

A New 1.5-Nanometer Titanium Treated Portland Cement

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Abstract

Patented modification of the surface of ordinary Portland cement with a 1.5-nanometer proprietary titanate coupling agent trade named Ken-React® KCM-3E produces a transformational Portland cement trade named Ken-Tec Portland cement allowing a 31% reduction in the water to cement ratio to equivalent flow (slump) while using significantly less time and energy to mix and providing new and novel material performance advantages important to sustainability and the infrastructure – such as: Greater compression strength; Efflorescence elimination; Faster mix cycles; Polymer compatibilization with epoxy, hydrocarbons such as oil, asphalt and plastics; 3-D Printing; Improved nano-adhesion to PE reinforcing fibers and fabric; Adhesion to graphite, aramid, and nano-reinforcements such as bauxite, 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; etc.

My Mission Statement for the last 46-years is *“...To teach the more efficient use of raw materials through the use of titanates and zirconates.”* The PowerPoint presentation will be an up-to-date review taken from: over 450-ACS CAS abstracted “Works by S.J. Monte”; several thousand ACS CAS abstracts of work by others applying “Ti/Zr Coupling Agents” – and their resultant commercial applications; and United States Patent 8591646 entitled, “CONSTRUCTION MATERIALS AND COMPOSITIONS FROM OIL CONTAMINATED PARTICLES” by Salvatore J. Monte.

Concrete and polymeric compositions are often filled or reinforced with inorganic & organic

fillers, pigments, fibers – some nano-sized. It will be shown that 1.5-nanometer heteroatom titanates/zirconates form functional atomic monolayers on the interface of non-silane reactive inorganics such as CaCO₃, CaSO₄, ZnO, TiO₂, hydroxyapatite, metal powders, carbon black, CNTs, BaSO₄, Portland cement, boron nitride, etc. via proton coordination – absent the need for hydrolysis of surface hydroxyls as with silanes. Smart sensor materials such as piezoelectric ceramics, graphene and PVDF can be dispersed to complete deagglomeration and compatibilization.

The author solved the challenges of the U.S. DoD Insensitive Munitions Program. Specifically, unplanned detonation of LOVA propellant for the Abrams A-1A tank rounds caused tragic explosions. A 1.5-nanometer atomic monolayer of a phosphorus heteroatom titanate on the RDX explosive allowed highly loaded CAB plastic-bonded propellant to be produced that was both safer and more powerful than the prior art. The author’s United States Patent 6197135 entitled “ENHANCED ENERGETIC COMPOSITES” was held under DoD Secrecy Orders for over 14-years.

Since the application of 1.5-nanometer titanium chemistry must be applied uniformly in atomic monolayers on to the surface of the Portland cement, a modern cement plant is needed. And the corporation owning the plant must be willing to license the Kenrich technology and have a cement, mortar and concrete lab capability to take existing ASTM test procedures and modify them to conform to the new and novel nano-technology requiring significant change in construction industry concrete practices and culture. Due to the proprietary nature of the process and chemistry, a formal NDA and license agreement needs to be negotiated as the first step.

Discussion

1.5-Nanometer Heteroatom Titanates and Zirconates form *in situ* monomolecular layers on the surface of any organic/inorganic via proton coordination as explained in their Six Functions and the References to four of the author's 450 ACS CAS Abstracted "Works" [1-4] – and Internet Web Links [1-5] spanning 46-years of our titanate R&D.

Since the 1950's, silane coupling agent technology has dominated surface modification technology [5]. Ti or Zr coupling agents can be differentiated from silanes by Six Functions:

<u>Titanate</u>		<u>Silane</u>	
(1)	(2) (3)(4)(5)(6)	(1)	(5)
$(\text{RO-})_n\text{-Ti-}(\text{-O X R' Y})_{4-n}$		$(\text{RO-})_3\text{-Si-}(\text{-R' Y})$	

Where,

(1) Coupling Function (RO)_n = hydrolyzable group or substrate reactive group with surface hydroxyl or protons. Function (1) concerns itself with filler/fiber substrate reaction mechanisms, while functions (2) to (6) are polymer/curative reactive. Organosilanes have long been used to enhance the chemical bonding of a variety of thermoset resins with siliceous surfaces. However, organosilanes are essentially non-functional as bonding agents when employing CaCO₃, CaO, Al₂O₃, Fe₂O₃, MgO, K₂O, Na₂O, SO₃, carbon black, boron nitride, graphite, aramid or other organic derived fibers.

