

WHY TITANATES & ZIRCONATES ARE DIFFERENT THAN SILANES

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ABSTRACT

Organometallic Ti or Zr coupling agents 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 titanate or zirconate 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 hydroxyl group availability from interface to interface. In addition, silane hydrolysis leaves water of condensation on the interface during siloxane formation, which may be detrimental to long term aging – particularly when composites are subjected to 240-hour 10% salt water boil wherein silanes fail at the interface while zirconates and titanates don't. E-Glass is the most widely used reinforcement in MEKP unsaturated polyester composites, but is it the best one? The paper will show why a zirconate can adhere silane sized E-Glass to a fluoro polymer such as ETFE, while the E-Glass alone doesn't. The paper will also address questions such as: How can a silane couple CNT's or graphene or sulfates or carbonates or cement that have no hydroxyl groups? How can nano-intumescence be achieved with a silane that does not have phosphato heteroatom functionality built into its ligands? The paper will also address the question: Why does the industry continue to use cobalt naphthenate as an accelerator in MEKP cured unsaturated polyester creating exothermic micro-bubbles and the subsequent problems of strength, aging and surface finishing, which can be eliminated by replacing the cobalt with certain titanate coupling agents thus utilizing titanium's latent cure effects, which in turn creates slower endothermic bubble-free cures that can use heat (40°C) or more aggressive peroxides to speed cures even faster than cobalt resulting in fourteen-fold increase in the impact strength of an unfilled and unreinforced unsaturated polyester? 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 CNT's will be reviewed using recent ACS CAS Abstracts.

Keywords: Coupling Agents, Titanate, Zirconate, Silane, Adhesion, Carbon, Interface, Catalysis, Anti-corrosion, Flame Retardance

INTRODUCTION

The author made his first public composites presentation [1] in February of 1976 at the annual meeting of the SPI Reinforced Plastics/Composites Institute at the Shoreham Americana in Washington, D.C. during the Interface Session chaired by Dr. Edwin Plueddemann, who later wrote the book in 1982 entitled, "Silanes" [2]. RP/CI evolved around 1999 into the ACMA

which subsequently joined with SAMPE to produce CAMX. Out of the six speakers in 1976, I was the only one not talking about silanes. Ed's comment after my presentation was somewhat deprecating as he apprised me of the fact that titanates weren't good coupling agents because of their poor hydrolytic stability and were better used as transesterification catalysts. But, Plueddemann was referring to older generation titanates such as tetraisopropyl titanate (TIPT), while I was introducing a new generation of heteroatom titanates using TIPT as a synthesis intermediate that were not only hydrolytically stable, but also water insoluble.

At the time, I did not have the data or understanding to counter Plueddemann (The Father of Silanes), and it wasn't until 1985 that we had gathered enough data and knowledge to write our own book [3] on titanates and zirconates. Nevertheless, the silane mindset persists in glass reinforced composites and silanes are used widely in all manner of polymeric compositions. Silanes are established art and have made the modern era of coatings and composites possible in thousands of proven applications. Physicist Max Planck wrote that "the new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it". I trust the speed of the internet enabling virtual transfer of information and this paper will enable me not to have to just outlive all the people who believe Silanes are better than Titanates. This paper is another in a series of almost five hundred ACS CAS Abstracted "Works by S.J. Monte" where I attempt to teach WHY TITANATES & ZIRCONATES ARE DIFFERENT THAN SILANES. Teachings that have led to over 3,000 patents and technical papers by others using subject organometallics.

DISCUSSION

The reason why titanates and zirconates may be different or even better adhesion promoters than silanes lies in the intrinsic multi-functional chemistry of tetravalent organometallic titanium and zirconium as compared to silicone at the nano-interface where dissimilar materials meet. The Titanate/Zirconate Six Functions is a useful collective method to teach why they do what they do where Silane Three Functions don't - see Figure 1.

If one looks at the Periodic Table in Figure 2 according to Atomic Number, there seems to be little in common between Si, Ti, and Zr.

But, look at the Periodic Table in Figure 3 according to Valence as drawn by Dow's James Franklin Hyde and there is much in common between tetravalent Si, Ti, and Zr. Hyde has been called the "Father of Silicones" and is credited with the launch of the silicone industry in the 1930s.

Si (Silanes), Ti (Titanates) and Zr (Zirconates) are tetravalent – but, different because of the Six Functions.

SIX FUNCTIONS

Function 1 "Coupling" Ti vs. Si Difference

Until his death in 1991 at the age of 75, Dr. Edwin P. Plueddemann was considered the world's foremost expert on silane coupling agents. In 1982, Ed wrote the book [2], "Silane Coupling Agents" (see Figure 4) and said on page 114: "... *Surfaces that showed little or no apparent response to Silane Coupling Agents include calcium carbonate, graphite and boron.*" Note:

organic substrates such as cellulose, Kevlar[®], azodicarbonamide blowing agents, nitramine explosives, nitrides, sulfates, sulfur, polymers, etc. are not listed.

