Contact Angle Analyzer using the Wilhelmy plate-wetting balance technique. The surface tensions of films and substrates have been determined using a video contact angle measurement. A sessile drop of liquid, in this case water and then methyl iodide, is placed on the surface and photographed. The drop profile is used to measure the contact angle and calculate the surface tension.

The flow and leveling of the OPVs was examined on Leneta paper, and polypropylene
To evaluate the effect of the formulations and the substrates, small droplets were placed on the Leneta paper and on the PP panel. The drop spread was followed using microscopy with software to measure the diameter of the drop. Typically, time lapses of 15 seconds over a two-minute time frame were used to follow the drop growth and the average diameter. The results are shown in Figure 1a-c

Figure 1a. Drop spread of OPV on Leneta paper

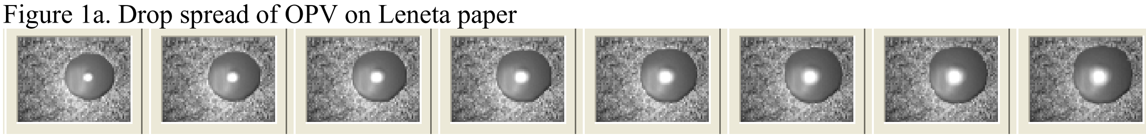


Figure 1b. Drop spread of OPV on TPO

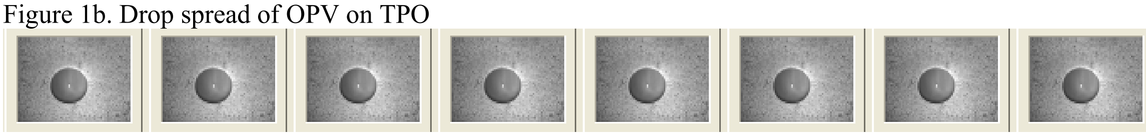
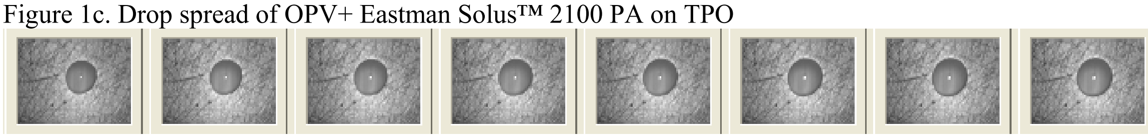
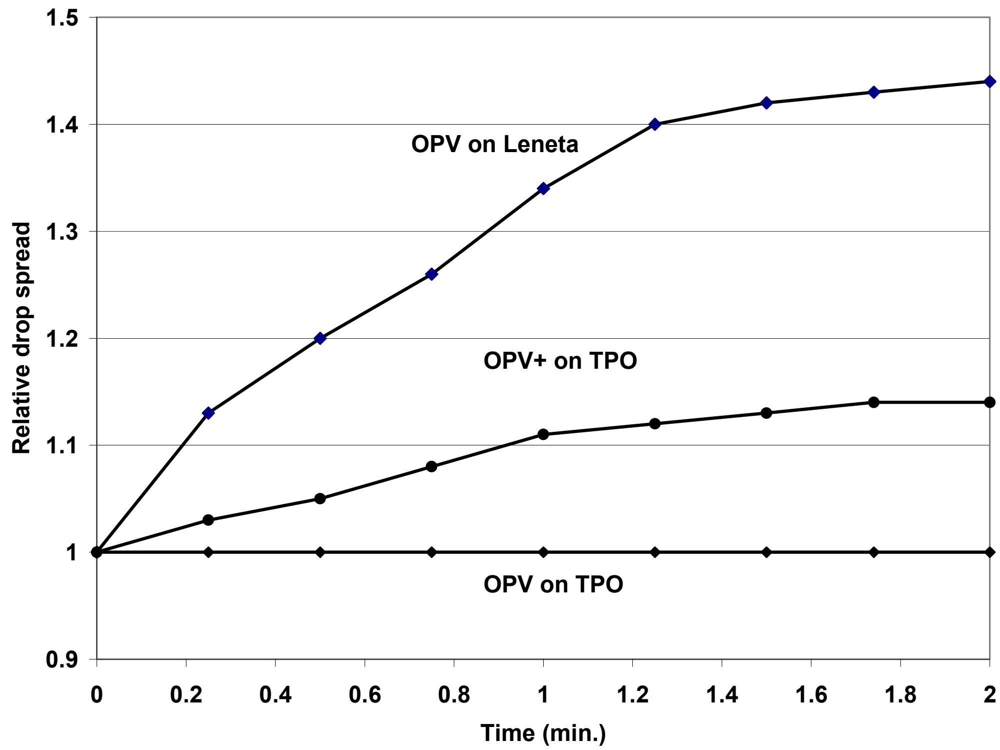


