As global environmental regulations continue to tighten restrictions on coatings containing volatile organic compounds (VOCs), the need for hydrolytically stable additives in waterborne coatings has never been greater. Organofunctional alkoxysilanes are a class of widely used additives in the coatings industry. They act as a bridge between an organic coating and an inorganic substrate, providing adhesion promotion and other important performance improvements.

Given the high moisture sensitivity of organofunctional alkoxysilanes, most silane additives rapidly undergo condensation in waterborne coatings, leading to unworkable viscosities and gelling of the waterborne coatings within the first few weeks or months on the shelf. This has posed a significant barrier to using silane additives in waterborne coatings for all types of applications.

Two organofunctional silane additives that demonstrated positive hydrolytic stability over an extended period of time in waterborne acrylic roof coatings are investigated here. These organofunctional silane additives include an epoxy-functional silane oligomer, VPS 4721, and an amine-functional silane monomer, Dynasylan® 1505 (Figure 1).

The oligomeric structure of the epoxy-functional silane oligomer allows for slower hydrolysis and condensation rates in a waterborne system compared to a monomeric epoxy-functional silane (such as glycidoxypropyltrimethoxysilane).

![Figure 1](https://example.com/figure1.png)

**FIGURE 1**—From left to right: Epoxy-functional silane oligomer (VPS 4721) and amine-functional silane monomer (Dynasylan® 1505). Me = methyl, EtO = ethyl, R = epoxy-based moiety, X = epoxy-based moiety.
Novel Hydrolytically Stable Silane Additives for Improving the Performance of Waterborne Acrylic Roof Coatings

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Furthermore, the epoxy groups on this silane oligomer may break open into diols in the presence of water, allowing for further stability in water over time. The presence of only two ethoxy groups and one methyl group on the amine-functional silane monomer allows for a slower, two-dimensional crosslinking mechanism when hydrolysis and condensation occur in a waterborne system. The primary amine group on this amine-functional silane monomer also shows positive stability in waterborne systems.

As the liquid-applied, cool-roof coating market continues to grow (specifically liquid-applied waterborne acrylic cool-roof coatings), this article will focus on the liquid-applied waterborne acrylic roof coating market. It will demonstrate that with the use of stable organofunctional silane additives, several crucial performance characteristics of waterborne acrylic roof coatings can be improved.

The mechanism behind an organofunctional silane adhering to a roofing membrane surface is an important process to understand before investigating the performance of the organofunctional silane additives into the waterborne acrylic roof coatings.

Organofunctional silanes contain a hydrolysable alkoxy silane (Si-OR) functional group that can bond with inorganic surfaces. In this work, the organofunctional silanes to be investigated have silicon functional groups that consist of alkoxy groups, typically ethoxy or methoxy groups.

Organofunctional silanes also consist of an organofunctional group that can react with organic systems, such as an acrylic resin. The simultaneous reaction of the silicon functional groups and organofunctional groups allow organofunctional silanes to act as an adhesion promoter between inorganic and organic materials.

For an organofunctional silane additive to provide adhesion promotion of a waterborne acrylic roof coating to a roofing membrane, hydrolysis must first take place at the alkoxy sites to form silanol groups. This process occurs within the first few hours of the organofunctional silane being added into a waterborne acrylic roof coating, given the excess water in this type of coating.

When the hydrolyzed organofunctional silane contacts an inorganic surface, the silanol groups can initially form hydrogen bonds with the hydroxyl groups on the inorganic surface. Upon removal of moisture from the system, these hydrogen bonds can form siloxane bonds between the organofunctional silane and roofing membrane. These siloxane bonds provide the strong adhesion characteristics that organofunctional silanes are known to have. Furthermore, siloxane bonds can form between silanol groups within the waterborne acrylic roof coating upon application, providing an increased crosslinking density for the coating that can lead to improved mechanical properties and other critical roof coating characteristics.

Several key coating properties will be investigated in accordance with ASTM D6083, the standard for liquid applied waterborne acrylic roof coatings. This includes shelf stability, dry and wet adhesion properties to various roofing membranes, ponding water resistance, dirt pickup resistance, tensile strength, flexibility, and UV weathering resistance.