The 1985 340-page Reference Manual by the author [3] starts by claiming, “Coupling agents are molecular bridges at the interface between two substrates, usually but not limited to an inorganic filler and an organic polymer matrix. Titanium derived coupling agents are unique in that their reaction with the free protons at the inorganic interface results in the formation of organic monomolecular layers on the inorganic surface. The absence of polymolecular layers at the interface together with the chemical structure of the titanates create novel substrate surface energy modification and polymer phase interactions often resulting in viscosity reductions in unfilled, as well as filled polymer composites. Typically, titanate-treated inorganics are hydrophobic (see Figure 1), organophilic and organofunctional. When incorporated into polymer systems they often promote adhesion; catalyze (see Figure 2); improve dispersion and rheology; improve strength; do not create embrittlement (see Figure 3); improve mechanical properties; make inorganic loadings above 50% desirable (see Figure 4); prevent phase separation; inhibit corrosion (see Figure 5); etc. Reactivity is possible with diverse substrates such as CaCO₃, BaSO₄, carbon black, azodicarbonamide, nitrates, hydrates, cellulose, phthalo and lake pigments, peroxides, aramid and carbon fibers, organics and polymers, as well as classical mineral and metal oxide-derived inorganics. See Figure 5.

Figure 6 shows in situ Function 1 Titanate Coupling and Function 2 Titanium Catalysis allow 70% 3-micron filled PP homopolymer to bend 180° without stress cracking. In the first decade – up until the mid-1980’s – the high filler loading was thought to be because of the Function 1 dispersion effect – until field tests and plant trials showed flow effects and faster injection mold cycles at lower temperatures in unfilled thermoplastic parts. Eureka! Polymer flow was also caused by Function 2 Catalysis.

Figure 7 shows the Function 1 dispersion effect of 0.35% titanate on non-Silane reactive 80% BaSO₄ filled non-polar Mineral Oil.

Space limits providing a reference for every reactable interface claim made above, so Figure 8 is taken from my 31st patent EP 2 614 040 B1 granted in the EU April 12, 2017 in which a titanate was added to water and dispersed followed by spent drilling mud (BaSO₄ saturated with hydrocarbon oil), and then Portland cement admixed to make a useful composition.

ASTM C150-Type I Portland cement consists of the following interfaces – some of which are non-silane reactive:

| Portland Cement | |
|---|------------------|
| <u>Oxide</u> | <u>% content</u> |
| CaO | 60.0–67.0 |
| SiO ₂ | 17.0–25.0 |
| Al ₂ O ₃ | 3.0–8.0 |
| Fe ₂ O ₃ | 0.5–6.0 |
| MgO | 0.1–4.0 |
| Alkalies (K ₂ O, Na ₂ O) | 0.4–1.3 |
| SO ₃ | 1.3–3.0 |

Figure 9 shows an emulsified titanate in water disperses added conductive carbon black (Cabot XC-72R) completely absent mechanical stirring. It also shows conductive carbon is well dispersed into non-polar 20 M.I. LLDPE on a 2-roll mill increasing volume conductivity ($\Omega\cdot\text{cm}$) twofold.

Figure 10 shows titanate modified ordinary Portland cement (ASTM C150 Type I) composition containing oil soaked sea water sand is made into a useful composition. Figure 11 is a lab photo of titanate treated Portland cement (ASTM C150 Type I) mortar mix (ASTM C778) preparation in order to conduct ASTM C305 cube compression tests wherein the cement to H_2O ratio is reduced by 31% to equivalent slump (flow) using a dynamic tap table.

The effects of the nano-titanium organo-functionality in ASTM lab tests and by analogy extrapolated from past materials experience and inventive skills results in – or will result in: Greater compression strength; Efflorescence elimination; Faster mix cycles; Polymer compatibilization with epoxy, hydrocarbons such as oil, asphalt and plastics – 3-D Printing; Improved adhesion to PE reinforcing fibers and fabric; Adhesion to graphite, aramid, and nano-reinforcements such as clays, graphene; rCB; etc.; Allow the incorporation of spent sulfur from refineries; Prevention of rebar corrosion; Less static build due to friction while flowing down metal chutes; More uniform cell structure in cement foam; More flexible structures for improved earthquake resistance; The creation of ageless and beautiful concrete structures and composites. Note: We are seeking a modern cement producer to license the technology since nano-titanate application requires precise cement plant applications art not practical in the field.

The Fiberglass Interface – Si vs. Zr

Practical commercial use of “coupling agents” began in 1953 using silane-sized fiberglass reinforced unsaturated polyester parts for the Corvette automobile. Let’s revisit fiberglass where silanes are proven performers and discuss Function 1 coupling at the glass interface.

