Why titanates and zirconates are different than silanes

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(Second of two parts)

Executive summary

In 1973, after more than a decade servicing the rubber industry with aromatic plasticizers and dispersions, Salvatore Monte, author of this paper, invented the first of many organometallic titanate or zirconate coupling agents while working on a zinc oxide masterbatch. He has spent 50 years teaching how they provide 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 interfacial coupling mechanism of a neoalkoxy organometallic via in situ surface proton (H+) coordination may be superior to silane (OH-) pretreatment condensation mechanisms because of the number of bonds and the differences in interfacial hydroxyl group availability.

In addition, silane hydrolysis leaves water of condensation on the interface during siloxane formation, which may be detrimental to long-term aging. For example, when inorganic and organic composites are subjected to a 240-hour, 10-percent saltwater boil, silanes often fail while zirconates and titanates do not. The paper will show why a zirconate can enable silane-sized E-Glass adhesion to a non-polar fluoropolymer.

The research also addresses questions such as: How can a silane couple CNTs, graphene, sulfates, carbonates or cement that have no hydroxyl groups? How can nano-intumescence be achieved with a silane with no phosphato heteroatom functionality built into its ligands?

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 CAS abstracts.

Function 2 Catalysis

Titanium- and zirconium-based organometallics are catalysts while silanes are not catalysts. Ti or Zr catalytic functionality works in unfilled polymers[7] 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 composites and also results in coatings with higher reverse impact strength and greater Mandrel flexibility.

TECHNICAL NOTEBOOK
Edited by John Dick

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-solvated 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 disc fractures while the titanate cured disc broke only after a second drop from a 6-foot height. (**Fig. 16B**)

Function 3 – Nano-Organometallic phosphorous anti-corrosive/flame retardance

The combination of the multi-functions of subject titanates and zirconates in nano-atomic monolayers 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 .[10]

For example, in **Fig. 17** wherein J.J. Jakubowski and R.V. Subramanian study the formation of fire retardant coatings of phosphorus compounds on graphite fibres[11]: "Fire retardant coatings of phosphorus compounds were formed on graphite fibers by a new electrochemical technique. Thus, tetrakis (hydroxymethyl)-phosphonium sulphate, ammonium polyphosphate, titanium di(dioctylpyrophosphate) oxyacetate, di(dioctylphosphato)ethylene titanate, and propargyltriphenyl-phosphonium bromide, were electro-deposited or electro-polymerized on commercial graphite fibers used for polymer reinforcement. The effect of these coatings on the thermal oxidative behavior of the coated carbon fibers, epoxy resin and composites prepared from them was studied by thermogravimetric analysis, and compared with that of polyimide coatings. Generally, the coated fibers showed higher decomposition temperature than the untreated carbon fibers.

"The fire retardant phosphorus compounds promoted the formation of char from the matrix resin, and accelerated the decomposition of char. Organophosphorus titanate coatings left an incombustible, white residual layer of titanium dioxide. The polyphosphate coating caused the decomposition of the fibers in the epoxy composite to occur at a reduced temperature compared to that in the absence of the matrix resin. A synergistic interaction between the polyphosphate and the amine-cured, epoxy resin to catalyze the decomposition of carbon fibers is inferred from this. Polyimide precursor coatings lowered the oxidation temperature of the carbon fibers, both as neat coatings and in the presence of epoxy matrix resin, thus reducing the temperature of survival of the fibers under combustion conditions. The results confirm the potential of this novel approach of forming precursor coatings on carbon fibers to minimize the release of conductive fiber fragments from carbon fiber-reinforced polymer composites exposed to fire."

