Patterns of Erosion from Acrylic and Fluoropolymer Coatings in Accelerated And Natural Weathering Tests

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Commercial poly(vinylidene difluoride) (PVDF)/acrylic coatings show minimal gloss loss or bulk chemical change even after sustained Florida or accelerated weathering testing. Previously, we showed that "QUV-B" weight loss rates can be used as an early predictor of the weatherability of fluoropolymer/acrylic blend clearcoats. In this work, we study the microscopic basis for differences seen between various blends and pure acrylic coatings. Scanning electron microscopy (SEM) images reveal different characteristic patterns of degradation.

INTRODUCTION

Architectural coatings based on polyvinylidene fluoride (PVDF) resins have a track record of durability which extends back over 30 years.[1] The excellent performance characteristics of such coatings have been obtained using a number of vinylidene fluoride copolymer resins, in addition to PVDF homopolymer. Commercial formulations also generally contain 20-30 wt% of a durable acrylic co-resin on total binder, but their outdoor weatherability approaches that of their pure fluoropolymer component when formulated using the most durable kinds of pigments. Industry standards for highly weatherable coatings commonly specify 5-10 years of South Florida exposure testing, and architectural coating warranties often extend for even longer periods. Therefore, the development of new products requires techniques to predict (within a period of months) the long-term weatherability of those coatings.

Coatings laboratories have used a variety of accelerated weathering techniques to evaluate the weatherability of coatings. *Figure* 1 illustrates the evolution in gloss for a white PVDF commercial-type paint, for three different types of testing: QUV-B, unshielded carbon arc, and Florida exposure. The accelerated techniques can cause significant coating degradation within a matter of months, days, or even minutes, depending on the technique. However, in many cases, the coating degradation through accelerated tests may not follow the same mechanism as natural weathering. In such cases, one would expect a poor correlation between accelerated testing and natural weathering results. (This is certainly the case for unshielded carbon arc testing, which is now rarely used in practice even for PVDF coatings).

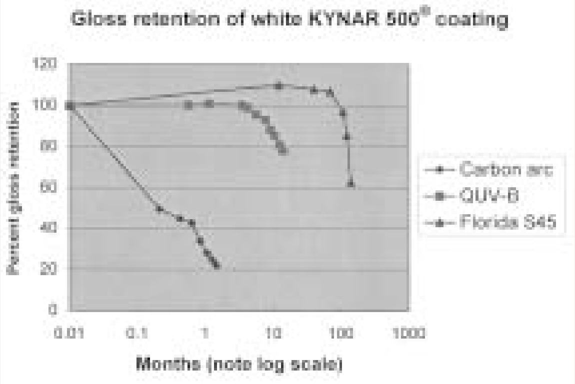

Figure 1—Degradation pattern observed under different types of testing: QUV-B, carbon arc, and Florida exposure.

To test whether accelerated weathering methods reproduce the dominant real life degradation pathways, an infrared analysis of the degrading coatings can generally be used.[2-7] For noncrosslinked coatings, measurements of soluble fraction and the molecular weight distribution can also provide valuable complementary information. For instance, recent work with acrylics has shown that compositional details can have a profound effect on the photodegradation pathway (changing the dominance of main chain scission versus crosslinking events).[8]

It has been difficult to use infrared analysis techniques to understand degradation mechanisms in PVDF coatings. PVDF itself does not degrade at solar UV wave-