See Figure 12 – The One-Step Coupling proton coordination of a neoalkoxy titanate vs. the Four-Step Hydrolysis of a trisalkoxy silane leaving water of condensation deposited on the silane coupled interface. Water at the interface is the Achilles Heel of aged compositions.

See Figure 13 – Plueddemann states [2] on page 114: *“From the above observations it must be concluded that water cannot be excluded from the interface between resin and a hydrophobic mineral reinforcement and the effect of water will vary with the nature of the mineral surface. Silane coupling agents do not exclude water from the interface, but somehow function to retain adhesion in the presence of water.”*

According to G.R. Kritchevsky [4], the islands of water shown on the surface of silica (glass fiber) are the points at which delamination, adhesive failure, and corrosion begin. Kritchevsky concluded: *“...boiled polystyrene samples show evidence of the diffusion of water through the resin. Islands are evident on fiber fracture surfaces in all polystyrene samples except for the titanate.”*

Zhi-Wen Wang et al. provide an instructive discussion of organic modification of nano-SiO₂ particles with pyrophosphato titanate [5]: *“Org. modification of nano-SiO₂ particles was performed with supercrit. CO₂ as solvent and a titanate coupling reagent KR 38S as the modification reagent. The surface of the nano-SiO₂ particles was changed after modification by the titanate coupling reagent from hydrophilic to hydrophobic. IR and thermo-gravimetric analyses indicate that the interaction between the titanate coupling reagent and the particle*

surface is mainly through chemical bonding. The influence of the apparent concentration of the titanate coupling reagent on the modification at 60° and 20.0 MPa was studied, in which the apparent concentration is the weight percent of the titanate coupling reagent added in the supercrit. solvent. The quantity of the titanate coupling reagent reacted on the particle surface reaches a maximum of $19.81 \times 10^{-7} \text{ mol/m}^2$, i.e. 1.19 mol titanate coupling reagent/nm², when the apparent concentration of titanate coupling reagent is 0.6% (weight).”

See Figure 14 – Monte states: “You do not want water boiling at the Nano-interface between fiber & polymer in a composite. In contradistinction to silanes, titanates and zirconates work better in the absence of water on the interface. Nano-Hydrophobicity is critical to anti-aging.”

R. Kraus et. al. stated [6]: “The ETFE matrix was a copolymer of ethylene (38.5%) and tetrafluoroethylene (61.5%) with a low fraction (0.4%) of perfluoropropylvinylether (PPVE) produced by Hoechst.

The fibres were glass fibres (E glass) with an average diameter of 10 μm and an average length of $L = 60 \mu\text{m}$. One fraction of the fibres was treated with the coupling agent NZ 44 (neopentyl(diallyl)oxytri(N-ethylenediamino) ethylzirconate) to improve the fibre-matrix interface. The specimens were prepared by melting the mixture of matrix and a weight fraction of 10% of fibres under pressure ($p = 25 \text{ bar}$) at a temperature of 295 °C, followed by cooling to RT (cooling rate $\sim 3 \text{ K min}^{-1}$).

The influence of the coupling agent on the fibre-matrix interface was studied by breaking composites at low temperature ($T = -190 \text{ }^\circ\text{C}$, liquid nitrogen) and analysing the fracture surface by scanning electron microscopy. Electron micrographs (Figs 1 and 2) show that in the composite made of fibres without coupling agent, the matrix is removed from the fibres. In the composite made of the fibres treated with coupling agent NZ 44 most of the fibres are covered with polymer matrix. This indicates that the fibre-matrix interface is improved by the coupling agent.

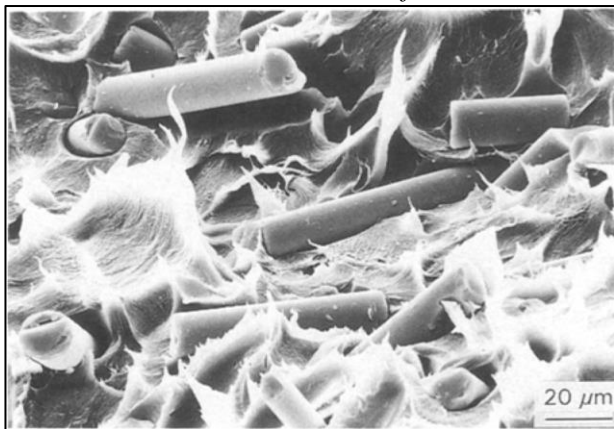


Figure 1. ETFE with fibres (E-Glass) not treated with coupling agent.

