Highly Weatherable Low-VOC Fluoropolymer Coatings for Building Restoration

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Highly weatherable, 70% PVDF fluorocarbon finishes are among the most popular coatings for exterior architectural metal, but when a need arises to make repairs or change colors, the options for restoration paints are often rather limited. Nonfluorocarbon restoration paints will not match the original PVDF finish in terms of color stability. Many of the fluorocarbon restoration paint options can have their own drawbacks, such as high VOC, adhesion issues over PVDF finishes, and potlife/material handling issues for systems which are two-component. We present here new studies to adapt PVDF-acrylic hybrid latex technology to the needs of the building restoration market. New one-pack formulations achieve outstanding weatherability and excellent wet and dry adhesion to new and aged PVDF finishes, at VOC levels in the 100 g/L range. Second generation latex materials under development are showing similar adhesion properties, in formulations meeting West Coast 50 g/L VOC requirements.

INTRODUCTION

Fluoropolymer-based coatings such as 70% poly vinylidene fluoride (PVDF) finishes are among the most popular coatings for exterior architectural building profiles,[1] including roofs. Coatings based on such resins are resistant to degradation by UV and environmental factors, and thus have superior durability and color fade resistance, compared to coatings made from nonfluorocarbon resins. Not infrequently, metal roofs and associated components coated with PVDF finishes may require color change to keep abreast of changing design trends, or to reduce building energy costs by installing "cool roof" reflective coating systems. In some other cases, the seams and joints of metal roofs may fail due to moisture and thermal cycling, thus requiring restoration.

The options are often limited for restoring PVDF-coated metal roofs with field-applied coatings. The faster degradation of the binder in nonfluorocarbon restoration paints means that they will not match the original PVDF finish in terms of color stability. Many of the fluorocarbon restoration paint options can have their own drawbacks. A good example is two-component, fluoropolymer-based solvent coatings crosslinked with polyisocyanates.

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Such systems can have good outdoor weathering performance, but suffer from relatively high VOC levels, which restricts their use in regions where VOC level regulations are tougher to achieve. In addition, isocyanate-crosslinked two-pack systems in general entail additional health and safety considerations, have a relatively short pot life (unless plural component equipment is used), and can be sensitive to application conditions—in particular, relative humidity.

To address some of the issues in the restoration coatings market, especially for metal restoration, we have developed water-based, PVDF-acrylic hybrid dispersions.[2] The morphology of individual latex particles in the dispersion enables the dried coating to have long-term durability and color retention characteristics similar to those of conventional solvent-based PVDF finishes.[3] Such a system allows for economical, lower-VOC, durable water-based coatings to restore existing PVDF finishes and extend the useful life of the building or structure.

Adhesion, which is a primary property for restoration coatings, can be challenging over aged/weathered PVDF coated metal roofs. Conventional PVDF finishes are 70–80% PVDF and 20–30% acrylic copolymer by resin weight. Studies have shown that exposure to UV selectively erodes away the acrylic component near the coating surface, leaving the surface rough and enriched in fluorine content.[4-6] Low energy and topographical features presented by the weathered surface can pose difficulties for adhesion of water-based restoration coatings. This article discusses one-pack formulations with PVDF-acrylic hybrid dispersions for restoration paints.

Table 1—PVDF-Acrylic Hybrid Physical Properties

	PVDF Hybrid A	PVDF Hybrid B
PVDF: acrylic mass ratio	70:30	50:50
Acrylic T_g	Higher	Lower
MFFT, °C	26	12

Approaches to achieve excellent adhesive properties of the PVDF-acrylic hybrid coatings over new and weathered PVDF finishes are presented. In addition, the role of surface energy and features of new and weathered PVDF finishes on adhesion of topcoats are investigated.

MATERIAL AND TEST CONDITIONS

In this study, two PVDF-acrylic hybrid emulsions, designated Hybrid A and Hybrid B, were used. The dispersions were made by a seeded emulsion polymerization process, using the same PVDF copolymer seed. The final latex particles consisted essentially of a physical alloy of a PVDF copolymer (with a T_g below 0°C) and a thermodynamically miscible acrylic copolymer. The final latex material properties were adjusted by varying the acrylic comonomer ratio to adjust the acrylic T_g, as well as the weight ratio of PVDF to acrylic, such that PVDF-Acrylic Hybrid B coatings were softer and lower in tensile-modulus than Hybrid A. The acrylic copolymer included a small amount of copolymerized acid-functional monomer, and the dispersions were neutralized with an organic amine base to a pH of 8–9, so that in each case the materials used in coating formulations were anionically stabilized. The resulting hybrid dispersions were unimodal in particle size, with an average particle size in the 130–190 nm range depending on the acrylic content. The properties of the two dispersions used in this study are summarized in *Table* 1.