SiO₂ coupling is better. R. Kraus et al. state (see Fig. 1): "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-silane sized) with an average diameter of 10 μm and an average length of L = 60 μm. One fraction of the fibres was treated with the coupling agent NZ 44 (neopentyl (diallyl)oxy tri(N-ethylenediamino)ethyl zirconate) to improve the fibre-matrix interface.

"Coupling" (Function 1) electro-chemically deagglomerates and exfoliates the filler interface and creates a shift in the Critical Pigment Concentration Point of filled polymer and concrete

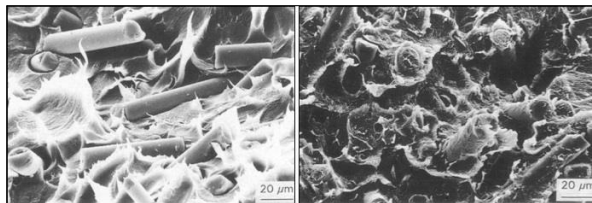


Figure 1: ETFE with silane treated E-Glass fibers (right) and with Ken-React® NZ® 44 zirconate (left).

composites, resulting in reduced resin or water demand to equivalent viscosity and increased inter-particulate contact transfer of forces.

The coupling of the titanate to the inorganic/organic substrate in 1.5-nanometer atomic monolayers allows for elimination of air voids, hydrophobicity, and a complete continuous phase for stress/strain transfer and resistance to long-term aging and efflorescence.

(2) Catalysis Function (Ti, Zr) = tetravalent titanium, zirconium or non-catalytic silicon (Si). The Ti-O (Zr-O) bond is capable of catalysis: disassociation, transesterification, transalkylation – see patented "Repolymerization" [2], while the Si-C bond is more stable and thus unreactive. The combination of (1) Coupling and (2) Catalysis provides a technical means to achieve the sustainability goals of recycling mixtures of cement, fillers and polymers (see Figure 2).

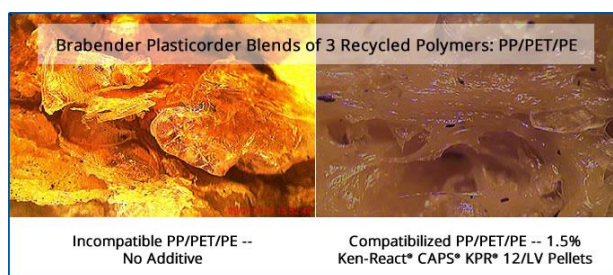


Figure 2: Incompatible materials obtained from post-industrial waste streams: LLDPE (fractional melt film), PP Copolymer (mixed 20-35 MFI inj. molded caps), and PET (thermoformed clamshell food packaging) made compatible.

(3) Hetero Atom Function (X) = Binder functional groups such as phosphato, pyrophosphato, sulfonyl, carboxyl, etc. impart intumescence, burn

rate control, anticorrosion, quaternization sites, electron transfer and pH control, etc. The nano-pyrophosphato titanium: acts as a sole flame retardant at levels of 2 to 7 wt. % of polymer or a synergist on non-FR fillers; increases the foamability of AZO in PP; reduces the IM cycle time of a CAB Screwdriver handle by 21%. RDX Nitramine/CAB LOVA Propellant for the Abrams A1A 120mm Tank Round uses a phosphato titanate to prevent unplanned detonation while allowing 85% RDX loading to be extruded through a 19-perf die with no pin drift – see Figure 3.