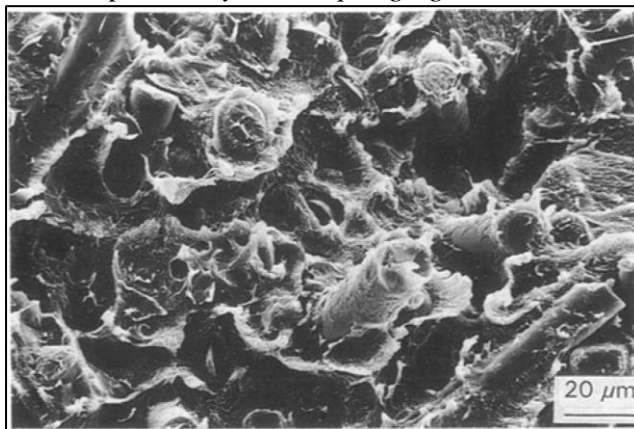


Figure 2. ETFE with fibres treated with NZ 44

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. See Figure 15 – Function 1 Adhesion, Function 2 Catalysis & Function 3 Anti-corrosion are demonstrated: 1-inch to ¼ 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® resulting in improved anti-corrosion performance at the scribe (right panel).

See Figure 16 – PP and PE are Addition polymers synthesized using Ti-Al (ZN) or titanocene / zirconocene (Kaminisky) catalysts. But they are incompatible with each other. PET is a Condensation polymer that can be synthesized with a coordinate titanate [8] PET is incompatible with Addition polymers. A Brabender mix of the three polymers in the presence of a Ti-Al catalyst causes a tri-polymerized composite [9]. The Ti-Al catalyst technology is one of the winners of the PIA 2020 Refocus Sustainability Innovation Award in Materials based on its innovation, environmental benefit, and market impact. See link:

<http://www.refocussummit.org/2020-award-submissions>

See Figure 17 – 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. 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 14x greater impact. See Figure 18 – Conventional cobalt cure disc fractures while the titanate cured disc broke only after a 2nd drop from a 6' height.

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, see Figure 19 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 fibres 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 electrodeposited or electropolymerized on commercial graphite fibres used for polymer reinforcement. The effect of these coatings on the thermal oxidative behaviour of the coated carbon fibres, epoxy resin, and composites prepared from them was studied by thermogravimetric analysis, and compared with that of polyimide coatings. Generally, the coated fibres showed higher decomposition temperature than the untreated carbon fibres. 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 fibres 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 catalyse the decomposition of carbon fibres is inferred from this. Polyimide precursor coatings lowered the oxidation temperature of the carbon fibres, both as neat coatings and in the*

presence of epoxy matrix resin, thus reducing the temperature of survival of the fibres under combustion conditions. The results confirm the potential of this novel approach of forming precursor coatings on carbon fibres to minimize the release of conductive fibre fragments from carbon fibre-reinforced polymer composites exposed to fire.”

See Figure. 20 – 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% 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 DOD Secrecy Orders for 14-years. [12]. Similarly, U.S. 5,753,853 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% salt water boil. The data reproduced in Table 1 shows the amino silane retains 65% of its original properties while the amino zirconate retains 93% of its original properties and is 2.1x better than the amino and epoxide silanes on aged Tensile Long Fiber Pullout Energy, J.

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 hetero-atom 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 1-second is a nanometer*” – see Figure 21.

This thumbnail visualization should register in your mind that you can’t see readily the growth or movement of 1-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 invention 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 Cambridge Scientific Instrument Company 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, a 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 SEM's. 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".

See Figure. 23 – An aromatic amino zirconate improves the flow and properties of 40% FG/PPS. China has filed 80% of the ACS CAS ABSTRACTED patents in carbon reinforced composites: Graphene-109; Graphite-177; CNTs-105 based on my teachings since 1974.

See Figure 24 – Graphite, Graphene and CNTs are the present and a good part of the nano-future of advanced thermoplastic and thermoset composites. The Ti/Zr effects on 40% FG/PPS translates to CNT/PPS increasing conductivity 10-fold using an titanate (KR TTS) Monte invented in 1973. The ACS CAS ABSTRACT in Figure 24 is from CAS IP SEARCH for: "*Ti/Zr Coupling Agents – July 25, 2013-Sept. 20, 2015*" reads:

L5 ANSWER 347 OF 439 CA COPYRIGHT 2016 ACS on STN
AN 160:415134 CA [Full-text](#)
TI Development of carbon nanotube and graphite filled polyphenylene sulfide based bipolar plates for all-vanadium redox flow batteries
AU Caglar, Burak; Fischer, Peter; Kauranen, Pertti; Karttunen, Mikko; Elsner, Peter
CS Applied Electrochemistry Department, Fraunhofer Institute for Chemical Technology (ICT), Pfingsttal, 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
AB 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% total conductive filler concentration, by addition of 2.5 weight% carbon nanotubes and 3 weight% 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, resp., 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 pos. affected. Flexural strength is improved 15% by addition of 1.25 weight% carbon nanotubes. Differential scanning calorimetry anal. shows nucleating effect of conductive fillers on polyphenylene sulfide matrix. Corrosion measurements, cyclic voltammetry and galvanostatic charge-discharge tests are performed to examine the electrochem. 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 (Uses)

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

As I complete this paper on May 11, 2020 during the beginning of Phase I of the COVID 19 pandemic, I included Figure 22 showing the 70-90 nanometer size of the COVID 19 virus – the so-called “invisible enemy” – to get a sense of the size of nano-titanates as being 1/5th the size of the 8-NM protein on the face of a COVID-19 virus.

