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TWO COATS IN ONE

Fluoropolymer blending optimises costs, performance and metallic effects. By Hongli Wang and Shun Saitoh, AGC Chemicals.

A blended powder coating containing FEVE fluoropolymer and superdurable polyester was dry blended with aluminium flakes. During cure, the coating self-stratified with FEVE forming the top layer and the flakes at the interface between the powders. This gave excellent appearance and performance at a much lower cost than pure fluoropolymer powder.

Fluoropolymers have superior chemical, corrosion and thermal resistance as well as excellent weathering, surface and optical properties when applied as coating materials on different substrates. Typical examples include:

- Aqueous dispersions of polytetrafluoroethylene (PTFE),
- Tetrafluoroethylene/hexafluoroethylene copolymers (FEP),
- Non-stick and anticorrosion applications using tetrafluoroethylene/perfluoroalkyl vinyl ether copolymers (PFA), [1] and
- High-performance polyvinylidene fluoride (PVDF)-based liquid paint for architectural applications.

However, these fluoropolymers are not necessarily suitable for use in powder coatings in architectural applications. PTFE cannot be used as a film former in powder coatings because of its physical properties. For example, it does not have a clean melt point, and it has to undergo pressure as well as heat to form a film [2]. Architectural substrates cannot sustain such heat. The melt point of a related polymer, ETFE (ethylene tetrafluoroethylene), is somewhat lower at 225 °C, which is still rather high even for an aluminium substrate [2]. Thermoplastic PVDF is tricky to process when used as a polymer for exterior durable powder coatings [2] as it requires cryogenic grinding. Because it is thermoplastic, the crystallinity of PVDF changes in the extruder, and a managed cooling period is required after compounding [2].

An alternative approach to incorporating the benefits of fluoropolymer technology in powder coatings at reasonable cost is described below. It is based on blending powders in such a way that the fluoropolymer component migrates to the surface during cure to optimise protection. Enhanced decorative effects can also be obtained when aluminium powders are incorporated.

ADVANTAGES OF FEVE COPOLYMER FOR POWDER COATINGS

Fluoro-olefin vinyl ether copolymer (abbreviated as FEVE copolymer, with the trade name of "Lumiflon") was developed in 1982 by Asahi Glass. FEVE is a thermoset polymer that can be processed through typical thermoset powder coating equipment. No liquid nitrogen is needed for cooling during the process, which makes it more process-tolerant [2].

FEVE is a better choice for powder coatings than other fluoropolymers. The resins have superior corrosion, chemical and UV resistance due to their unique chemical structure. The resins are amorphous A-B type copolymers with repeating units of fluoroethylene and substituted vinyl ethers. The energy of the C-F bond is around 486 kJ/mol, while the energy of UV radiation at 300 nm is some 400 kJ/mol [3]. The

unique alternating pattern of FEVE resins is critical for their extreme UV resistance properties. The chemically stable and UV-resistant fluoroethylene unit sterically and chemically protects the neighbouring vinyl ether unit [3].
The vinyl ether groups make FEVE polymers usable as resins for powder coatings by providing high gloss, hardness, transparency and flexibility as well as pigment compatibility and adhesion. The vinyl ether groups also allow for functional groups, such as hydroxyl groups, to be incorporated into the structure for crosslinkability [4].

THE CHALLENGES OF OBTAINING METALLIC POWDER FINISHES

Approximately 10 % of all powder coatings have a metallic effect, and strong commercial growth is evident due to developments in higher performance metallic pigments and market trends in colour and aesthetics. However, formulating becomes a challenge when very bright, reflective, sparkling metallic effects are required.
In the co-extrusion process, the metallic pigment granules are added to the other raw material at the premix stage and then pass to the extruder and onwards to the chill roll, kibbling, milling, sieving and packing stages. Due to the high shear in the extruder, the metallic pigments may be fractured, which results in a darker appearance with increased opacity [5]. When a leafing grade of metallic pigment is chosen, coating with leafing effects can be achieved — the metallic pigment migrates to the upper surface of the coating during the cure cycle and orients parallel to the surface.
Because metallic pigments such as aluminium are soft and non-durable, a clear coating applied through a separate process is then needed for protection. However, this virtually doubles the cost and film thickness, which limits their usage. Poor adhesion between the clear coat and base coating is another challenge.

