Why titanates and zirconates are different than silanes

By Salvatore J. Monte
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(Second of two parts)

Function 2 Catalysis
Titanium- and zirconium-based organometallics are catalysts while silanes are not catalysts. Ti or Zr catalytic functionality works in unfilled polymers and changes the morphology of the polymer at the nano-interface of a filled polymer resulting in polymers with slightly higher tensile strength (F/A) and significantly higher elongation (e/l), which produces a tougher (defined as the area under the plot of stress vs. strain) polymer composite and also results in coatings with higher reverse impact strength and greater Mandrel flexibility.

Fig. 15 demonstrates Function 1 Adhesion, Function 2 Catalysis and Function 3 Anti-corrosion are demonstrated. It involves a 1-inch to quarter-inch mandrel flexibility and anti-corrosion using a co-soluted neoalkoxy pyrophosphato zirconate in an Unfilled WB Acrylic (Joncryl 537) on automotive tin plate. Realizing that the amine used to quaternize the otherwise water insoluble Ti/Zr blend might be causing a degree of hydrophilicity, it was decided to cosolvate the neat neoalkoxy pyrophosphate zirconate (NZ 38) with Texanol. That resulted in improved anti-corrosion performance at the scribe (right panel).

The use of a titanate absent cobalt naphthenate slows the rate of cure at 25°C, but not the state of cure of an unfilled MEK peroxide cured UP (Fig. 16A). The result is the elimination of the heat of exotherm and the resultant micro-bubbles formed when cobalt catalyst is used. At 40°C, the heat accelerated cure with titanate is faster than cobalt, and the state of cure is much higher as the unfilled MEK peroxide-cured composite has 14 times greater impact. Conventional cobalt cure discs fractures while the titanate cured disc broke micro after a second drop from a 6-foot height. (Fig. 16B)

Function 3 – Nano-Organometallic phosphorous anti-corrosion
The combination of the multi-functions of subject titanates and zirconates in nano-atomic mono-layers on any organic or organic substrate in any thermoplastic or thermoset polymer matrix provides a means to formulate all manner of anti-corrosive FR compositions.

For example, in Fig. 17 where in J.J. Jakubowski and R.V. Subramanian study the formation of fire retardant coatings of phosphorus compounds on graphite fibres: "Fire retardant coatings of phosphorus compounds were electro-deposited or electro-po-lymerized on commercial graphite fibres used for polymer reinforcement. The effect of these coatings on the thermal oxidative behavior of the coated carbon fi-
Why titanates and zirconates or visit

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Current work from the literature will be shown and some of the more interesting developments in the field of alternate interface technologies such as graphite, graphene and CNTs will be reviewed using recent ACS no phosphato heteroatom functionality built into its ligands? The paper will show why a zirconate can enable silane-sized E-Glass adhesion to a non-polar fluoropolymer. Subjection to a 240-hour, 10-percent saltwater boil, silanes often fail while zirconates and titanates do not. Be superior to silane (OH-) pretreatment condensation mechanisms because of the number of bonds and the facial coupling mechanism of a neoalkoxy organometallic via in situ surface proton (H+) coordination may significantly different alternative coupling mechanisms when compared to silanes.

Fig. 15: Unfilled WB acrylic increased adhesion, flexibility and anti-corrosion.

Fig. 16A: Titanate replaces cobalt naphthenate accelerator in MEK peroxide-cured unsaturated polyester.

Fig. 16B: Titanate increases impact strength of unsaturated polyester 14-fold.

Fig. 17: Flame-retarding effect of phosphorus titanate on carbon fiber/epoxy.