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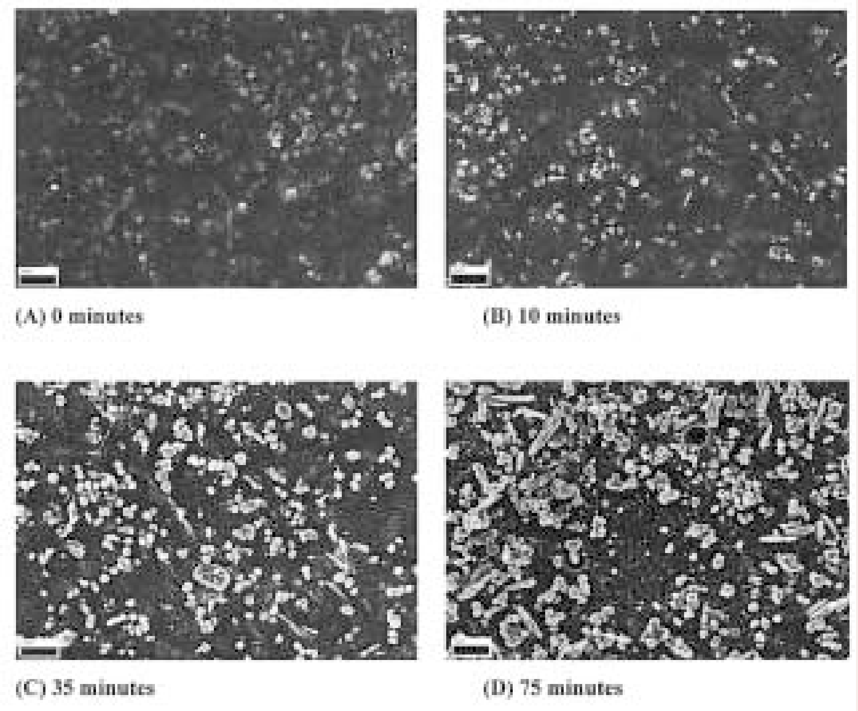


(A) 0 minutes

(B) 10 minutes

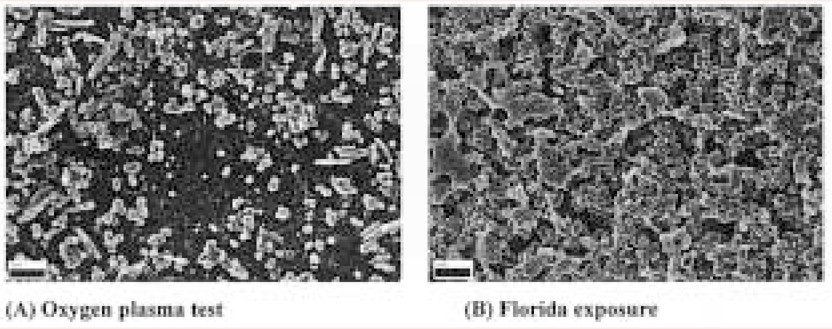
(C) 35 minutes

(D) 75 minutes

Figure 2—PVDF/acrylic dispersion coating under plasma erosion test. Gloss loss begins at 35 min; color change begins at 60 min; chalking begins at 50 min. Scale = 1 µm, Mag. = 10 kX.

lengths,[9] while a study of weathered Florida panels saw only very small changes in the infrared spectrum.[10] Moreover, more surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS), when applied to weathered Florida panels, can be more sensitive to surface contamination than to actual chemical changes in the coating. In such cases, other ways to compare degradation mechanisms are needed.

If an accelerated technique reproduces the dominant degradation pathways occurring in outdoor weathering of a coating, the appearances of the degraded coating surfaces should be similar, at microscopic length scales. Therefore a necessary (but not sufficient) condition for the relevancy of a particular accelerated technique, when applied to a given coating, is that micrographs of the accelerated and naturally weathered coatings should look the same. This criterion can be used to evaluate accelerated techniques.



(A) Oxygen plasma test

(B) Florida exposure

Figure 3—Comparison between oxygen plasma degradation and Florida exposure for highly weathered PVDF dispersion coatings (after onset of chalking). Scale = 1 µm, Mag. = 10 kX.

For example, one can see that the pattern observed for a PVDF coating after oxygen plasma exposure (*Figures* 2 and 3a) is totally different from that observed after Florida exposure (*Figure* 3b). The mechanism of binder erosion seems to be limited to the surface in the case of the plasma method, but a subsurface component appears to contribute in the case of the naturally weathered panel. From the micrographs, it is immediately apparent that the plasma erosion technique, for this coating, does not accurately reproduce natural weathering conditions. It is also possible to distinguish between erosion and contraction models of coating degradation using techniques other than imaging, such as a careful comparison of the relative rates of coating weight loss, gloss loss, and chalking.[11] However, the use of microscopic analysis as a screening tool is surprisingly infrequent.