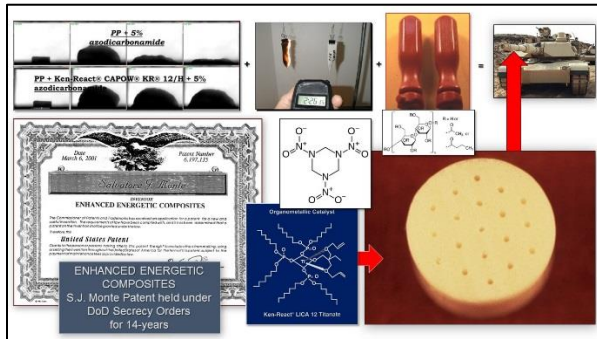


Figure 3: (1) More efficient N₂ gassing; (2) Catalytic CAB plastic flow; (3) Nano-Ti-O-Phosphatizing = self-detonation resistant LOVA Gun Propellant.

(4) Thermoplastic Function (R') = thermoplastic functional groups such as: aliphatic and non-polar octyl, isostearoyl groups; naphthenic dodecylbenzyl groups; or aromatic benzyl, cumyl phenyl groups optimize bonding based on polarity. **(5) Thermoset Function (Y)** = thermoset functional groups such as acryl, methacryl, mercapto, amino, etc. increase x-link network density.

(6) 4-n = mono, di or tri-organofunctional hybrid titanates are possible, such as containing 1-mole of an aliphatic isostearoyl ligand (function 4) and 2-moles of acryl ligands (function 5).

The discussed Six Functions effects at the nano-interface of dissimilar materials provide almost unlimited avenues for more efficient use of raw materials – sustainability and innovation. Figure 4 shows how Functions 1, 2 & 3 of a pyrophosphato zirconate (NZ[®] 38) allow a waterbased clear acrylic coating to (1) promote adhesion to metal (automotive tin plate); (2) increase mandrel bend

flexibility-1-inch to ¼-inch; (3) prevent corrosion at the scribe – and compatibilize oil-sea water soaked sand (oil spill such as Deepwater Horizon) with water & ordinary Portland cement [6].

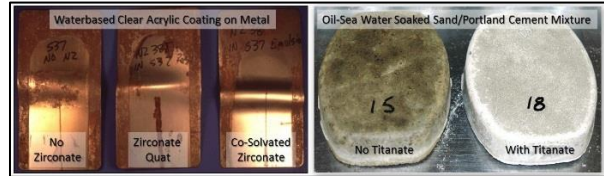


Figure 4: The Six Functions of 1.5-nanometer heteroatom titanates and zirconate enables infrastructure sustainability and innovation by compatibilizing the interface of dissimilar materials such as waterbased polymers and ordinary Portland cement.

Space limits providing a reference, data or figure for each claim herein, so I used the Six Functions as a theoretical basis for the effects next shown in Figures 5-7 supported by Reference [5].

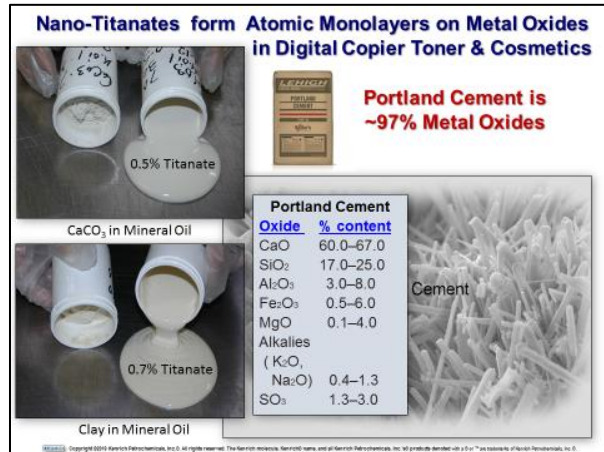


Figure 5: Titanates Function 1 Couple to all the mineral surfaces in ordinary Portland cement.



Figure 6: (Left) non-silane reactive BaSO₄ dispersed in mineral oil without & with 0.35% titanate. Function 1 Coupling achieved in situ absent silane hydrolysis. (Right) Oil-soaked spent drilling mud (BaSO₄) compatibilized in a water-Portland cement mixture using subject titanates.