The hybrid dispersions were formulated into white paints, using standard grades of pigments, dispersants, coalescents, and other additives such as are commonly used with acrylic latex products. Specifically, coatings based on four white formulations were studied (*Table* 2). Coatings C1, C2, and C3 were prepared from PVDF-Acrylic Hybrid A with rutile TiO_2, and also contained some blended low T_g acrylic coresin to bring the final PVDF copolymer content of the binder into the 50–60 wt% range, for more direct comparison with Coating C4, which was made with PVDF-Acrylic Hybrid B. Coating C1 contained TiO_2 only at 15 PVC, while Coating C2, in addition to a similar level of TiO_2, also contained a barium sulfate extender, which increased the total pigment volume concentration to 21%. Coating C3 had the same PVC and pigment package as C2, but incorporated some additional coalescent, in particular, N-methyl pyrrolidone (NMP), which is not only a rather high boiling point coalescent, but also is an active solvent for PVDF. Finally, Coating C4 was prepared from the lower T_g PVDF-Acrylic Hybrid B, using TiO_2 as the only pigment. The coatings formulations are provided in *Table* 2.

Three types of PVDF finish substrate were used to test the adhesion of the four waterborne formulations

Table 2—Details of Waterborne Test Formulations Using PVDF-Acrylic Hybrid Emulsions

	C1	C2	C3	C4
Water	58.2	58.2	58.2	59.4
Rutile TiO_2	215.0	125.4	125.4	215.0
Extender	0.0	89.6	89.6	0.0
Dispersant	13.5	13.5	13.5	13.4
Defoamer	0.5	0.5	0.5	0.5
Co-surfactant	2.2	2.2	2.2	2.2
PVDF-Acrylic Hybrid A	734.0	458.0	458.0	0.0
PVDF-Acrylic Hybrid B	0.0	0.0	0.0	653.3
Coalescent (DPM)	53.3	47.5	47.5	16.4
Acrylic coresin	183.5	115.0	115.0	0.0
HEUR thickener	4.1	2.6	2.6	1.9
High boiling coalescent (NMP)	0.0	0.0	11.0	0.0
% Pigment Volume Concentration[a]	15	21	21	18

(a) Pigment Volume Concentration (PVC) = (Volume of Pigment + Filler)/(Volume of Pigment + Filler + Binder).

described in *Table* 2. Commercially available new PVDF finished coil stock was obtained from McElroy Metal and designated as S1. The other two substrates, S2 and S3, were prepared in our laboratory, using a simple lab formulation without any coating additives. For substrates S2 and S3, a PVDF finish (based on 70 wt% PVDF polymer, 30 wt% acrylic copolymer) was applied directly over chromated aluminum, without the use of a primer, and baked using a coil bake schedule. Substrate S2 was prepared fresh in the lab a few days before applying the waterborne test formulations, while substrate S3 had been exposed in southern Florida at south facing 45° for 14 years prior to applying the waterborne test formulation.

The three substrates were characterized by dynamic water contact angle measurements, using a Kruss Contact Angle Measuring System G10. The panels were cleaned with water and allowed to air dry before measuring the D.I. water contact angle. In addition, their surface roughness was determined by an optical interferometry technique, using the WYKO NT1100 optical profiling system from Veeco. The measurements were performed in the vertical scanning interferometry mode, and an area of 242 × 184 microns was analyzed at 25× magnification.

All four waterborne test formulations were applied over the three PVDF-coated substrates using a draw down blade, to obtain a dry film thickness of 75 microns. Before the waterborne formulations were applied, the substrates were cleaned with soapy water, thoroughly rinsed with tap water, and allowed to dry. All coatings were air-dried under ambient conditions for two weeks before testing adhesion. Adhesion was tested using a cross-hatch tape pull method according to ASTM standard D3359. Ratings of 0B and 5B implied poor and excellent adhesion, respectively. Dry adhesion was tested before soaking the coated panels in water. Samples were tested for water blisters and wet adhesion immediately after immersion of panels in water for 24 hr. Water blisters were rated according to ASTM D714, with 10 being no blisters and 0 being very large blisters. Also, the number of blisters on the surface was rated on a "few" to "dense" scale, in accordance with the standard.