QUV-B testing (described in ASTM G53-95) is generally not useful when the goal is to predict the relative durability of *different* resin types. The lamps employed substantially over-emphasize the most energetic part of the solar UV spectrum, and some resins are more sensitive to these wavelengths than others.[12,13] However, we showed in a recent study[10] that QUV-B testing could be a useful tool when developing PVDF-based coatings. Fluoropolymer/acrylic clearcoats (70% PVDF homopolymer or copolymer/30% acrylic), weathered in a QUV-B unit, can in many cases display characteristic changes in steady state weight loss rate, long before any changes in gloss are evident. For the same acrylic polymer, the weight loss rate appears to correlate directly with the resin coating morphology, and so can be used for the early prediction of the blend's weatherability.

In this paper, we use optical microscopy and scanning electron microscopy (SEM) imaging to track changes in the coating surface morphology of fluoropolymer and acrylic clearcoats weathered in Florida and in a QUV-B unit. The images are used to assess the validity of the QUV-B weight loss method, and to probe in general the relevancy of QUV-B testing of fluoropolymer coatings.

EXPERIMENTAL

Clearcoatings, as described in reference 3, were applied over a baked low gloss KYNAR 500® black primer coat on

Table 1—Clear Coatings: Gloss and Weight Loss After QUV-B Exposure

	Hours to 50% Gloss Loss (60°gloss)	Weight Loss Rate after 500 hr Conditioning (μg /1000 hr/ cm²)
Acrylic latex I	3,200	352
Acrylic latex II	5,700	222
Fluoropolymer/acrylic (no UV package, baked dispersion coating)	> 10,000	< 10
Fluoropolymer/acrylic, blend I , air dry (continuous fluoropolymer phase)	> 12,000	55
Fluoropolymer/acrylic, blend II, air dry (acrylic continuous phase, with fluoropolymer crystallites)	1,700	260

chromated aluminum test panels. The clearcoat dry film thickness was in the range of 15-30 microns. The thermoplastic coatings did not contain a UV stabilization package. Panels were exposed in South Florida for 28 months facing south at a 45° angle, and were not washed prior to microscopy analysis. QUV-B exposure panels were cut to a size of approximately 15 × 8 cm to fit in the QUV sample holders. The area exposed to radiation was roughly 9 × 6 cm. Samples were exposed according to ASTM G53, UVB 313 lamps, eight hours light @ 60°C/four hours condensation @ 45°C. The total exposure time for the samples was 4000 or 5800 hr.

Optical microscopy images were taken in reflection mode at a magnification of 10x. SEM images were obtained with an accelerating voltage of 5 keV, at various magnifications, after coating with 50 nm of gold/palladium to reduce surface charging in the SEM. Atomic force microscopy (AFM) images were collected in Phase Imaging mode, and both height and phase data were recorded. The scan rate was 1.0 Hz and the set point (force exerted on the sample) was adjusted to optimize the image.

DISCUSSION

PVDF/acrylic blend coatings can often meet 10-year South Florida gloss retention specifications, unlike most nonfluoropolymer coatings, including pure acrylics.[1] In our previous study, we noted that various acrylic and fluoropolymer clearcoats had different characteristic QUV-B steady state weight loss rates. In addition to a variety of fluoropolymer/acrylic blend coatings, with resin ratios typical of commercial PVDF coatings (70 wt% fluoropolymer/30% acrylic), we looked at four different all-acrylic coatings (two latex coatings, a thermoplastic solution coating, and a two-component solvent acrylic-urethane). Weight and gloss loss rates for some of those coatings are shown in *Table* 1. The coating weight loss rates could be measured long before any change of gloss was apparent. In fact, for some of the acrylic clearcoats, gloss loss occurred only when, according to mass loss, most of the coating had eroded. The early weight loss rate (in the period 500-2500 hr exposure) correlated well with the time until QUV-B gloss loss. For known coating compositions, the early weight loss rate also appeared to be consistent with general trends for Florida gloss retention. It was therefore concluded that for reasonably well understood systems, measuring weight loss rates is a useful tool, especially for screening new polymers and formulations.