In **Fig. 18,** a neoalkoxy phosphato titanate prevents unplanned detonation of LOVA tank round propellant via Function 1 coupling to 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]

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

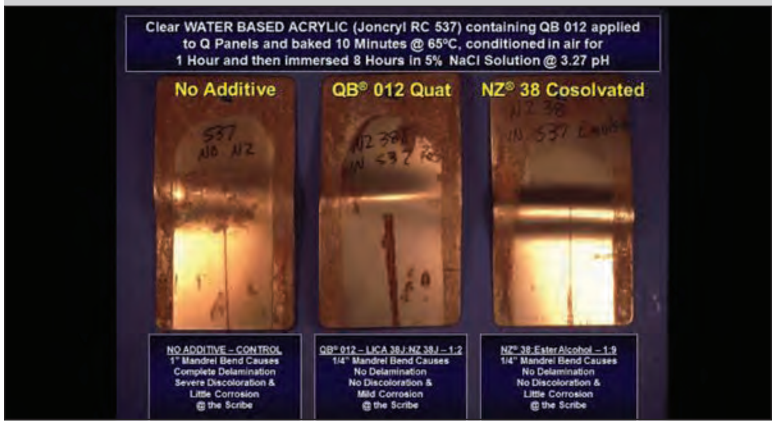


Fig. 16A: Titanate replaces cobalt naphthenate accelerator in MEK peroxide-cured unsaturated polyester.

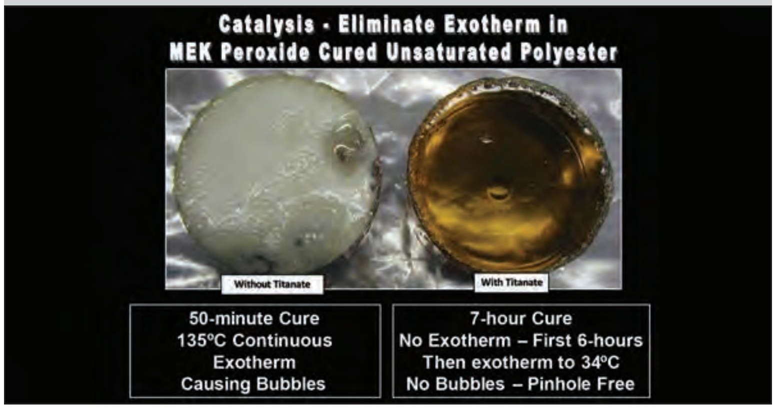
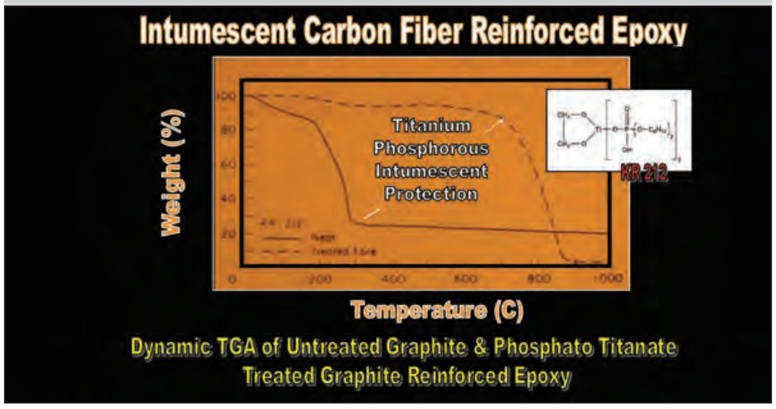


Fig. 16B: Titanate increases impact strength of unsaturated polyester 14-fold.

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

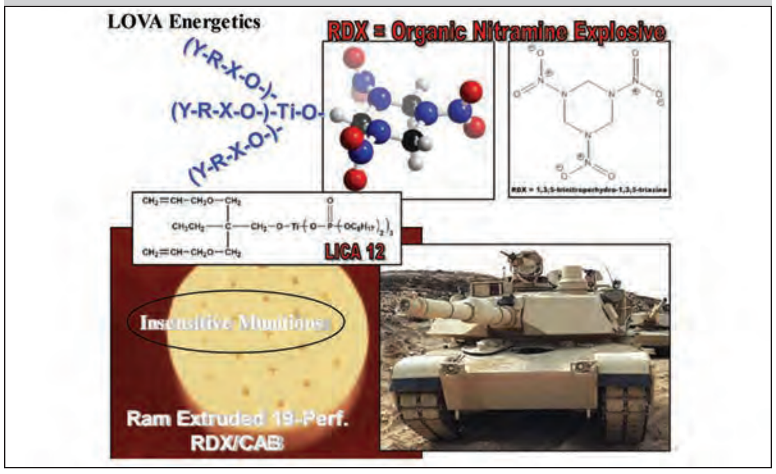


Similarly, U.S. patent 5,753,853 was issued for controlling the burn rate and burn rate exponent of a solid rocket fuel composition consisting of rocket grade aluminum powder/ammonium perchlorate/HTPB PU was held under DOD secrecy orders for 11 years.[13]