SUBSTRATE CHARACTERIZATION

Dynamic water contact angle measurements of the three substrates used in this study showed differences, even though they were based on the same materials (*Figure* 1). The advancing water contact angle of substrate S1 was at 94.8°, which was considerably higher than a contact angle measured for PVDF homopolymer, which was at 85° (not shown). In comparison, substrate S2, which was prepared fresh in the lab, showed an advancing water contact angle of 76.4°. This value was between the contact angles of the PVDF homopolymer and acrylic copolymers used in the finish formulation (the latter being in the 70° range), and suggests that the surface contains at least 30% or even higher levels of the acrylic copolymer component, consistent with other reports in the literature.[4] The aged substrate, S3, had a lower advancing water contact angle, ~ 62.3°, despite the fact that surfaces

Figure 1—Advancing and receding water contact angles of the three substrates. The contact angle hysteresis, which is the difference between the advancing and receding contact angles, was 48.1°, 31.8°, and 35.4° for substrates S1, S2, and S3, respectively.

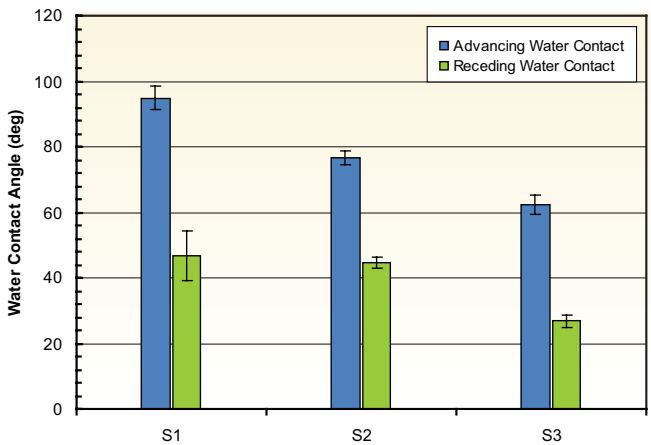
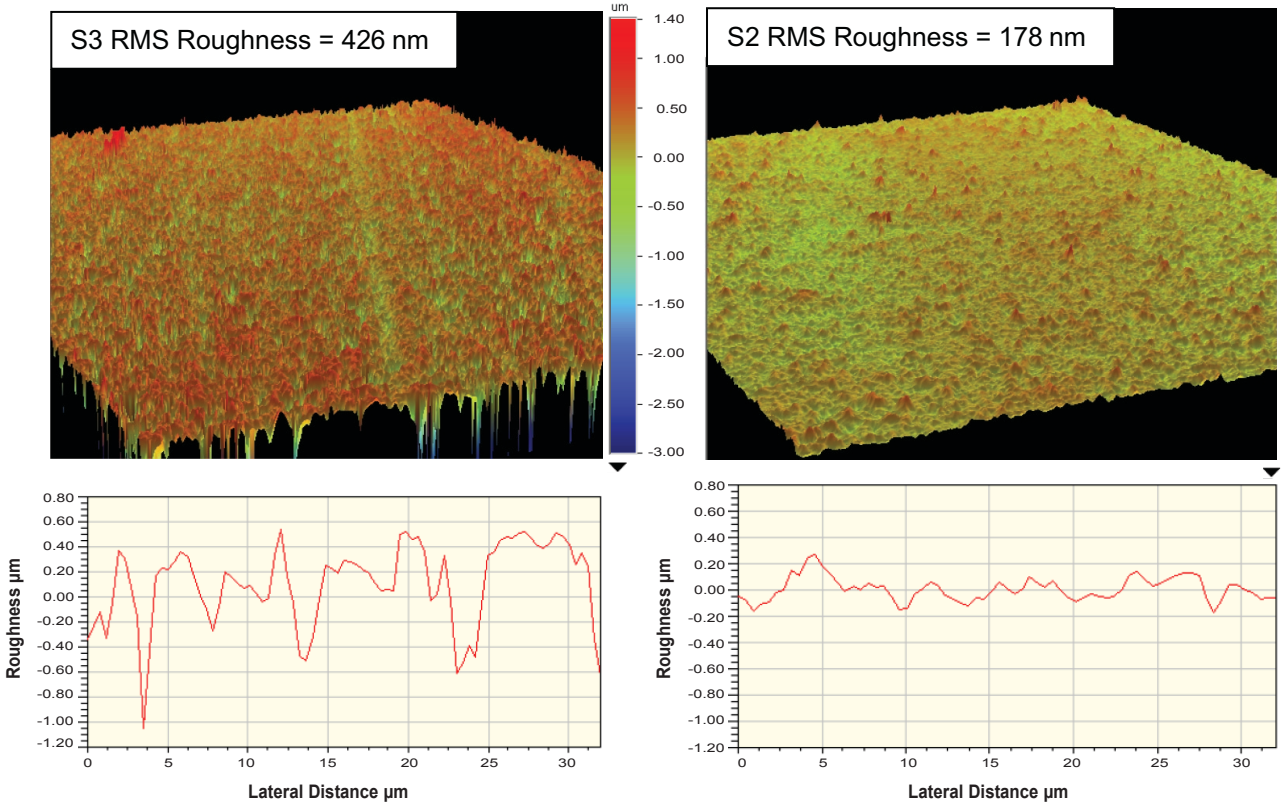