The SEM images presented here reveal that coating weight loss is a very complicated phenomenon. For all the acrylic coatings studied (both crosslinked and thermoplastic, waterborne and solvent), the QUV-B coating degradation is not spatially homogeneous, even for clearcoats, after an initial induction period. During the initial high gloss period, the acrylics have a very smooth surface (*Figures* 4a and 4b), indicating that a spatially homogeneous loss of mass is occurring during this period (e.g., from surface degradation, diffusion of volatile materials from the coating interior, etc.). However, dramatic changes are seen in the micrographs of the QUV-B weathered acrylic samples once gloss loss begins to occur (*Figures* 4c, 5).

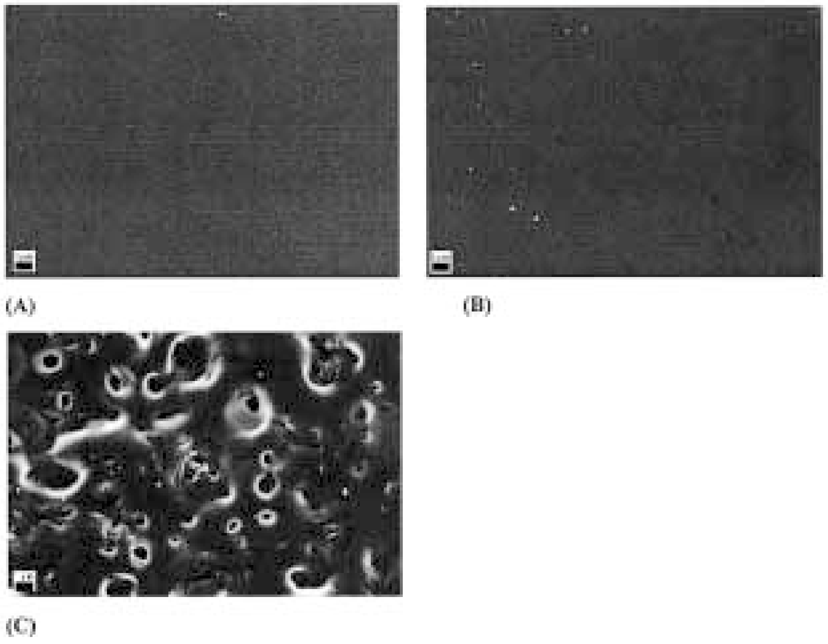


Figure 4—Thermoplastic acrylic latex I: (A) unexposed; (B) after 460 hr QUV-B exposure; (C) after 4,000 hr QUV-B exposure. Scale = 1 μm, Mag. = 5 kX.

Figure 5—Thermoplastic acrylic latex II, after 5,800 hr QUV-B exposure. Scale = 1 µm, Mag. = 5 kX.

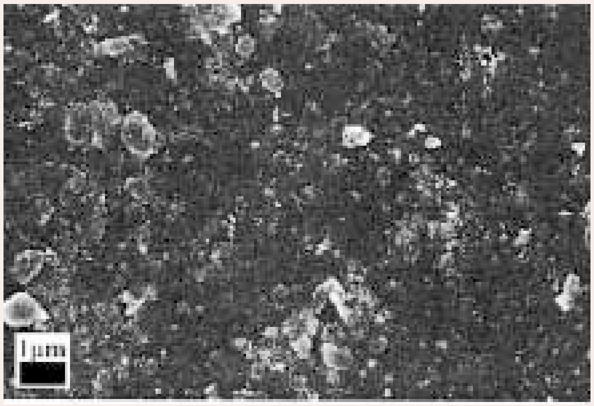


Figure 7—PVDF/acrylic dispersion clearcoat, after two years of Florida exposure. Scale = 1 µm, Mag. = 5 kX.

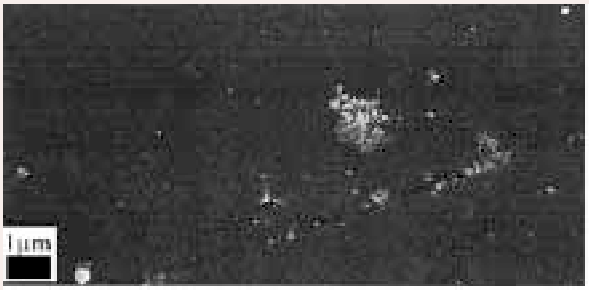


Figure 8—PVDF/acrylic dispersion coating, after 4,000 hr QUV-B. Scale = 1 µm, Mag. = 5 kX.