EXPERIMENTAL METHODS

Materials

Polyvinyl chloride (PVC) and ethylene propylene diene monomer (EPDM) roofing membranes were purchased from McMaster-Carr. Aluminum wire mesh 304 grade (with 28 openings per inch) was also purchased from McMaster-Carr. Liquid asphalt (Fibered Black Roof Coating 201) was purchased from Henry Company. Samples of carbon black Lamp Black 101 was obtained from Orion Engineered Carbons.
Samples of Rhoplex™ EC-1791 and Bioban™ O-45 were obtained by Dow. Samples of potassium triopolyphosphate were obtained by ICP Phosphate Specialty. The Displex® AA 4144 was sampled from BASF. Hubercarb® W325 was obtained from Huber Engineered Materials. Ti Pure® R-960 was sampled from Chemours. Samples of zinc oxide, propylene glycol, red iron oxide powder (<5 mm >96%), and aqueous ammonia were obtained from Sigma Aldrich. The Natrosol™ 250 was obtained from Ashland. Texanol™ ester alcohol was obtained from Eastman. Dynasylan 1505 and VPS 4721 are commercially available products from Evonik Corporation.

**Formulation Preparation**

After adding a small amount of dispersants and thinning the viscous resin down with deionized (DI) water, three different types of fillers were added into the grind under high shear (using a disperm#mat) and mixed for 15 minutes.

After returning the disperm to a lower mixing speed, a waterborne acrylic resin was added to the formulation, followed by a coalescent and preservative. At this stage in the formulation, a thickener was mixed with propylene glycol and stirred for several minutes in a separate container. After slowly adding in 28% aqueous ammonia, this solvent/thickener combination was immediately added.

As the final step, the silane was post-added into the formulation under low shear and the entire formulation was mixed for several minutes before use. In this example, only 0.2 wt % of silane additive was used relative to the total formulation (1 wt % relative to resin solids in the coating). Previous studies have shown that only a small amount of active silane content, ranging from 0.2-2.0 wt % solids, is necessary for improving the adhesion of a coating system.3

**Roofing Membrane Substrate Preparation**

Three roofing membranes are evaluated in this article, including PVC, EPDM, and asphalt. While the PVC and EPDM substrates were purchased in their ready-to-use solid form, the asphalt substrate was prepared by applying a liquid asphalt coating onto an aluminum substrate (at 50 mil dry film thickness) and allowed to cure and harden at room temperature for 3 months before use.

Before applying the waterborne acrylic roof coatings onto the PVC and EPDM roofing membrane substrates, these substrates were aged in an accelerated weathering instrument (QUV) for 350 hours.

This accelerated weathering procedure cycles between a humidity cycle at 50 °C and a QUV-A exposure cycle at 70 °C (based on ASTM G154). This provides a realistic aged roofing membrane surface that a waterborne acrylic roof coating would be applied to in the field. While wash primers are sometimes used for EPDM roofing membranes, these EPDM wash primers were not used for this work.

After aging the roofing membrane substrates, they were rinsed with water and dried with compressed air before applying the waterborne acrylic roof coatings onto the substrates.

**Curing Procedure**

Once the coatings were applied to the aged roofing substrates (by pouring on the coatings and leveling out to the desired film thickness with a trowel), they were cured at ambient temperature (23 °C) and constant humidity (40% relative humidity) for a minimum of 14 days before any test methods were performed.

**Testing Procedures**

**Contact Angle Measurement Procedure**

Once the coatings were fully cured, a goniometer (Ramé-Hart, Inc.) was used to measure the contact angle of DI water on the coated substrate surfaces. Each measurement reported in this article is the average of 10 contact angle measurements to ensure the accuracy of this method.

**Accelerated Stability Testing Procedure**

The silane was added to the waterborne acrylic resin (1 wt% silane relative to resin solids) at room temperature and mixed by hand for 1 minute. The mixture was then placed in an oven at 45 °C for several weeks. One week in the oven at 45 °C is approximately equivalent to 6 weeks stability at room temperature. The samples were monitored for gelling, particle formation, and viscosity over time. A Brookfield viscometer (Spindle #4, RPM = 6) was used for these viscosity measurements.