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 H₂O 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,

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TABLE 1 – EVALUATION OF VARIOUS COUPLING AGENTS IN GLASS FIBER REINFORCED EPOXY COMPOSITES (ORIGINAL/AGED PROPERTIES)

| <u>Formulation</u> | <u>Parts by Weight</u> |
|---|------------------------|
| 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 | | | |
|-----------------|------------|--|--|---|---|
| | | 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 |

FIGURES

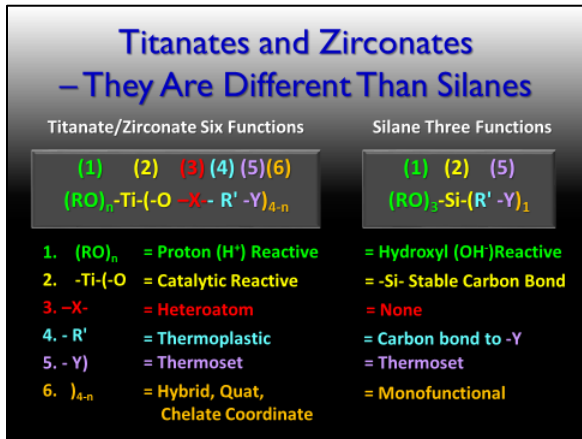


Fig. 1 – A comparison of the titanates-zirconates with silanes according to their Functionalities.

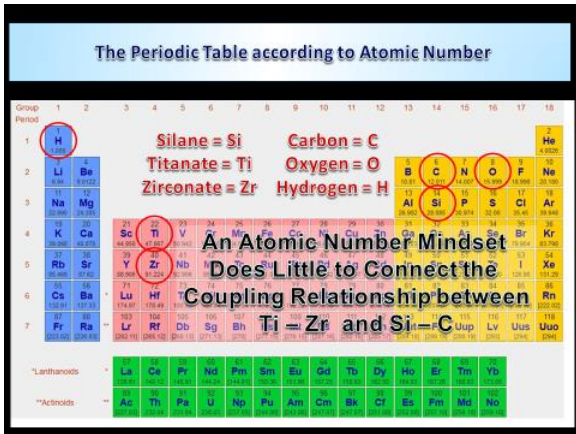


Fig. 2 – A comparison of the titanates-zirconates with silanes according to their Atomic Number.

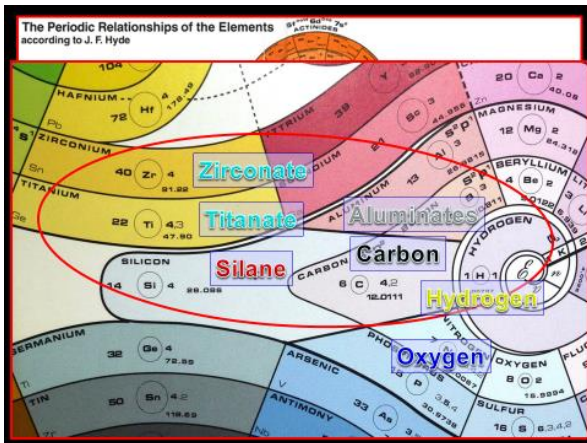


Fig. 3 – A comparison by their Valence.

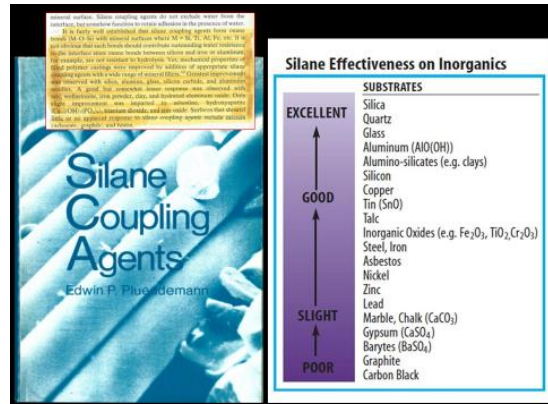


Fig. 4 – A comparison of the effectiveness of silanes according to inorganic substrate.