Figure 2—Top figures represent the surface topography and RMS roughness of substrates S3 (left) and S2 (right) obtained using optical profilometer. Bottom insets represent the linear roughness of the two surfaces over a lateral distance of 30 microns. The RMS roughness was also measured for substrate S1 and was 235 nm.



of weathered PVDF finishes become enriched in PVDF homopolymer.[4,5] This lower advancing contact angle of S3 is no doubt at least partly attributable to the presence of photooxidized species on the surface.

Another likely reason for the S2-S3 contact angle difference is the surface roughness. Optical profilometry showed that the aged substrate, S3, had a much higher root mean surface roughness compared to the freshly prepared substrate S2 (*Figure* 2), consistent with the generally accepted mechanism for weathering-induced gloss loss in coatings, and also with specific published results for PVDF finishes.[6] The contact angle hysteresis value (the difference between advancing and receding values), which tends to be correlated with surface roughness, was higher for substrate S3 than S2, and was in line with the trend of RMS roughness for the two panels. So, the high surface roughness may also contribute in lowering the advancing contact angle of substrate S3 well below the PVDF homopolymer levels.

Compared with lab-prepared substrates S2 and S3, the commercially prepared substrate S1 had a much higher advancing water contact angle, and a larger value for the contact angle hysteresis. Since the gloss and surface roughness for substrate S1 are roughly comparable to those of S2, it is postulated that the surface of the commercially produced substrate also has present on it some additional, nonbinder hydrophobic species: for instance, some kind of low molecular weight silicone species like those which were recently reported in another study,[7] which were traced back in that case to the primer formulation. The high value of the contact angle hysteresis for substrate S1 also suggests that this additional hydrophobic material is inhomogeneously distributed on the surface. Both these factors would be expected to make it more difficult to achieve adhesion to S1, compared to S2.

RESTORATION COATING ADHESION RESULTS AND DISCUSSION

Formulation Effects

The dry and wet adhesion results for coating C1 over the three PVDF substrates showed striking differences. The adhesion, both dry and wet, was poor over S1, the fresh commercial PVDF finish. Also, the coating showed a high density of water blisters during the water soak test. By contrast, the same formulation had excellent dry and wet adhesion with no water blisters over the freshly prepared substrate, S2. Over the aged lab prepared sub-

Table 3—Dry, Wet Adhesion, and Water Blister Resistance of Waterborne Restoration Coating Formulations (C1–C4) over Three PVDF-Coated Substrates (S1–S3).

	Comm-PVDF (S1)			Lab-PVDF (S2)			S. FL weathered Lab-PVDF (S3)		
	Dry	Wet	Water Blisters	Dry	Wet	Water Blisters	Dry	Wet	Water Blisters
C1	0B	0B	4/Medium	5B	5B	10	5B	0B	4/Medium
C2	0B	0B	6/Few	5B	5B	10	5B	0B	6/Few
C3	0B	0B	6/Few	5B	5B	10	5B	5B	10
C4	0B	0B	10	5B	5B	10	5B	5B	10

Note: Adhesion of 0B and 5B indicates poor and excellent adhesion respectively. The ranking of water blistering is on a scale of 0 to 10 with 10 being no blistering and 0 being large blister. Quantity of water blisters are graded from "few" to "dense."

strate, S3, it had excellent dry adhesion, but numerous water blisters and poor wet adhesion were observed after the water soak (*Table* 3, Row 1).