**Water Ponding Resistance Testing Procedure**

In accordance with ASTM D471, the waterborne acrylic coatings were applied to an aluminum metal surface (which was wiped with a solvent) at 20 mil dry film thickness. These coatings were cured and the resulting sample weighed. The coated aluminum was then immersed in room temperature DI water for 7 days (168 hours). After this immersion period, the film was removed from the DI water bath, dried with air, and weighed again. After the water immersion, the percentage difference in weight was reported and pictures were taken of any observable surface defects.
Elongation at Break Measurement Procedure
In accordance with ASTM D2370, the waterborne acrylic roof coatings were poured into a Teflon mold (length: 150 mm, width: 60 mm, depth: 5 mm) and left to cure for a minimum of 14 days at 23 °C and 40% humidity. These cured films were then cut into a dogbone and evaluated on a Tinius Olsen tensile-testing instrument for elongation at break. This measurement is the calculation of the percent change in length at breakage when strained at a constant rate on the Tinius Olsen instrument. This elongation at break measurement was performed within a few days of curing the waterborne acrylic roof coating films and after 1,000 hours of accelerated weathering using the QUV instrument (running in accordance to ASTM G154).

Tensile Strength Measurement Procedure
In accordance with ASTM D2370, the waterborne acrylic roof coatings were poured into a Teflon mold (length: 150 mm, width: 60 mm, depth: 5 mm) and left to cure for a minimum of 14 days at 23 °C and 40% humidity. These cured films were then cut into a dogbone and evaluated on a Tinius Olsen machine for tensile strength. This measurement is the calculation of the maximum pull strength on the Tinius Olsen (in MPa) when strained at a constant rate until break. This tensile strength measurement was performed within a few days of curing the waterborne acrylic roof coating films and after 1,000 hours of accelerated weathering using the QUV instrument (running in accordance to ASTM G154).

Dry Adhesion Testing Procedure
In accordance with ASTM C794, an aluminum wire mesh was embedded between two 10 mil dry film thickness coatings on several different roofing membrane substrates. This system was then cured at room temperature and 40% relative humidity for a minimum of 14 days before placing the sample in a Tinius Olsen tension-testing machine. The aluminum wire mesh was then peeled back from the substrate at an 180° angle as the force required to peel back the aluminum wire mesh from the roofing membrane substrate was measured. The mode of failure (adhesion failure, cohesion failure, or mixed failure) was observed and reported.

Wet Adhesion Testing Procedure
The wet adhesion testing procedure was identical to the dry adhesion testing procedure above, with the exception that the adhesion measurements were taken immediately after the cured coating system has been immersed in DI water for 7 days (168 hours).

Dirt Pickup Resistance Testing Procedure
As derived from ASTM D3719, a hydrophobic dirt slurry was prepared by mixing 13 wt % carbon black pigment in DI water and mixing for 1 hour at room temperature. A hydrophilic dirt slurry was prepared by mixing 25 wt % red iron oxide pigment in DI water and mixing for 1 hour at room temperature. These dirt slurries were then applied to the cured coatings with a paint brush and allowed to dry at room temperature for 4 hours. After this 4-hour dry period, the dirt was lightly rinsed with DI water and lightly wiped with a wet sponge. The resulting surface was then photographed for comparison.

Accelerated Weathering Aging Procedure
In accordance with ASTM D6083 requirements, the cured waterborne acrylic roof coatings must show no cracking or checking after accelerated weathering for 1,000 hours. The cured waterborne acrylic roof coatings was placed in a QUV instrument (Q-lab) that cycles between a humidity cycle at 50 °C and a QUV-A exposure cycle at 70 °C (based on ASTM G154).

RESULTS AND DISCUSSION
Accelerated Stability Results
As silanes tend to undergo hydrolysis and condensation in the presence of water, most organofunctional silanes crosslink in a waterborne coating over time. This condensation of the silane occurring over time increases the
viscosity of the coating, eventually leading to gelling and unworkable viscosities for proper application of the coating.

It is crucial that silane additives in waterborne coatings exhibit low condensation rates throughout the shelf life of the coating. This stability performance was evaluated with an accelerated stability test, where the viscosity of the coatings was monitored in an elevated temperature environment over time (Figure 2).