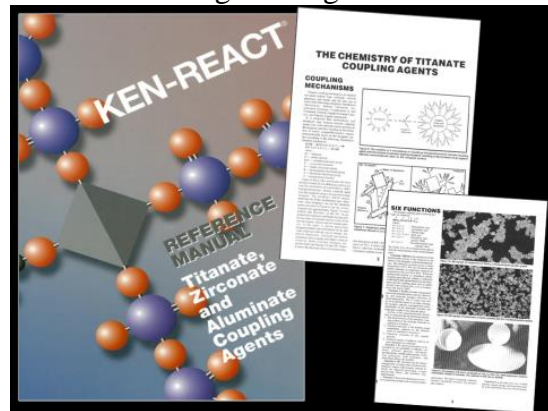


Fig.5 – 340-pg. Reference Manual coupling & deagglomeration effect on CaCO₃ & TiO₂.

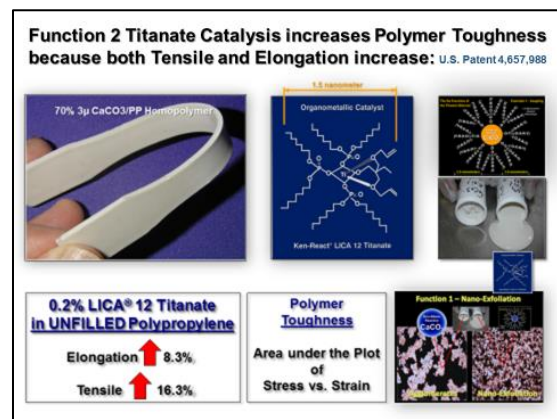


Fig. 6 – In situ Titanate Coupling & Titanium Catalysis allow 70% 3-micron filled PP to bend 180° without stress cracking.



Fig. 7 – Effect of 0.35% titanate on non-Silane reactive 80% BaSO₄ filled non-polar Mineral Oil.

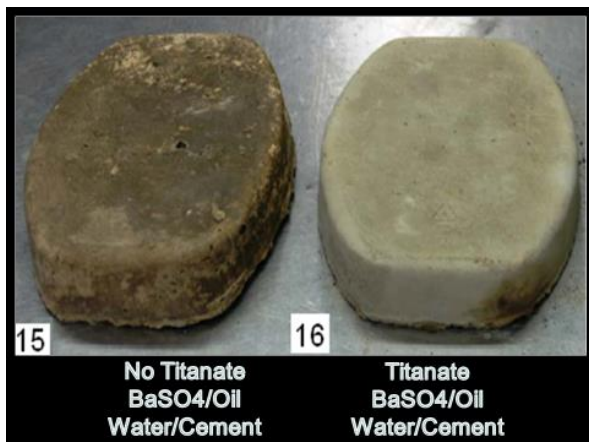


Fig. 8 – The use of titanate in situ to compatibilize oil, water, BaSO₄, and Type I Portland cement.

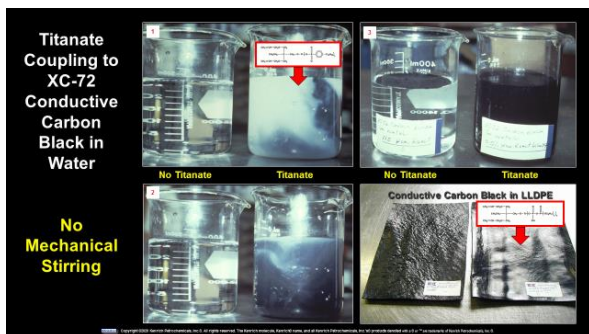


Fig. 9 – Emulsified titanate in water disperses conductive Carbon completely absent mechanical stirring. Conductive carbon is well dispersed into non-polar LLDPE on 2-roll mill increasing volume conductivity ($\Omega\cdot\text{cm}$) by a factor of two.



Fig. 10 Titanate modified ordinary Portland cement composition containing oil soaked sea water sand is made compatible in H₂O.



Fig. 11 – Titanate treated Portland cement (ASTM C150 Type I) reduces the cement H₂O ratio by 31% to equivalent slump.

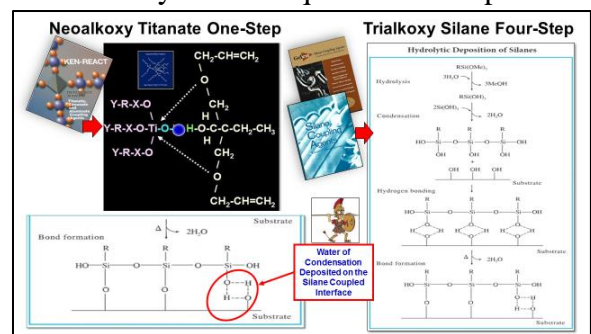


Fig. 12 – The One-Step Coupling proton coordination of a neoalkoxy titanate vs. the Four-Step Hydrolysis of a trisalkoxy silane leaving water of condensation deposited on the silane coupled interface – the Achilles Heel of aged compositions.