RESULTS AT A GLANCE

→ Fluoropolymers have advantages wherever high levels of corrosion, weathering or chemical resistance are required. However, none of the common types are readily usable as powder coatings.

→ Fluoro-olefin vinyl ether (FEVE) copolymer is a thermoset powder coating resin with exceptional UV resistance. It can be extruded in a blend with superdurable polyester powder.

→ If this is correctly formulated, aluminium flakes can be dry blended (avoiding any damage due to the extrusion process) and the coating will self-stratify during cure. Aluminium will migrate to the interface, creating a bright metallic finish with the FEVE copolymer forming a top layer that gives maximum protection to both flakes and polyester with a lower cost than a pure FEVE coating.

→ Stratified coatings performed well in a severe accelerated weathering test and showed better alkali resistance than the pure polyester.

BLENDING CREATES HIGH-PERFORMANCE METALLIC FINISHES

For this study, a low-cost fluoroethylene vinyl ether (FEVE)/polyester blending technology was examined — a coating blend of 30 % FEVE resin and 70% superdurable polyester that can be stratified into two distinct layers with FEVE clear coating on the surface as a protective layer. Metallic pigment was incorporated in the FEVE/polyester blend to form a unique structure with metallic flakes staying at the interface of FEVE and polyester.
In this novel process aluminium (Al) pigments can be incorporated into the FEVE and polyester blend powder formulations through post dry blending (*Figure 1*). FEVE and polyester resins are pre-blended with other ingredients. The fluoropolymer and polyester powders are generated through the traditional powder coating process (Step 1). The extrusion can be done on a twin-screw extruder. Extrusion conditions are: 120 °C, 250 rpm and 50 % shear.
Aluminium flakes are dry blended with the fluoropolymer/polyester powders (Step 2). The metallic formulations are electrostatically coated on a substrate (Step 3), and the coated panels are cured in the oven using similar conditions to FEVE coating formulations without aluminium flakes (200 °C for 20 minutes) (Step 4). When the proper raw materials are chosen, a stratification structure can be achieved (*Figure 2*). FEVE migrates to the surface of the coating during curing. Aluminium flakes stay at the interface of pigmented polyester and FEVE layer. The clear FEVE topcoat serves as a protective layer for both polyester and aluminium flakes. The photocatalytic reaction of TiO_2 can be reduced in this structure, thus improving the durability of the coating. The photocatalytic effect happens when TiO_2 generates free radicals with existence of UV light, moisture and oxygen. Free redicals degredate binder polymer in the coating and damage the coating durability. Photocatalytic effects all coatings which contains TiO_2 or other pigments which have photocatalytic activity.

BENEFITS AND HOW TO MAXIMISE THEM

There are several advantages with this structure:

› Aluminium flakes oriented at the interface of the two polymer layers result in very bright, reflective and sparkling metallic effects. The

ADDITIVES

Figure 1: Schematic representation of the process of incorporating Al flakes in FEVE/polyester powder formulations through dry blending