Both the amine-functional silane monomer and epoxy-functional silane oligomer, when added to the waterborne acrylic roof coating at 1 wt % relative to resin solids (0.2 wt % on total formulation), showed evidence of hydrolytic stability over time in this accelerated stability test as suggested by the moderate increase in viscosity compared to the control sample.

One week at this elevated temperature is approximately equivalent to 6 weeks at room temperature, so these waterborne acrylic roof coatings with the silane additives should exhibit good stability for at least 12 months at room temperature (at least 8 weeks at an elevated temperature). As the resin without the silane additives started to show significant viscosity increase eight weeks into this study, this increase can be attributed to the instability of the resin, not the silane additives.

Several other organofunctional silanes commonly used in waterborne coatings as additives for adhesion promotion, notably aminopropyltriethoxysilane and glycidoxypropyltriethoxysilane, exhibited gelling in this accelerated stability test within the first few weeks. This demonstrates the significantly improved stability of the amine-functional silane monomer and epoxy-functional silane oligomer compared to the traditional commercial additives for waterborne acrylic roof coatings.

Water Ponding Resistance Results

Waterborne acrylic roof coatings are notoriously susceptible to water ponding damage. When rainwater is left to sit on a roof for extended periods of time, especially in high-rainfall regions, this water can prematurely age roof coatings and the roofing membranes beneath the coatings. Furthermore, this ponding water can encourage mildew and algae growth on the roof, leading to additional surface defects and breakdown of the roof coatings. While there are several solutions to minimize ponding water, such as sloped roofing, the addition of a silane into the coating can increase the crosslinking density of the system through condensation, resulting in a less penetrable coating for water to soak into the coating and potentially damage it (Figure 3).

The cured waterborne acrylic roof coating without any silane additive in the system (control) showed blistering on the coating surface after being immersed in room temperature DI water for 7 days. A significant water weight gain of 7.2% was also observed after this water immersion period for the control.

With the addition of 0.2 wt % of the amine-functional silane monomer (relative to total formulation) into the waterborne acrylic roof coating, the water uptake of the coating was reduced by approximately 40% compared to the control without any silane additives in the coating. However, delamination between the coating and the aluminum surface was observed after this water immersion period with the amine-functional silane monomer in the coating.

With the addition of 0.2 wt % epoxy-functional silane oligomer (relative to total formulation) into the waterborne acrylic roof coating, the water uptake of the coating was reduced by approximately 60% compared to the control without any silane additives in the coating. Furthermore, no blistering or delamination of the coating was observed with the epoxy-functional silane oligomer added in the coating.

Dry and Wet Adhesion Results on Aged PVC

The dry and wet adhesion properties of the waterborne acrylic roof coatings were investigated on several roofing membranes, including aged PVC. The force required to pull the aluminum wire mesh out of the waterborne acrylic roof coatings on aged PVC at a 180° angle was measured in pounds per linear inch (PLI) and the type of failure was recorded (Figure 4).
For the dry and wet adhesion tests, cohesion failure was observed on all the waterborne acrylic roof coating samples, with and without the silane additives. While adding the amine-functional silane monomer to the waterborne acrylic roof coating did not have a significant impact on the dry or wet adhesion force measured, the addition of the epoxy-functional silane oligomer into the waterborne acrylic roof coating resulted in an approximate 40% increase in dry adhesion force and 40% increase in wet adhesion force.

**Dry and Wet Adhesion Results on Aged EPDM**

The dry and wet adhesion properties of the waterborne acrylic roof coatings were investigated on several roofing membranes, including aged EPDM. The force required to pull the aluminum wire mesh out of the waterborne acrylic roof coatings on aged EPDM at a 180° angle was measured in PLI and the type of failure was recorded (Figure 5).

While the addition of the amine-functional silane monomer into the waterborne acrylic roof coating resulted in a decrease in the dry and wet adhesion performance compared to the control, adding the epoxy-functional silane oligomer to the waterborne acrylic roof coating resulted in an approximate 160% increase in wet adhesion force compared to the control.

It is important to note that ASTM D6083 requires a minimum wet adhesion force of 2 PLI to pass the standard requirements. Without the epoxy-functional silane oligomer added to the waterborne acrylic roof coating, this ASTM D6083 requirement is not met, however with 1 wt % (relative to resin solids) of VPS 4721 added into the system, this wet adhesion requirement is met on aged EPDM.