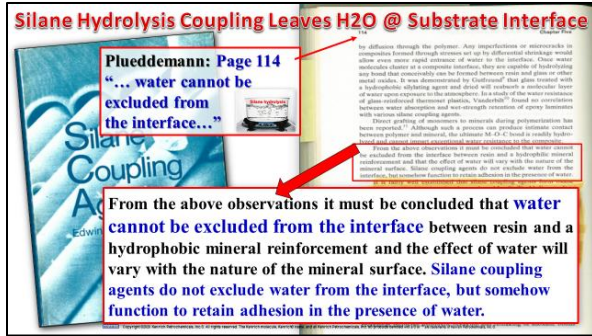


Fig. 13 – Plueddemann: “...Silane coupling agents do not exclude water from the interface, but somehow function to retain adhesion in the presence of water.”

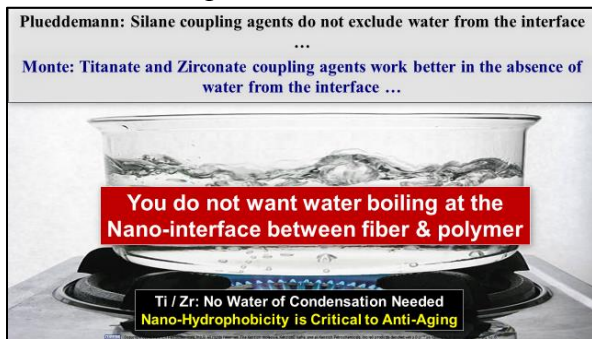


Fig. 14 – Monte: “You do not want water boiling at the Nano-interface between fiber & polymer in a composite. Nanohydrophobicity is critical to anti-aging. TI / Zr chemistry obviates the need for Hydrolysis.

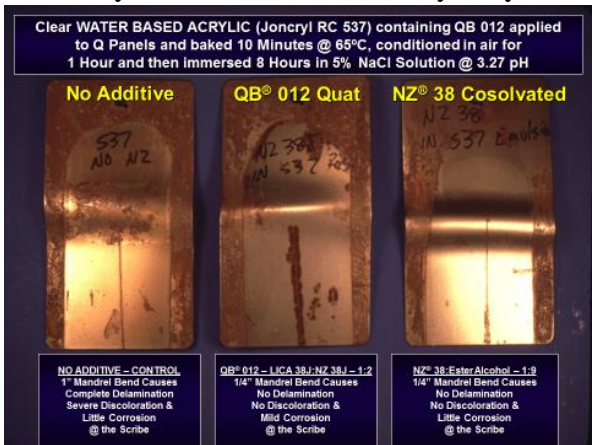


Fig. 15 – Function 1 Adhesion, Function 2 Catalysis & Function 3 Anti-corrosion demonstrated for an unfilled WB Acrylic coating using a co-solvated Neoalkoxy pyrophosphato zirconate .

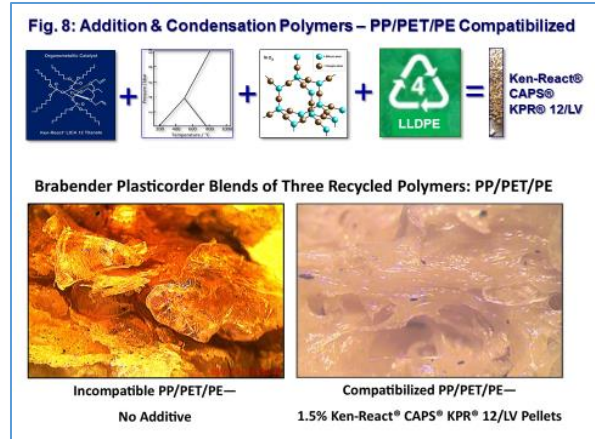


Fig. 16 – PP and PE are Addition polymers, but are incompatible with each other. PET is a Condensation polymer that is incompatible with Addition polymers. A Babender mix of the three polymers in the presence of titanate causes a tri-polymerized composite.



Fig. 17 – The use of a titanate absent cobalt naphthenate slows the cure at 25°C – but eliminates the heat of exotherm and the resultant micro-bubbles. At 40°C, the heat accelerated cure is faster than cobalt.



Fig. 18 – Conventional cobalt cure disc fractures while the titanate cured disc broke only after a 2nd drop from a 6' height.