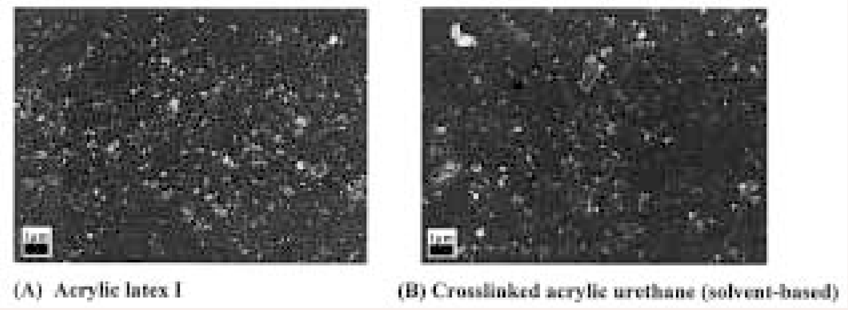
Pitting, and, in some extreme cases, holes and delamination, were observed in these samples.

The same acrylic clearcoats, after two years of Florida exposure, have not yet lost much gloss. Microscopic images show a generally smooth surface (*Figure* 6), with some fine scale structure (irregular adherent particles and patches of material apparently sticking out of the surface). This fine scale structure is commonly seen for many types of coatings after short-term Florida exposure (cf. a PVDF dispersion coating, *Figure* 7). Based on limited XPS analyses of the surface elemental composition, and the observation that such features are ubiquitous in Florida-exposed coatings but absent in accelerated-test coatings, the fine scale structure is believed to be caused by "dirt" contamination.

Apart from the apparent surface contamination, the acrylic coatings show little or no evidence of pitting—consistent with their gloss retention. Thus, the acrylics show the same pattern of minimal surface degradation seen in the early stages of QUV-B exposure (*Figure* 4b). At this stage, if any weight loss from the coatings is occurring, it must be occurring in a spatially uniform fashion. As the coatings begin to lose gloss in Florida during the next year or two, additional SEM images should reveal whether the pitting and porous degradation morphology, seen in the later stages of QUV-B, also occur in Florida exposures.

For a PVDF/acrylic dispersion coating, the SEM micrographs (*Figures* 7 and 8) did not show any changes for either Florida exposure or QUV-B exposure (after 12 months). This was not surprising since these coatings are known for their excellent long-term durability. The PVDF appears to protect the acrylic co-resin from the effects of weathering.

However, coatings having a heterogeneous PVDF/acrylic blend morphology, without a PVDF continuous phase, show dramatic patterns of erosion in SEM micrographs at early times, both in the QUV-B and in Florida exposure, due apparently to differential erosion rates for the acrylic and PVDF polymers. *Figures* 9 and 10 show the surface of a waterborne fluoropolymer/acrylic coating prepared for this study, which possessed small PVDF crystallites dispersed in a continuous acrylic phase. The coating exhibited rates of QUV-B weight loss similar to those of pure acrylics. The SEM micrographs show a highly porous, irregular arrangement of small spheres, which have the same diameter as the original PVDF crystallites. The same degradation pattern is observed after both Florida exposure and QUV-B exposure. These images support the idea that QUV-B exposure is adequate in many respects to mimic the net differential chemical changes



(A) Acrylic latex I

(B) Crosslinked acrylic urethane (solvent-based)

Figure 6—Acrylic-based coatings, after two years of Florida exposure (south 45°). Scale = 1 µm, Mag. = 5 kX.

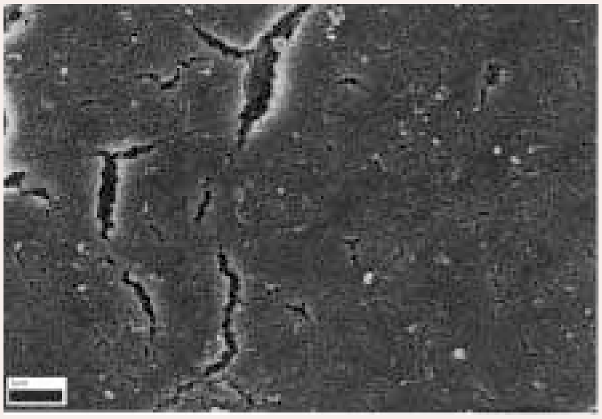


Figure 9—Fluoropolymer/acrylic blend II, after 24 months Florida exposure. Scale = 1 µm, Mag. = 10 kX.