For the dry adhesion tests, adhesion failure was observed with the waterborne acrylic roof coatings without any silane in the system and with the amine-functional silane monomer added to the system.

However, adding the epoxy-functional silane oligomer to the waterborne acrylic roof coating resulted in cohesion failure—a more preferable type of adhesion failure given the stronger crosslinking.
between the coating and the aged EPDM surface (Figure 6).
This held true for the wet adhesion tests as well, where adhesion failure was observed with the waterborne acrylic roof coatings without any silane in the system and with the amine-functional silane monomer added to the system, but a mixed failure mode was observed with the epoxy-functional silane oligomer added to the system.

Dry and Wet Adhesion Results on Aged Asphalt
The dry and wet adhesion properties of the waterborne acrylic roof coatings were investigated on several roofing membranes, including aged asphalt. The force required to pull the aluminum wire mesh out of the waterborne acrylic roof coatings on aged asphalt at a 180° angle was measured pli and the failure type was recorded (Figure 7).

For the dry adhesion tests performed on aged asphalt, adding the amine-functional silane monomer to the waterborne acrylic roof coating resulted in an approximate 170% improvement in the adhesion force measurement compared to the control.

The waterborne acrylic roof coating with the epoxy-functional silane oligomer in the system showed an approximate 210% improvement in the dry adhesion force compared to the control.

For the wet adhesion tests performed on aged asphalt, adding the amine-functional silane monomer to the waterborne acrylic roof coating resulted in an approximate 80% improvement in the adhesion force measurement compared to the control.

While the epoxy-functional silane oligomer being present in...
the waterborne acrylic roof coating decreased the wet adhesion by approximately 10% on aged asphalt, the mode of failure was more preferable, as described below.

For the dry and wet adhesion tests, adhesion failure was observed with the waterborne acrylic roof coatings without any silane in the system. The addition of either the amine-functional silane monomer or the epoxy-functional silane oligomer into the waterborne acrylic roof coating resulted in cohesion failure—a more preferable type of adhesion failure given the stronger crosslinking between the coating and the aged asphalt surface (Figure 8).

**Elongation at Break Results**

As silanes tend to undergo hydrolysis and condensation in the presence of water, such as in these waterborne acrylic coatings, they will form siloxane bonds with any hydroxyl functionality in the system and increase the crosslinking density over time.

As the elastomeric properties of waterborne acrylic roof coatings are a crucial property to maintain, the elongation at break properties of the coatings with and without silane additives was investigated (Figure 9).

Although silanes typically increase the crosslinking density of a coating when used as an additive, adding either the amine-functional silane monomer or

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**FIGURE 8**—Failure mode analysis of the waterborne acrylic roof coatings during dry and wet adhesion testing on aged asphalt. Adhesion failure was observed on both control samples, while cohesion failure was observed when the epoxy-functional silane oligomer was present in the coating.

**FIGURE 9**—Elongation at break percentages for the waterborne acrylic roof coatings initially and after 1,000 hours aging in an accelerated weathering test.
epoxy-functional silane oligomer to the coating did not significantly impact the elongation at break properties.

This held true for both the waterborne acrylic coatings tested within a few weeks of formulating and the waterborne acrylic coatings aged in an accelerated weathering test for 1,000 hours.

It is important to note that this accelerated weathering exposure reduced the elongation at break of the waterborne acrylic roof coating without any silane in the system by approximately 70%, while the waterborne acrylic roof coatings with the silane additives were only reduced by approximately 60%.

The low loading levels of the silanes may be one potential reason the elastomeric properties of these waterborne acrylic roof coatings were not impacted with these additives.

**Tensile Strength Results**

As previously discussed, silanes will undergo hydrolysis and condensation in waterborne acrylic roof coatings, thus forming siloxane bonds in the system and increasing the crosslinking density over time. This increased crosslinking density can lead to improved toughness and durability of the coating, which can be measured and correlated with the tensile strength of the system (Figure 10).