Figure 1c. Drop spread of OPV+ Eastman Solus™ 2100 PA on TPO



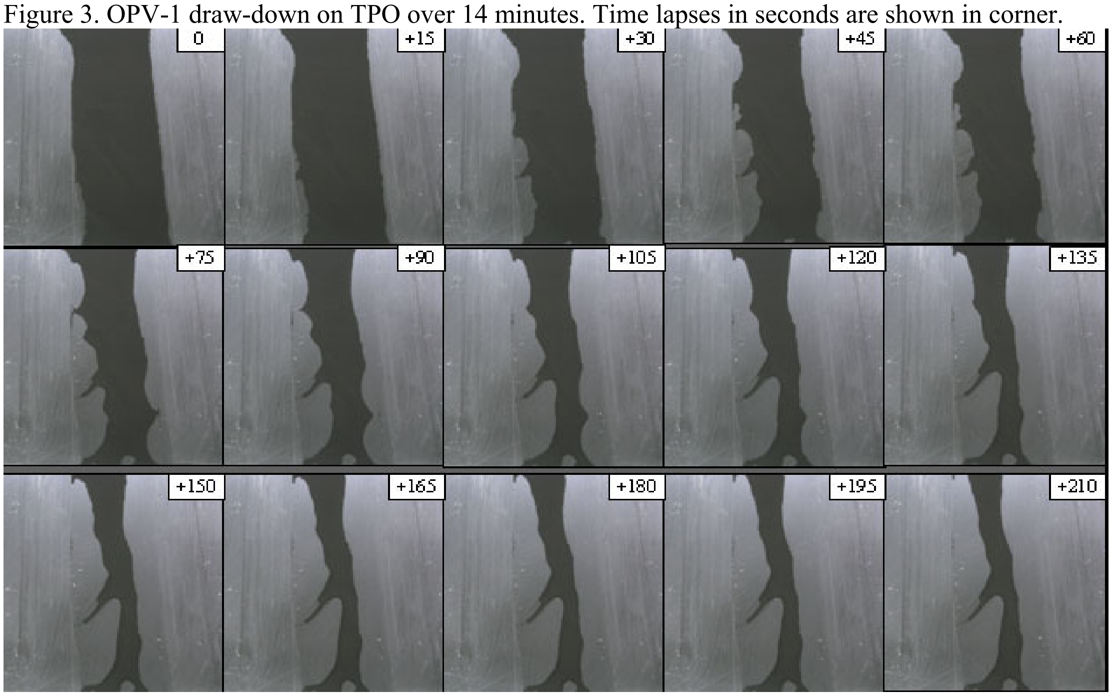
These results are graphically represented in Figure 2 below. The drop sizes were normalized and the percentage growth is plotted on the y-axis.