The phenomenon of water blistering, although very well covered in the literature, can be complicated due to the influence of numerous factors. Osmotic pressure is often cited in the literature as the main mechanism[8,9] for blistering. Most organic coatings are semi-permeable membranes. Minute pockets of water-soluble organic and inorganic compounds present at the coating-substrate interface, such as chloride and sulfate salts and corrosion products, draw in water by the process of osmosis. As more and more water is drawn into these pockets, blisters appear when the adhesive forces at the interface are weaker than the force created by osmotic pressure. Subsequently, the film delaminates. In water-based latex or dispersion coatings, another source of osmotic pressure buildup may be operative. Typically, water–based systems are formulated with additives and solvents, which are hydrophilic in nature. As these coatings dry, mobile hydrophilic materials can be concentrated, and possibly trapped, in small interstitial regions that are created during the particle packing phase of the film-formation process.[10] These regions can then become a second osmotic sink for water absorption. These two factors may both be operative in the case of the water blistering observed here.

Coating C2, which incorporated a filler and had a higher pigment volume concentration than C1, had similar adhesion results, but improved greatly in water blistering characteristics (*Table* 3, Row 2). The higher pigment loading of coating C2 gives it a higher elastic modulus than C1, as measured by mechanical testing, and this is thought to contribute to an improved ability to mechanically resist the formation of blisters due to osmotic pressure.[11] In addition, fillers and pigments often tend to aggregate and distribute heterogeneously in the dried coatings.[12] Such a distribution can create microscopic channels in the coating, which will make it more permeable and thus allow easier pathways for the dissolved impurities at the interface, and hydrophilic moieties in the coating, to diffuse out into the water phase. This will reduce osmotic pressure buildup and reduce blister size and density.

Formulation C3 was similar to C1, except that it contained an additional quantity of a second coalescent—N-methyl pyrrolidone (NMP)—which was also an active solvent for the PVDF in the substrate. Formulation C3 not only showed excellent water blistering resistance over both the fresh and the weathered lab PVDF substrates (S2 and S3), but also excellent wet adhesion (*Table* 3, Row 3). In additional studies, two separate factors were found to be important for this second added coalescent: it needed to have a low evaporation rate, and it needed to have good solvency for PVDF polymers. Alternative formulations where the NMP was replaced with other good coalescents for the binder, such as DPM, which were not active solvents for PVDF homopolymer, did not see a significant improvement of the adhesion or blister resistance. Likewise, the replacement of NMP with acetone, a fast-evaporating active solvent for PVDF polymers, did not improve the adhesion and water blistering properties to the same extent as NMP. These results point to the idea that adhesion to PVDF finishes can be significantly enhanced by choosing a topcoat coalescent or cosolvent which can effectively cause some softening or plasticization of the substrate.

In other studies not reported in detail here, a two-pack, solvent-based epoxy primer was also evaluated as a primer layer between the coating C1 and PVDF aged panel S3. The solvent primer also gave excellent system wet and dry adhesion, and excellent blister resistance, when used with the C1 topcoat. This would represent another potential approach for restoration coatings over PVDF finishes in regions of the world where such primers could be used.

Increasing the pigment loading and the incorporation of active cosolvents definitely improved the water blistering and wet adhesion of PVDF-Acrylic Hybrid A coatings over new and aged PVDF finishes, but the incorporation of additional solvents inevitably increases coating VOC levels, which goes in a direction opposite the trend in today's coatings markets. Two other alternative practical approaches to improve the adhe-

sion over PVDF finishes have also been demonstrated, which do not involve significant VOCs. The most effective solution, in fact, may be the simplest: a thorough cleaning of the surface, followed by scuff sanding. This procedure seems to be very effective in generating a contamination-free PVDF surface that can be readily adhered to by PVDF-acrylic hybrid dispersion formulations; in fact, excellent adhesion and water blister resistance was obtained by even formulation C1, directly applied over the fresh commercial PVDF substrate S1, when this substrate preparation strategy was followed. For situations involving the touch up or repair of relatively new PVDF finishes, scuff sanding the substrate is very highly recommended.

Another low-VOC strategy which seems to be effective in many cases is to use a waterborne primer based on a low T_g acrylic emulsion polymer. These kinds of primers can dramatically improve the water blistering and adhesive properties of PVDF-Acrylic Hybrid A coatings.