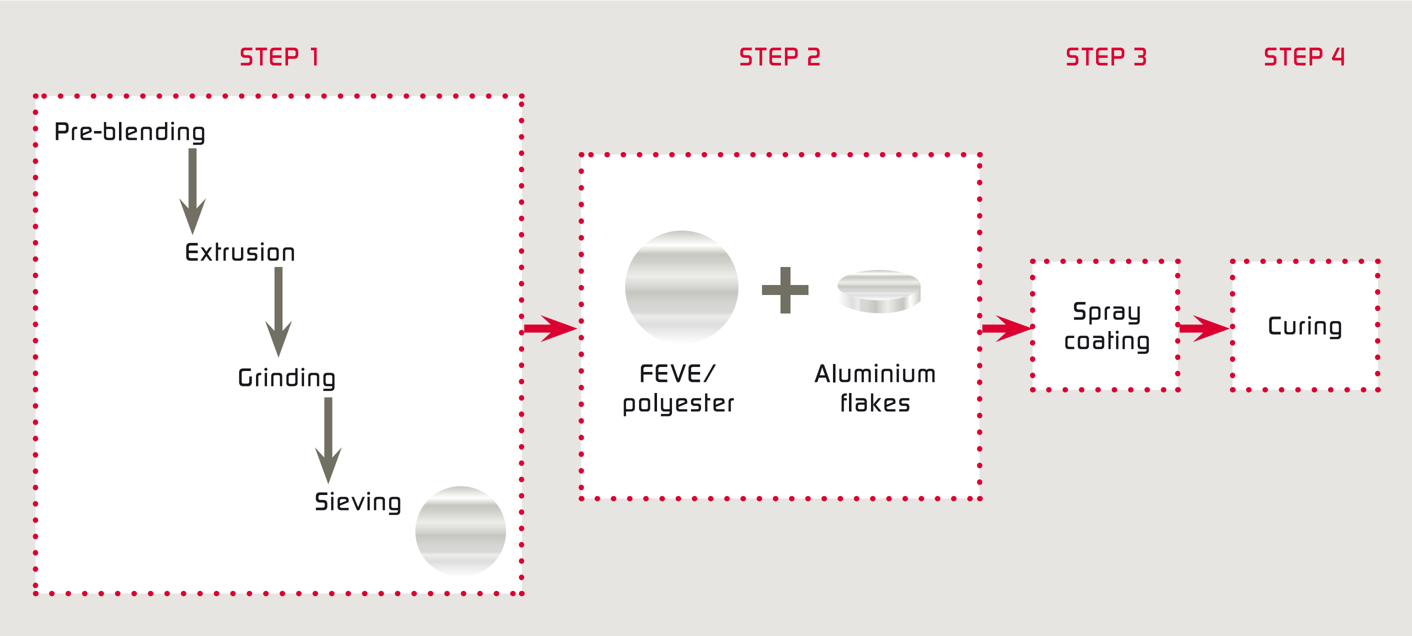


Figure 2: Energy-dispersive X-ray spectroscopy (EDX) analysis of a cross section of FEVE/polyester metallic coating.

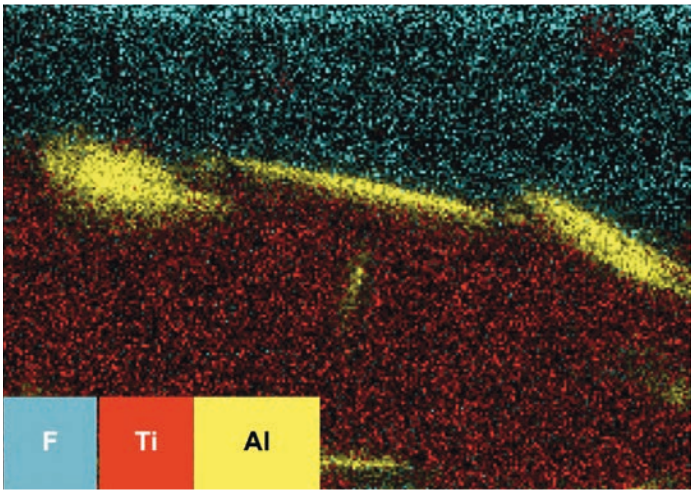


Figure 3: Hybrid exposure xenon weather meter (HE-XWM).