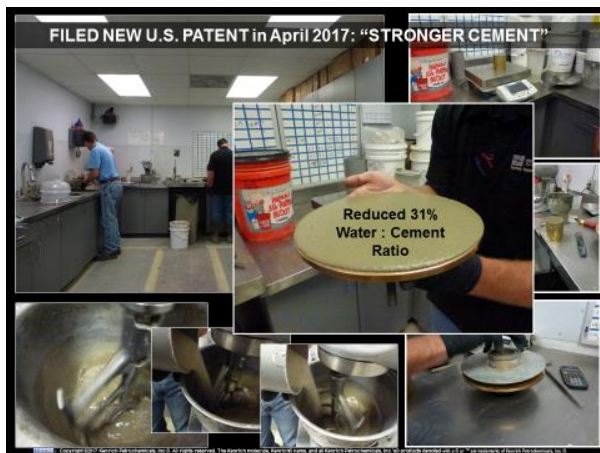


Figure 7: A New 1.5-Nanometer Titanium Treated Portland cement (ASTM C150 – Type I) reduces the cement water ratio by 31% to equivalent slump (flow). Tests conducted at TEC Services Laboratory.

Conclusion

The author's family were cement masons and bricklayers. As a result, I attended Manhattan College - studied Structures-Civil Engineering and went to work for Turner Construction Co. My wife's family had a chemical business and made me a VP (it pays to marry the bosses' daughter) – so, I went back to Brooklyn Poly and got a M.S. in Polymeric Materials. The degree was useful as Kenrich served the rubber, wire & cable, plastic, adhesives and coatings industries.

At the atomic level, the demands for complete deagglomeration and compatibilization of all the compound formulation ingredients are the same whether the composition is cosmetic, dental, polymeric, energetic or concrete.

Leading edge is bleeding edge and we seek market savvy partners to accelerate commercialization of this new & novel technology.

References

[1] Monte, S.J., Kenrich Petrochemicals, Inc., "KenReact Reference Manual - Titanate, Zirconate and Aluminate Coupling Agents", 3rd Rev. Edition, March 1995, 340 pgs.

[2] Monte, S.J., Sugerman, G., Kenrich Petrochemicals, Inc., "Repolymerization", U.S. Patent 4,657,988, April 14, 1987.

[3] Monte, S.J. & Sugerman, G., Kenrich Petrochem., Inc.: S.M. Gabayson & W.E. Chitwood, General Dynamics, "Enhanced Bonding of Fiber Reinforcements to Thermoset Resins", 33rd Int'l SAMPE Symposium, Anaheim, CA, March 7-10, 1988.

[4] Monte, S. – Chapter 5 – Titanates – "Functional Fillers for Plastics", edited by Xanthos, M., Wiley-VCH Verlag GmbH & Co. KGaA, 2005, ISBN 3-527-31054-1.

[5] Plueddemann, Edwin P., "Silane Coupling Agents", Pg. 114, 1982 Plenum Press.

[6] Monte, S.J., "Construction Materials and Compositions from Oil-Containing Filler", EP 2614040 B1 dated 12.04.2017.

Links

[1] <https://4kenrich.com/wp-content/uploads/2018/09/Review-of-titanate-coupling-agents-and-their-application-for-dental-composite-fabrication-Dental-Materials-Journal-2017-365-539-552.pdf>.

[2] <https://4kenrich.com/wpcontent/uploads/2017/10/pci1017p48-Kenrich-FT-PCI-Oct2017-Issue-PCI-Approved-for-Publication.pdf>.

[3] http://digital.ipcprintservices.com/publication/?m=9911&l=1#{%22issue_id%22:476701,%22page%22:34}.

[4] <https://4kenrich.com/wp-content/uploads/2018/02/KenReact-KPR-Global-Plastics-Summit-2015-Chicago-MultiSlidesTitanate-Catalyst-for-PC.pdf>.

[5] <https://4kenrich.com/wpcontent/uploads/2018/12/PROCESSING-AND-MOLDINGPOLYMERS-WITH-1.5-NANOMETER-TITANATESZIRCONATES-IN-PELLET-FORM-NOV-2018-w.-Cover.pdf>