Phosphorus-based titanates were subsequently approved in 92-Insensitive Munitions programs in place at that time. The solution to unplanned detonation of energetics, propellants and explosives had been 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. The author is a lifetime member of the NDIA.

Table 1 is the FG/epoxy portion of a 1988 SAMPE paper[15] 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, J.

Fig. 18: Phosphato titanate prevents unplanned detonation of 12omm tank round propellant consisting of 85-percent nitramine extruded with CAB through a 19-perf die.



1.5-Nanometer Ti/Zr nanotechnology: Meeting the nano-challenge of graphene

Sometimes the meaning of "nano" gets lost in numerical definitions such as: "one nanometer equals 1E-09 meters" or "one-billionth of a meter." In organic carbon terms, one nanometer is the length of 10 carbon atoms. Most subject heteroatom titanates and zirconates invented by the author are about 15 carbons in length—hence, 1.5 nanometers. I like to use a more visual description for the length of a nanometer by saying: "Look at your thumbnail. The length it grows in one second is a nanometer." **(Fig. 19.)**

This thumbnail visualization should register in your mind that you can't see readily the growth or movement of one nanometer. When things on the nanometer scale such as a virus (30-50 nm), DNA (2.5 nm), CNT (~1 nm in diameter) are this small, you can't see them with your eyes, or a light microscope and analytical SPM (scanning probe microscopy) methodologies such as STM (scanning tunneling microscopy) and AFM (atomic force microscopy) are used. AFM techniques include: contact AFM; non-contact AFM; dynamic contact AFM; tapping AFM; and AFM-IR.

The first commercially available atomic-force microscope was introduced in 1989—16 years after I was trying to figure out how my invented titanate products "worked." The AFM is one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale.

The first commercial instrument for SEM photos was by

See **Different**, *page 20*

Clausen steps down as Danfoss chairman

Rubber News Staff

NORDBERG, Denmark—Generations may pass but leadership remains in the family for global power management company Danfoss Co., as it has since its founding 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

Clausen stepped down as chairman at the March 25 annual general meeting for Danfoss, at which time other changes were instituted as part of the planned generational shift in family ownership.

Clausen was succeeded as chairman by Jens 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 green transition and combating climate change with our energy-efficient products and solutions," Clausen said. "This is a result of our business strategy, which is now being updated with an ambitious sustainability strategy."

Though he no longer will be on the board of directors, Clausen said in a March 21 release that he will continue to be accessible, embodying a post-leadership legacy begun by Bitten Clausen, widow of Danfoss founder Mads Clausen.

"Both my siblings and my wife and I are delighted that the third generation of the family is showing their commitment to Danfoss by taking on greater responsibility," Clausen said.

He said Sorensen possesses the right leadership traits and a unique understanding of the Danfoss culture.

"He can take Danfoss to new levels, together with the rest of the board, management and our employees," Clausen added.

Sorensen previously served as CEO of Schouw and Co.—a Denmark-based engineering services firm—since 2000, and has served 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 now has a decisive influence on whether the world succeeds in the green transition."

Other changes at the top

Additional transitions included:

- William Erwin Hoover Jr. stepped down, to be replaced by Karin Dohm on the board of directors. Dohm has served as global head of government and regulatory affairs at Deutsche Bank and a partner 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 2014; and
- 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 unit for Dublin, Ireland-based Eaton Corp.

The Aug. 2, 2021, acquisition brought about 10,000 former Eaton employees into the Danfoss fold and adds about $1.8 billion in annual revenue to Danfoss, specifically to the Danfoss Power Solutions segment, which doubled in size with the Eaton Hydraulics addition. Danfoss leadership has said that hydraulics remains a priority for the company moving forward.