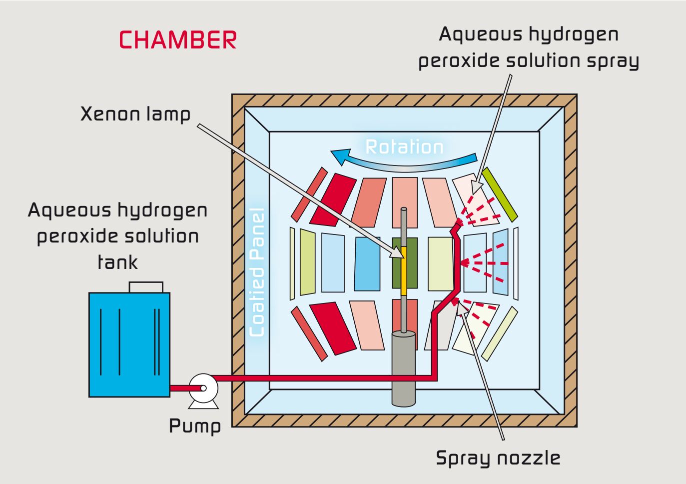
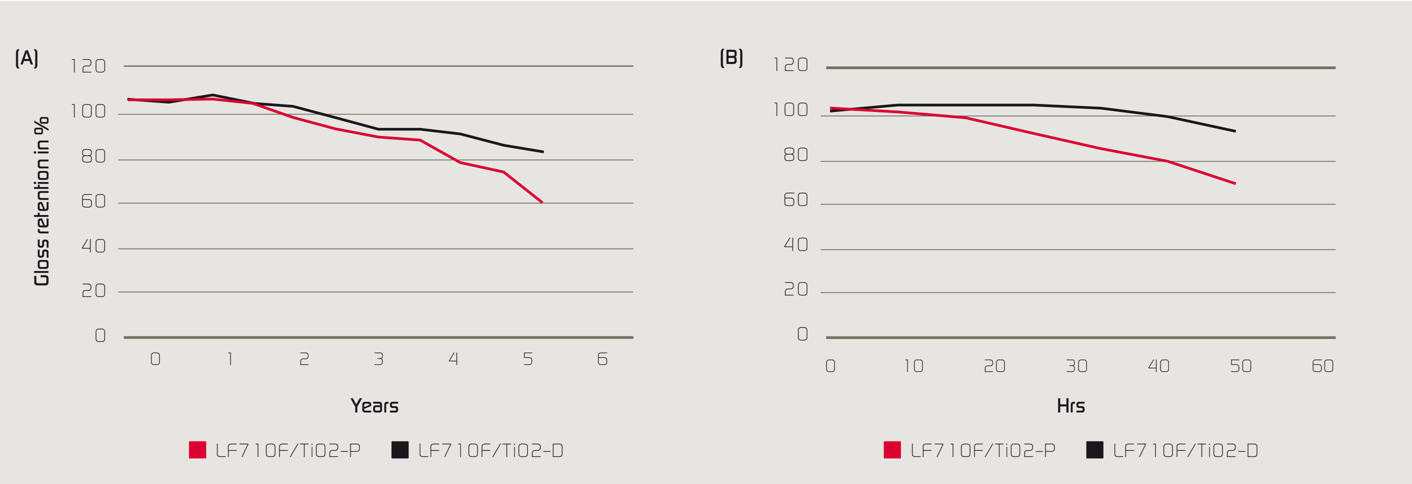


Figure 4: HE-XWM and Southern Florida exposure results compared.



aluminium flakes are protected by the thin FEVE layer. There is no need for a separate coating to protect the metallic pigments, which reduces the process cost.

- Only 3% to 5% of aluminium flakes are needed to achieve the bright effects, while in metallic liquid coatings three times more aluminium pigment is required to achieve similar effects.
- Polyester has better adhesion to metal substrates than fluoropolymers.
- Polyester and TiO_2 pigments are protected by a very durable FEVE top layer. Coatings with this special structure can provide weatherability comparable to pure FEVE coatings.
- The total raw material cost is much lower than pure FEVE coatings, because polyester accounts for 70% of the resin materials in the formulations.

There are some requirements for the coating ingredients in order to achieve the stratification structures. The solubility parameter of the polyester has to be different from that of the FEVE. The greater the difference, the greater the chance there is to achieve the desired structure. The solubility parameter (calculated by Fedors' method, involving molar volumes and energy of vapourisation) of the FEVE powder grade is 9.1 (SI units).

Suitable polyester candidates for this formulation should have a solubility parameter very different to that of FEVE. "Crylcoat 4890" by Allnex is one such candidate. The metallic aluminium flakes need to be acrylic coated. Eckart "PCU" aluminium grades (specifically formulated for powder coatings) are good choices for these stratification formulations.

COATINGS PERFORM WELL IN TOUGH HYBRID WEATHERING TEST

Accelerated weathering tests, such as the "QUV" and xenon arc, are used to screen formulations and predict performance under real-life

Figure 5: HE-XWM exposure results of a FEVE/polyester metallic coating and a pure polyester coating.