Figure 2. Drop spread of over-print-varnishes on Leneta paper and TPO



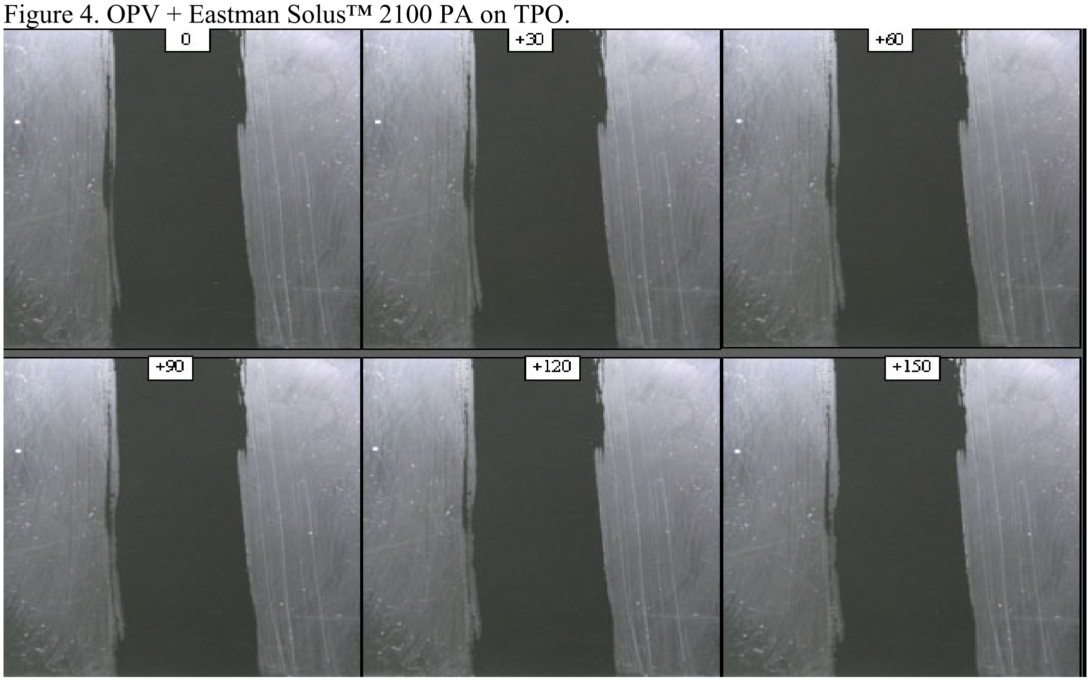
The effect of Eastman Solus™ 2100 PA on flow is even more clearly demonstrated by applying draw-downs of the two OPVs on the same TPO panels. As soon as the standard OPV is applied to the TPO substrate it starts to draw in and the integrity of the film is gone, as can be seen in Figure 3 below. Adhesion on the TPO is zero; the film remaining after curing falls off the panel.

Figure 3. OPV-1 draw-down on TPO over 14 minutes. Time lapses in seconds are shown in corner.



The Picture below shows OPV with 5 weight % of Eastman Solus™ 2100 performance additive. The film once applied does not change and the film integrity is preserved. The adhesion is improved to around 40% with the cross hatch test.

Figure 4. OPV + Eastman Solus™ 2100 PA on TPO.



Adhesion and film formation

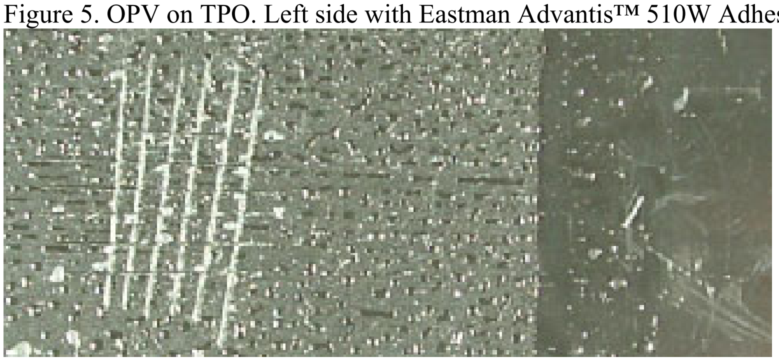
In the first part of this discussion on providing adhesion of UV coatings on PP substrates, solvent borne chlorinated adhesion promoters were used as primer coats. Due to the "green" nature of radiation curing, use of solvents is not desirable. In 2006 a new water-borne and chlorine-free adhesion promoter, Eastman Eastman Advantis™ 510W waterborne chlorine-free adhesion promoter (AP), was introduced in the automotive industry as well. This environmentally acceptable adhesion promoter was evaluated with the two OPVs for both film formation and adhesion. Two TPO panels were taped such that half of the panels were spray coated with a 5 micron film of the adhesion promoter. Surface tensions were measured on the substrates and the cured films as shown in Table 6. The increase in surface tension due to the Eastman Advantis™ 510W adhesion promoter on the TPO and the decrease in surface tension in the cured OPV are large and are likely to be a major contributor to the observed adhesion and film formation.