For the waterborne acrylic roof coatings tested within a few weeks of formulating, adding the amine-functional silane monomer to the system resulted in an approximately 25% drop in tensile strength. However, adding the epoxy-functional silane oligomer to the system resulted in an approximate 20% increase in the tensile strength of the system. After aging the waterborne acrylic roof coatings in an accelerated weathering test for 1,000 hours, the tensile strength of all three systems increased significantly. The epoxy-functional silane oligomer containing coating still exhibited the highest tensile strength after this accelerated weathering test.

**Dirt Pickup Resistance Results**

Given the importance of solar reflectance for a cool-roof coating, waterborne acrylic roof coatings are typically pigmented white, as this color is most efficient at reflecting incoming sunlight. If dirt were to stain the surface of the cool-roof coatings, the solar reflectance properties of the coating surface will likely decrease, leading to a less efficient cool roof coating. For this reason, investigating the use of silane additives to improve the dirt pickup resistance of waterborne acrylic roof coatings is a crucial property to explore (Figure 11).

The amine-functional silane monomer and epoxy-functional silane oligomer significantly improved the carbon black resistance of the waterborne acrylic roof coatings, as less black pigment is left behind after the stain test on these surfaces. However, the silanes demonstrated a less-noticeable, stain-resistance effect with the red iron oxide stains. One potential explanation for this improved
FIGURE 11—Dirt pickup resistance results after wiping stains off the waterborne acrylic roof coating surfaces. The top portion indicates the red iron oxide stain, the middle portion is left unstained, and the bottom portion indicates the carbon black stain.

FIGURE 12—Contact angles of water on the surface of the waterborne acrylic coatings.
dirt pickup resistance with the addition of the silanes is the increased crosslinking density of the waterborne acrylic roof coatings. As the crosslinking density of the coatings increase, it becomes more difficult for these hydrophobic and hydrophilic stains to penetrate the coating surface and become unremovable.

**Surface Hydrophobicity Results**

The surface hydrophobicity of the waterborne acrylic roof coatings was also investigated in this work. The contact angle of DI water on newly formulated waterborne acrylic roof coatings and waterborne acrylic roof coatings aged in an accelerated weathering test were measured.

The addition of a silane into the waterborne acrylic roof coatings did not have a significant impact on the surface hydrophobicity properties. All the contact angle measurements were <90° and >60°, indicating a moderately hydrophobic surface (Figure 12).

While it was previously shown that adding the epoxy-functional silane oligomer and amine-functional silane monomer improved the water ponding resistance of the waterborne acrylic roof coatings, this was likely due to the increased crosslinking density of the coatings via silane condensation.

This improved water ponding resistance was not likely due to the increased hydrophobicity of the coating surface, as no significant impact on this property was observed in these contact angle tests.

**Accelerated Weathering Results**

The waterborne acrylic roof coatings were subject to 1,000 hours in an accelerated weathering environment, which exposed the coatings to humidity, elevated temperatures, and UV light in a cyclic manner. After 1,000 hours in the accelerated weathering environment, no surface defects were observed on any of the waterborne acrylic roof coatings (Figure 13).

**CONCLUSION**

While this work is not the first demonstration of silane additives improving the performance of coatings, these new findings demonstrate significant progress in overcoming the biggest obstacle for the use of silane additives in waterborne roof coatings: stability.

Not only did the addition of the silane additives improve several crucial coating properties of the waterborne acrylic roof coatings, but the silane additives were also stable in the waterborne coating over time. Specifically, adding only 0.2 wt % of the epoxy-functional silane oligomer (relative to the total formulation) to the waterborne acrylic roof coating, the water ponding resistance was improved by over 60%, the tensile strength was improved by over 20%, and the primerless adhesion to EPDM and asphalt was achieved without sacrificing any elongation performance of the system.

Furthermore, by adding only 0.2 wt % of the amine-functional silane monomer (relative to the total formulation) to the waterborne acrylic roof coating, the water ponding resistance was improved by more than 40% and primerless adhesion to asphalt was achieved without significantly impacting the mechanical properties of the coating.

Coating manufacturers that previously could not use silane adhesion promoters in waterborne systems due to stability issues can now explore this technology with a significantly increased probability of success. As roof coating regulations and specifications continue to become more stringent across the United States, these silane additives will play an important role in achieving better performance of these waterborne coatings without impacting shelf life.

**References**


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