The above approaches to enhance adhesion generally can be used in combination as well. Finally, as was observed in this study, attention must be focused on the formulation details because the excessive use of hydrophilic surfactants and rheology modifiers can greatly influence the water sensitivity of a coating, especially with latex-based systems. Such ingredients should be used judiciously and in limited amounts.

Acrylic T_g Effect

Coating C4, prepared from the lower T_g PVDF-Acrylic Hybrid B, showed much better adhesion and high water-blister resistance on top of the S3 (aged Lab-PVDF) substrate, compared to C1 with PVDF-Acrylic Hybrid A. Since the lower T_g latex particles in the Hybrid B gave lower modulus coatings, as demonstrated by mechanical testing, we hypothesize that the adhesion improvement is due at least in part[13] to improved contact between the topcoat and the aged PVDF finish, resulting from the lower coating modulus. An additional factor contributing to the improved wet adhesion may be the much lower level of coalescent used in Coating C4 (about one third the amount used in C1; see *Table* 2), which could help reduce the total residual hydrophilic content of C4 relative to the other coatings tested (a lower acrylic T_g would also tend to promote a lower residual hydrophilic content, by enhancing the diffusion rate).

Whatever the exact reason for the improvement, the good adhesion performance of Coating C4, based on the PVDF-Acrylic Hybrid B, is especially noteworthy as this formulation is below the 50 g/L VOC limit that is in effect for restoration coatings in the South Coast Air Quality Management District (SCAQMD) region.

Influence of Substrate

The wetting properties and roughness of surfaces play a dominant role in adhesion between coatings and surfaces.[13] In this study, the adhesion of PVDF-acrylic hybrid coatings on a new commercial PVDF finish was poor (*Table* 3), unless some mechanical means like scuff sanding was used to prepare the surface. In a series of publications, Hinder et al.[7] have shown that the low molecular weight wetting and flow agents which are often used in the primer and topcoat layers of commercial PVDF finishes, such as siliconized additives, can migrate to the topcoat surface. Such species would reduce the surface energy, potentially reducing the wetting of the surface by any subsequent overcoat and reducing the adhesive energy, and could also impede the generation of mechanical linkages across the interface due to polymer reptation. The high advancing water contact angle of Substrate S1, as described in the section on surface characterization, strongly suggests the presence of low energy species on the commercial finish S1, and explains why careful cleaning and mechanical treatments are required to achieve good adhesion in such cases, even when waterborne PVDF-acrylic hybrid coatings are applied to them.

On the other hand, when a PVDF finish is made in the absence of such additives, as was the case for lab prepared Substrate S2, there seems to be sufficient wetting and adhesive force that a PVDF-acrylic hybrid dispersion topcoat can achieve excellent adhesion in both dry and wet conditions, even without scuff sanding and other mechanical treatments. The wet adhesive properties are largely lost, however, when the same substrate has been weathered for an extended period of time in the outdoors (Substrate S3), despite an increase in the surface roughness which might normally be expected to improve the adhesion (see *Figure* 2). In this case, it seems likely that photooxidized materials on the surface, which are hydrophilic enough to lead to a reduction in the water contact angle, provide pockets at the interface where water and hydrophilic components can migrate and reside. This leads to a build up in the osmotic pressure which causes the observed blistering and wet adhesion failure. In the case of aged PVDF finishes, however, it appears that these impediments can be rather easily overcome, either through careful surface preparation, the use of primers, formulation (as demonstrated with PVDF-Acrylic Hybrid Dispersion A), or by the optimization of the PVDF-Acrylic Hybrid Dispersion itself (Coating C4, based on Hybrid Dispersion B).

CONCLUDING REMARKS

In this study, we have discussed approaches to improve the adhesion of restoration coatings based on newly developed, water-based PVDF-acrylic hybrid

dispersions. Coatings with higher pigment volume concentration, and containing a coalescent which has good solvency for PVDF, showed dramatically improved water-blister resistance and wet adhesion over aged PVDF finishes. Several mechanisms may be operative in accounting for these results. Improvements in the adhesion may also be obtained through the use of a variant hybrid dispersion with lower T_g. This lower T_g version has the added benefit that it may be formulated at very low VOC content. Finally, the influence of surface topographic features and composition of the PVDF finish were also discussed, and found to play crucial roles in adhesion of restoration coatings based on PVDF-acrylic hybrids.

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