Danfoss Power Solutions had about $4.7 billion in sales revenue in 2021.

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Cambridge Scientific Instrument Co. as the "Stereoscan" in 1965. Conventional SEM requires samples to be imaged under vacuum. Processes involving phase transitions, such as the drying of adhesives or melting of alloys, liquid transport, chemical reactions and solid-air gas systems, in general cannot be observed. In fact, an SEM can only show the effect and not the actual "coupling agent" itself. So again (*repetitio est mater studiorum*), we must rethink "complete coupling" if we are to achieve optimal performance of materials used in composites and coatings.

So much of what we think we know about how coupling agents work are based on SEMs. And they only tell you what you see at a non-nano level—and it certainly isn't the nano-water of condensation left on the interface from silane hydrolysis coupling. To quote Mark Twain: "It's not what you don't know that will get you in trouble. It's what you know that ain't so."

In **Fig. 20,** an aromatic amino zirconate improves the flow and properties of 40-percent FG/PPS. China has filed 80 percent of the ACS CAS abstracted patents in carbon reinforced composites: graphene-109; graphite-177; CNTs-105 based on my teachings since 1974.

Graphite, graphene and CNTs are the present and a good part of the nano-future of advanced thermoplastic and thermoset composites such as EV batteries. The Ti/Zr effects on 40 percent FG/PPS translates to CNT/PPS increasing conductivity 10-fold using a titanate (KR TTS) Monte invented in 1973. The ACS CAS abstract that follows is from CAS IP SEARCH:

Title: Development of carbon nanotube- and graphite-filled polyphenylene sulfide-based bipolar plates for all-vanadium redox flow batteries.

Author: Caglar, Burak; Fischer, Peter; Kauranen, Pertti; Karttunen, Mikko; Elsner, Peter.

CS: Applied Electrochemistry Department, Fraunhofer Institute for Chemical Technology (ICT), Pfinztal, 76327, Germany.

SO: Journal of Power Sources (2014), 256, 88-95.

DOI: 10.1016/j.jpowsour.2014.01.060.

PB: Elsevier B.V.

DT: Journal; (online computer file).

LA: English

Abstract: In this study, synthetic graphite and carbon nanotubes filled polyphenylene sulfide-based bipolar plates are produced by using co-rotating twin-screw extruder and injection molding. Graphite is the main conductive filler and carbon nanotubes are used as bridging filler between graphite particles. To improve the dispersion of the fillers and the flow behavior of the composite, titanate coupling agent (KR-TTS) is used.

The concentration effect of carbon nanotubes and coupling agent on the properties of bipolar plates are examined at 72.5 weight percent total conductive filler concentration, by addition of 2.5 weight percent carbon nanotubes and 3 weight percent KR-TTS, through-plane and in-plane elec. conductivities increase from 1.42 S/cm to 20 S/cm and 6.4 S/cm to 57.3 S/cm, respectively, compared to sample without carbon nanotubes and additive. Extruder torque value and apparent viscosity of samples decrease significantly with coupling agent and as a result the flow behavior is positively affected. Flexural strength is improved 15 percent by addition of 1.25 weight percent carbon nanotubes. Differential scanning calorimetry analysis shows nucleating effect of conductive fillers on polyphenylene sulfide matrix. Corrosion measurements, cyclic voltammetry and galvanostatic charge-discharge tests are performed to examine the electrochemical stability and the performance of produced bipolar plates in all-vanadium redox flow battery.

IT: 61417-49-0, KR-TTS

RL: NUU (Other use, unclassified);

Uses: Coupling agent; development of carbon nanotubes and graphite-filled polyphenylene sulfide-based bipolar plates for all-vanadium redox flow batteries)

Summary

Subject titanates and zirconates are different and may be better adhesion promoters than silanes because their Six Function chemistry works differently:

- No hydroxyl (OH-) groups or H_2O needed as with silanes.
- No pH sensitivity—special pretreatment conditions needed—add directly to the organic or water phase.
- Proton (H+) reactive with organic/inorganic substrates of all types.
- Add directly into mix for in situ coupling and polymer catalysis for repolymerization and copolymerization compatibilizing dissimilar polymers.[4]
- Form 1.5-nanometer atomic monolayers for complete adhesion.
- Resist aging and provide nano-phosphorus anti-corrosion and flame retardance at the nano-interface.
- Act as coupling agents and catalysts to compatibilize dissimilar interfaces found in composites.
- Compatibilize addition and condensation polymers and couple inorganics and organics enabling mechanical recycling sustainability goals to be achieved through the same chemistry used to make the polymers.