Fig. 18: Phosphato titanate prevents unplanned detonation of 120mm tank round propellant containing 85-percent nitramine extruded with RDX nitramine explosive while detonation of LOVA tank round propellant via Function 1 coupling detonation of LOVA tank round propellant consisting of 85-percent nitramine extruded with RDX nitramine explosive while catalyzing CAB plastic binder to allow 85-percent RDX/CAB to be ram extruded through a 19-Perf die without pin drift. The subsequent U.S. 6,197,135 patent by Monte was held under Department of Defense secrecy orders for 15 years and one month.12 Similarly, U.S. patent 5,753,853 was issued for controlling the burn rate and burn rate exponent of a solid rocket fuel composition consisting of rocket grade aluminum powder/ammonium perchlorate/HTTP FU was held under DOD secrecy orders for 11 years.13 Phosphorus-based titanates were subsequently approved in 92-In sensitive Munitions programs in place at that time. The solution to unplanned detonation of LOVA tank round propellant via Function 1 coupling was worked on from 1967 to 1983 with little success until Monte presented a paper at an American Defense Preparedness Association Symposium on June 1, 1982.14 Note, the ADPA changed its name to NDIA (National Defense Industrial Association) in October 1997.

Table 1 is the FG/epoxy portion of a 1988 SAMPE paper studying the effects of various titanates, zirconates and silanes on glass, carbon and Kevlar short- and long-fiber reinforced epoxy, vinyl ester, polyester and urethane composites. It establishes titanate and zirconate efficacy on the organic carbon and aramid interfaces as they outperformed the silanes on fiberglass long fiber pull-out tensile strength after being aged 240 hours in 10-percent salt water boil. The data reproduced in Table 1 shows the amino silane retains 65 percent of its original properties while the amino zirconate retains 93 percent of its original properties and is 2.1 times better than the amino and epoxide silanes on aged tensile long fiber pullout energy.

Fig. 18:

The paper also shows that being aged 240 hours in 10-percent salt water boil, silanes often fail while zirconates and titanates do not. Be superior to silane (OH-) pretreatment condensation mechanisms because of the number of bonds and the "facial coupling mechanism of a neoalkoxy organometallic via in situ surface proton (H+) coordination may significantly different alternative coupling mechanisms when compared to silanes."

The differences are explained through their chemistry and six functions. It will be shown that the inter

The author is a lifetime member of the American Chemical Society (ACS) and presented a paper at an American Chemical Society (ACS) Symposium on June 1, 1982.14

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Rubber News  •  April 4, 2022
Rubber News Staff
NORDBERG, Denmark—Generations may pass but leadership remains in the family for global power management company Danfoss Co., which was founded in 1933. Since 1996, Jorgen Mads Clausen has been at the helm for Danfoss, serving as CEO from 1996 to 2008, and as chairman of the board since 2009. Clausen stepped down as chairman at the March 25 annual general meeting for Danfoss shareholders, at which time the other changes were instituted as part of the planned generational shift in family ownership. Clausen was succeeded as chairman by Bjerg Sorensen, former vice chairman, who was chosen by the board in a session following the annual meeting. “Danfoss is now a stronger, bigger and more global company, but also one with a clear goal of contributing to the solution and combating climate change with our energy-efficient products and solutions,” Clausen added. “This is a result of a leadership strategy, which is now being updated with an ambitious sustainability strategy.” Though he no longer will be the chairman of the board, Clausen said in a March 21 release that he will continue to be president, as well as chairman of the board for a number of major companies. “Danfoss has an impressive history,” Sorensen said. “The foundation-based, long-term ownership and the family’s strong values are one of the main reasons why Danfoss has the influence we have on the world succeeds in the green transition.” Other changes at the top Additional transitions included: • William Erwin Hoover Jr. stepped down as president as directed by Clausen on the board of directors. Dohm has served as global head of government and regulatory affairs, as a team leader in financial services for Deloitte. • Mads-Peter Clausen, son of Peter Mads Clausen, will continue to serve on the board of directors for Danfoss A/S, of which he has been a member since 2015. • Mads Clausen, son of Jorgen Mads Clausen, will join the board of directors at Danfoss A/S. Stronger together New Board Chairman Sorensen noted that Danfoss “is financially stronger than ever,” as evidenced by Danfoss’ $3.3 billion acquisition of the hydraulics division for Dubl, Ireland-based Eaton Corp. The Aug. 2, 2021, acquisition brought about $1.5 billion in annual revenue to Danfoss, specifically to the division that serves the wind segment, which doubled in size with the Eaton Hydraulics acquisition. Danfoss leadership transition and combating climate change with an emphasis strategy, which is now being updated to include the company’s priorities for the company moving forward. Danfoss Power Solutions had about $4.7 billion in sales revenue in 2021.

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