Table 6. Surface tension measurements

Surface measured	Surface tension in dynes/cm
Polypropylene (TPO)	27.6
TPO + Eastman Advantis™ 510W adhesion promoter	43.1
Leneta paper	52.8
OPV	49.3
OPV+ Eastman Solus™ 2100 PA	32.9

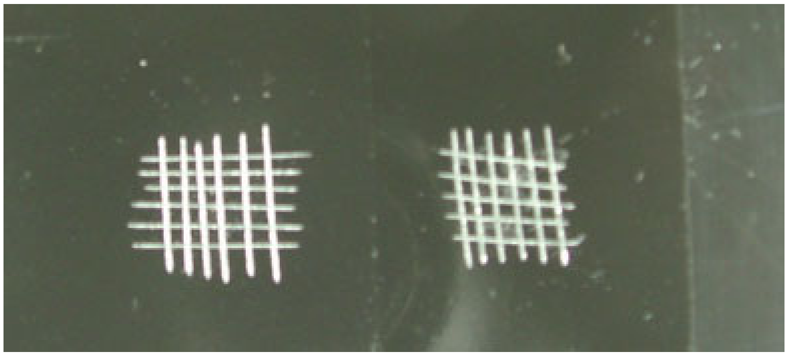
Both OPVs were applied using an the RK automated draw down machine using wire-wound rod #6, resulting in an approximately 2-mil thick cured coating. The two panels were cured with the a made by American Ultraviolet UV cure machine, using a belt speed of 20 ft/min and irradiation with a 300 watts-per-inch medium-pressure mercury lamp, resulting in exposure of approximately 650 mJ/cm2. The left side of the panel has been treated with adhesion promoter. Although no film was formed, the individual droplets did exhibit good adhesion. On the right untreated side of the panels the individual droplets just fell of the substrate.

Figure 5. OPV on TPO. Left side with Eastman Advantis™ 510W Adhesion Promoter



Repeating this same experiment with OPV with Eastman Solus™ 2100 PA, excellent film formation occurred over the treated and untreated surface. The adhesion of the coating on the untreated side was similar to that in the previous experiment, i.e. around 40%. The adhesion on the treated side was 100%.

Figure 6. OPV + Eastman Solus™ 2100 PA on TPO. Left side with Eastman Advantis™ 510W Adhesion Promoter



Summary and conclusions

This work is best summarized in Table 7.

Table 7. Benefits of adhesion promoter and performance additive

	TPO	TPO + Eastman Advantis™ 510W Adhesion Promoter
OPV	No film No adhesion	No film Good adhesion
OPV + Eastman Solus™ 2100 PA	Good film 40% adhesion	Good film 100% adhesion

Adhesion promoters applied as primers are very effective in adhering radiation curable coatings to polyolefinic substrates. The new environmentally friendly water borne and chlorine free adhesion promoter Eastman ™ Advantis 510W adhesion promoter has been shown to provide excellent adhesion of a RC OPV to a TPO substrate. Furthermore the addition of Eastman Solus™ 2100 PA in a UV OPV can greatly enhance film formation and to a lesser extent adhesion. The combination of the additive and the adhesion promoter can solve many adhesion and film formation issues faced by the UV formulator.