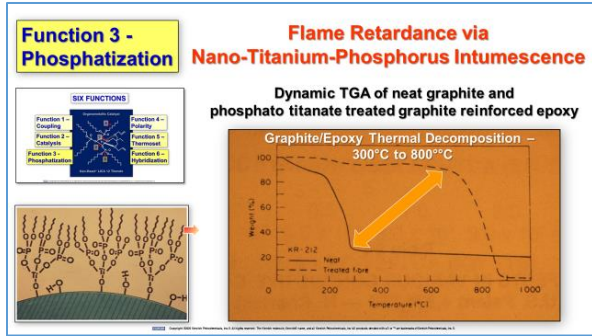


Fig. 19 – Di(dioctylphosphato)ethylene titanate (KR 212) coating increases graphite FR 300°C to 800°C

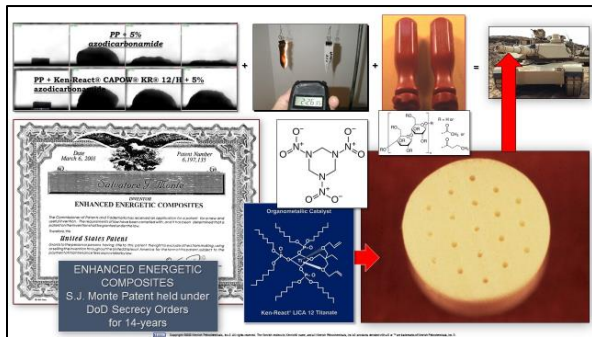


Fig. 20 – Neoalkoxy phosphato titanate prevents unplanned detonation of LOVA tank round propellant via Function 1 coupling to RDX nitramine explosive while catalyzing CAB plastic binder. Patent held under DOD Secrecy Orders for 14-years.

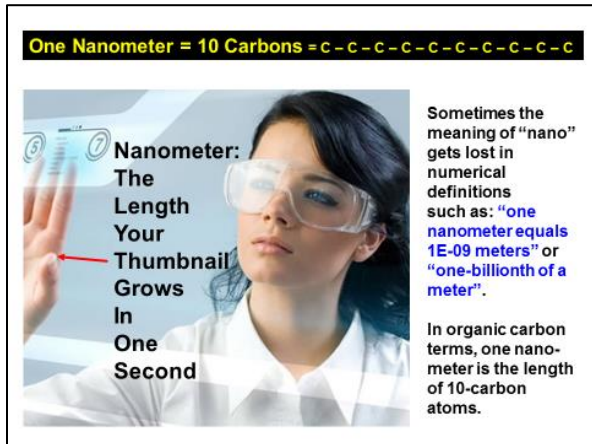


Fig. 21 – Nano is the length your fingernail grows in a second and cannot be “seen” with conventional microscopic techniques. Proper application procedures are critical to success.

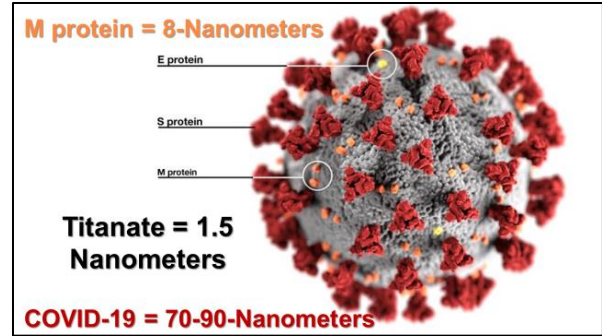


Fig. 22 – The nano-nature of titanates presents a challenge in characterizing their workings at the interface.

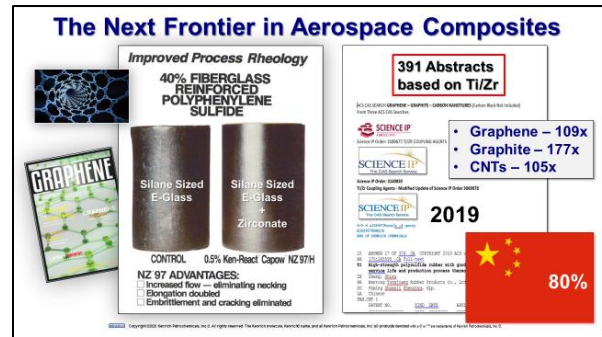


Fig. 23 An aromatic amino zirconate improves the flow and properties of 40% FG/PPS. China has filed 80% of the ACS CAS ABSTRACTED patents in carbon reinforced composites: Graphene-109; Graphite-177; CNTs-105.

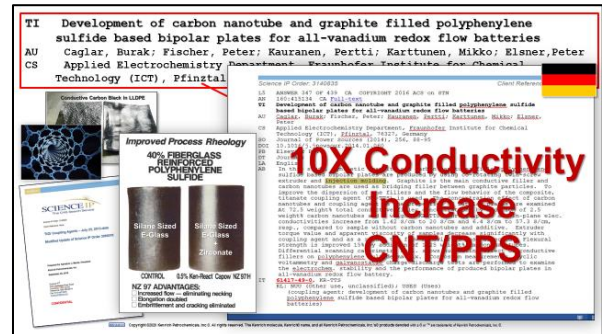


Fig. 24 – Graphite, Graphene and CNTs are the present and a good part of the future of advanced thermoplastic and thermoset composites. The Ti/Zr effect on 40% FG/PPS translates to CNT/PPS increasing conductivity 10-fold with an isostearoyl titanate Monte invented in 1973.