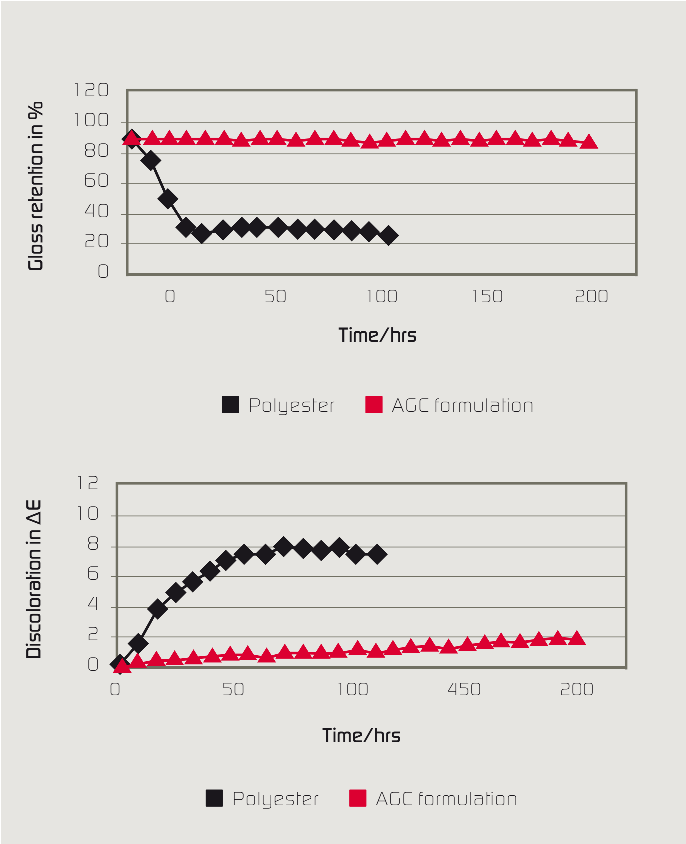


Table 1: Impact resistance and flexibility results comparing FEVE/polyester with PVDF.

Test type	FEVE/polyester	PVDF
T-bend test (ASTM D 4145)	2T	2T
Direct impact (cm)*	100	100
Reverse impact (cm)*	100	100

(* Qualicoat specifications).

PIGMENTS

FUNCTIONAL FILLERS

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exposure conditions in the coating industry. The challenge is to find an efficient and effective accelerated test that has a good correlation with natural exposure results [6]. For exterior coatings, performance is compromised primarily by degradation of the binder [7]. There are two types of binder degradation: direct degradation through UV light and TiO_2 photocatalytic degradation [8]. Considering the UV stability of fluoropolymers, the binder degradation of fluoropolymer coatings is mostly due to TiO_2 photocatalytic reactions. Current accelerated tests ("QUV A", "QUV B" and xenon) are designed to detect resin degradation by UV only.
In this study, accelerated exposure tests were performed by using a hybrid exposure xenon weather meter (HE-XWM) (*Figure 3*). The method was developed by Toyota Central R&D Labs.
Unlike the traditional QUV and xenon arc accelerated tests, the hybrid test also subjects a coating to hydrogen peroxide spray. H_2O_2 reacts with the electrons generated from the photocatalytic reactions of TiO_2 and produces hydroxyl radicals (Equation 1).

$$e^- + H_2O_2 \rightarrow HO\cdot + OH^-$$

The hydroxyl radical level is much higher under the hybrid testing conditions than in traditional exposure tests without H_2O_2. The extra hydroxyl radicals accelerate the degradation rate of the coatings. The maximum testing time of the hybrid system is only 200 hours. Testing results from the hybrid system have a very good correlation with the results of southern Florida exposure (*Figure 4*).
Figure 5 shows the HE-XWM exposure results of a FEVE/polyester metallic coating and a polyester coating using the hybrid system. The AGC formulation is the metallic FEVE/polyester coating prepared through post dry blending as shown in *Figure 2*. Although the majority of the resin (70%) in the metallic formulation is polyester, weatherability was significantly improved due to the protection from the stratified FEVE top layer. Chemical resistance of the FEVE/polyester metallic coating and polyester coating are compared in *Figure 6*. The coatings were exposed to alkaline (10% NaOH) aqueous solution at 80 °C for four hours. The FEVE/polyester blend coating has significantly better chemical resistance to alkali due to the protection of the FEVE top layer.

IMPACT RESISTANCE, FLEXIBILITY AND GLOSS CONTROL

FEVE powder coatings are widely used in architectural applications. Coatings with good impact resistance and flexibility are very critical during transport and construction. Because it is a thermoset polymer, FEVE coating is brittle. Conversely, PVDF is thermoplastic with a higher molecular weight, so coatings with PVDF are flexible.
This study demonstrates that with the proper additives, FEVE/polyester powder coatings can achieve the same level of flexibility as PVDF coatings. The impact resistance modifier evaluated was "Staphyloid AC-4040", a core-shell structured polymer with an elastomer as core and a glassy shell [9]. The results are shown in *Table 1*.
FEVE coatings offer high gloss due to their unique chemistry. However, many highly durable powder coating applications require low gloss. This study shows that "Tospearl 145", a silicone micro-resin, can help reduce gloss to meet the requirements of architectural applications without sacrificing other coating performance attributes (*Figure 7*).