Fig. 19: The 1.5-nanometer atomic monolayer of titanate is equivalent to the length a thumbnail grows in one second and cannot be seen with TEM or SEM images.

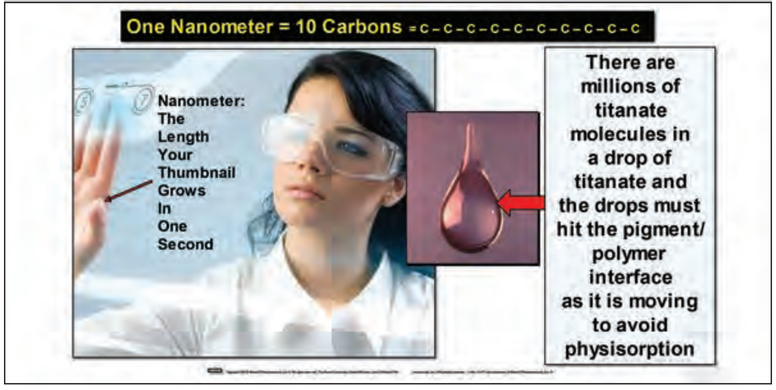

Fig. 20: An aromatic amino zirconate improves the flow and properties of 40-percent FG/PPS.

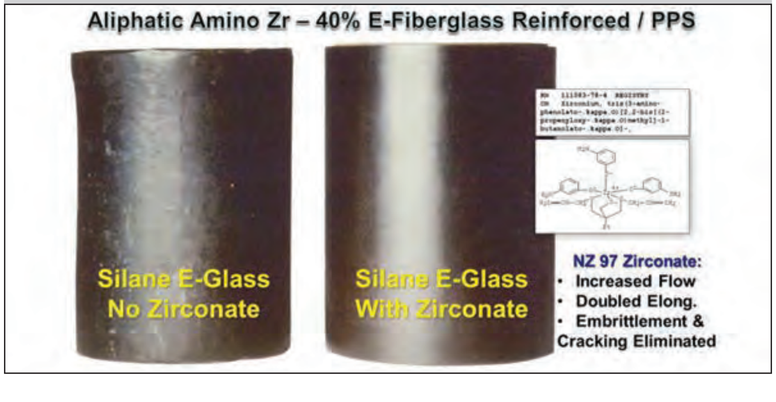

Table 1: Evaluation of various coupling agents in glass fiber-reinforced epoxy composites (original/aged properties).

Formulation	Parts by Weight
Resin, DEN 438 (Novalak - Dow)	100.0
Hardener, Methyl Nadic Anhydride	87.5
Glass Fiber As shown (Short - 5 mm)	40.0
Additive(s)	0.4

Brookfield Viscosity measured @ 80°C; Cure 30 min. @ 150°C.
Post Cure: 4 hr. @ 180°C.
Aging 240 hr. in boiling 10% aqueous salt solution.

Additive	Long Fiber	Short Fiber Vehicle Only			
	Tensile Pullout Energy, J Orig. / Aged	Viscosity 0.2 rpm/2 rpm: Mega poise	Flexural Strength, gPa Orig. / Aged	Compressive Strength, gPa Orig. / Aged	Falling Ball Impact Str. kJ/m Orig. / Aged
Control	54 / 14	0.67 : 0.43	0.82 / 0.40	1.54/1.21	1.7/1.0
Amino Silane	63 / 41	0.63 : 0.48	0.96 / 0.69	1.69/1.43	1.9/1.5
Epoxide Silane	65 / 37	0.58 : 0.45	0.92 / 0.74	1.58/1.51	1.9/1.6
Amino Zirconate	92 / 86	0.39 : 0.34	1.31 / 1.23	1.92/1.80	1.9/1.7

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