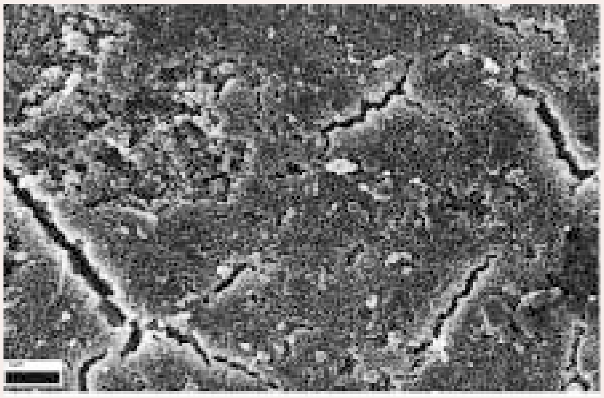


Figure 10—Fluoropolymer /acrylic blend II, after 4000 hr QUV-B exposure. Scale = 1 µm, Mag. = 5 kX.

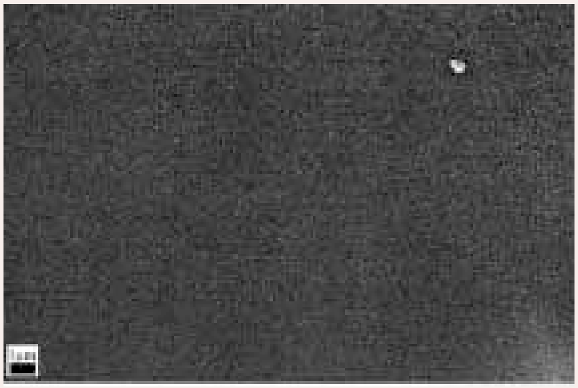


Figure 12—Fluoropolymer /acrylic blend I, after 5800 hr QUV-B exposure. Scale = 1 µm, Mag. = 5 kX.

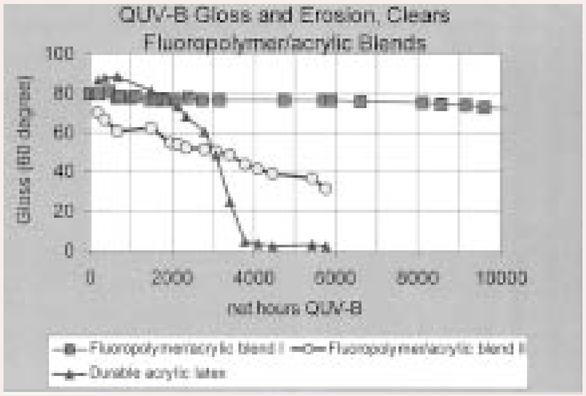


Figure 13—Effect of fluoropolymer/acrylic blend morphology on durability.

that occur in Florida exposures of such coatings. For this particular coating, weight loss seems to be occurring mainly through the differential loss of the acrylic component, gradually leading to a rough, porous surface and concurrent gloss loss. The mechanism is shown schematically in *Figure* 11. In *Figure* 11a, the acrylic covers the PVDF crystallites, resulting in a smooth surface and high gloss, while in *Figure* 11b, the binder erosion leads to exposure of the PVDF crystallites, resulting in chalking, surface roughening, and loss of gloss. In contrast, the thermoplastic acrylic latex II, which loses weight upon QUV-B exposure at a comparable rate, does not initially lose gloss because the erosion is spatially uniform.

As another example of the importance of the coating morphology on weatherability, *Figure* 12 shows the surface of a waterborne fluoropolymer/acrylic coating having a fluoropolymer continuous phase, after 5800 hr of QUV-B exposure. This coating survived 12,000 hr of QUV-B exposure with very little gloss loss (*Figure* 13). The surface is seen to be very smooth, and the QUV-B weight loss of this sample was minimal. In fact, recent atomic force microscopy results reveal that the surface of this coating possesses only a small pattern of corrugation (6 nm in amplitude) arising from the original latex particles. The corrugation pattern is retained after a year of QUV-B exposure, with an increase in the degree of rms surface roughness of only 1 nm (*Figure* 14). Therefore, QUV-B surface erosion in this fluoropolymer system appears to be minimal.