THE LOW-COST ROUTE TO ENHANCED POWDER PERFORMANCE

Because of its unique chemical structure, FEVE is a better choice for powder coatings than other fluoropolymers. Developing powder coatings by adding superdurable polyester resin to FEVE-based formulas creates added consumer value over traditional coatings. These relatively low-cost FEVE/polyester blended formulas require no solvents, offer lower material costs, and deliver the performance, strength and gloss control end-users expect from fluoropolymer-based coatings.

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Figure 6: Chemical resistance comparison: (A) polyester coating and (B) FEVE/polyester metallic coating.

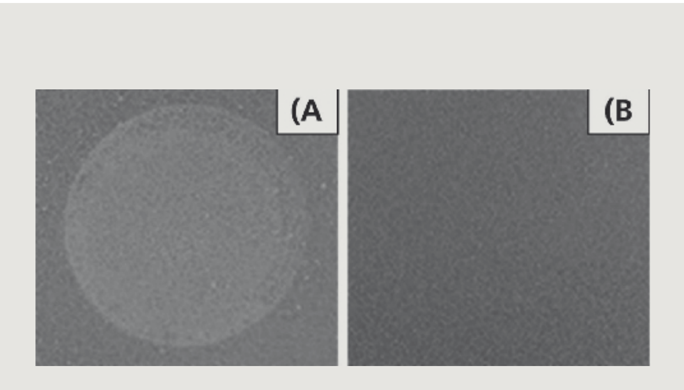
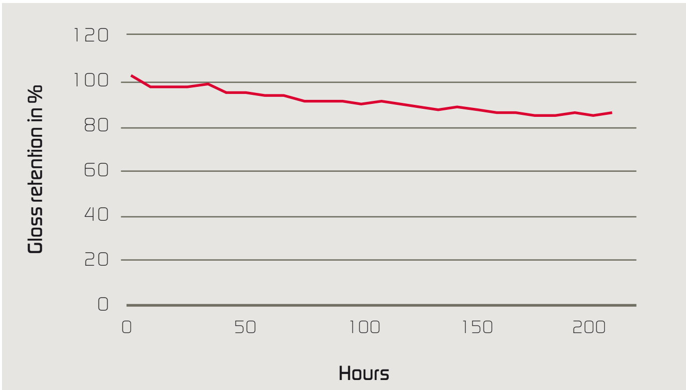
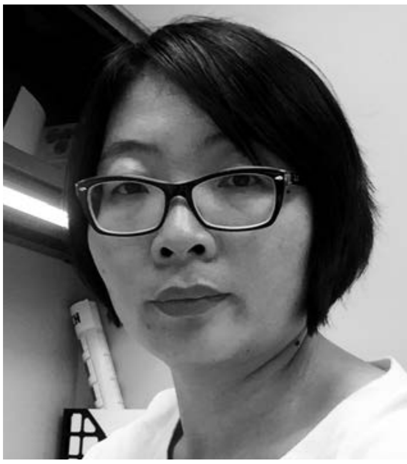


Figure 7: HE-XWM weathering results on matting formulations.





Hongli Wang
AGC Chemicals
Hongli.Wang@us.agc.com

"We have not seen any delamination in the stratification structure."

2 questions to Hongli Wang

Can the product be easily overcoated, for instance when maintenance work is necessary? *It is possible to do touch up repair by using "Lumiflon" liquid coatings. Our customers in Japan always use it for maintenance and repair during packaging or transportation of metallic powder coated products.*

What were your test results regarding interlayer adhesion? *We do not have experience testing interlayer adhesion between the product and a polyester layer. However, we have not seen any delamination in the stratification structure. Both our product and polyester have OH functional group reacting with an NCO group with isocyanate. The reason for the good adhesion between the two distinctive layers could be due to the thermoset networks formed between the product and the polyester at the interface.*

ADDITIVES

BOOK TIP

POWDER COATINGS CHEMISTRY AND TECHNOLOGY

3rd Revised Edition
By Emmouil Sypyrou
384 pages

PRODUCTION EQUIPMENT