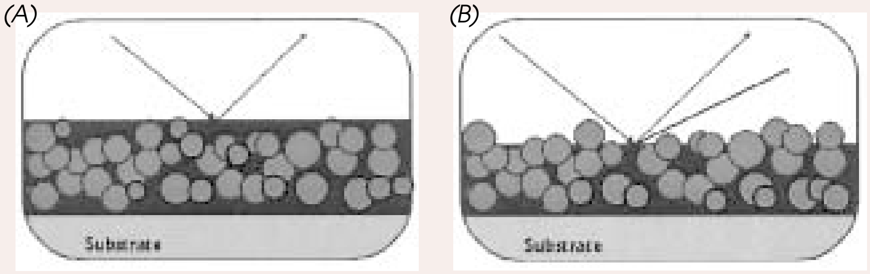


Figure 11—(A) Acrylic covers PVDF crystallites. (B) PVDF crystallites exposed after acrylic erosion.

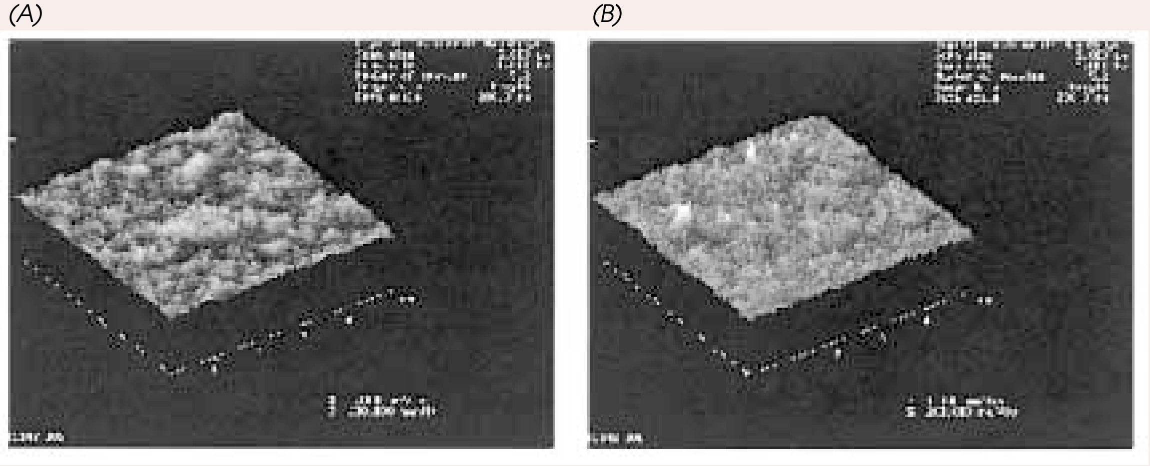


Figure 14—Atomic force micrographs of fluoropolymer/acrylic blend I surface: (A): initial; (B): after 8,500 hr QUV-B exposure.

The presence of pigments in a coating significantly alters the importance of various degradation pathways, as a comparison of PVDF/acrylic paints and clearcoats weathered in Florida (*Figures* 3 and 7) illustrates clearly. So while the above results, for clearcoats, provide important information about the relative weatherability of the different resin systems being tested, a complementary effort with full paints will also be required, to assess the effect of pigments on the coating weatherability.

CONCLUSIONS

Monitoring QUV-B gloss loss alone may not be sufficient to predict the outdoor performance of acrylic or fluoropolymer coatings, but the use of complementary techniques such as weight loss measurements and imaging can provide valuable information about the degradation mechanisms of a coating. SEM imaging can also be used to probe the extent to which accelerated weathering methods reproduce the degradation mechanisms of outdoor exposure. For fluoropolymer-acrylic systems with a fluoropolymer continuous phase—whether formed from solution or from latex—the inherent blend weatherability of clearcoats appears to be outstanding, with the fluoropolymer resin substantially preventing the erosion of the acrylic.

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