

THE USE OF TITANATES AND ZIRCONATES IN FLAME RETARDED COMPOSITIONS

Salvatore J. Monte
Kenrich Petrochemicals, Inc.
Bayonne, NJ 07002 USA
sjmonte@4kenrich.com www.4kenrich.com

ABSTRACT

Phosphato and pyrophosphato functional titanates and zirconates work alone or as 2-nanometer atomic interfacial coupling agents between two dissimilar species – including ATH, Mg(OH)₂, Sb₂O₃, halogenated species, phosphates, nano materials of all types, polymers, and organic fibers and particulates such as graphite, blowing agents and nitramine explosives – to form intumescent monolayers. For example, it will be shown that 44% CaCO₃ (pretreated with 3% of a neoalkoxy pyrophosphato titanate) filled LLDPE will exhibit FR intumescence on vertical burn and extinguish approximately half way through the burn while the control without titanate burns to completion. It will therefore be the focus of the paper and PowerPoint presentation to establish new thinking in FR polymer additives art based on the organometallic heteroatom molecule's Six Functions: Function 1-*Coupling*; Function 2-*Catalysis*; Function 3-*Intumescence*; Function 4-*Polarity/Compatibility*; Function 5-*UV and Free Radical Reactivity*; and Function 6-*Hybrid Multifunctionality*. Data will show use in diverse applications such as injection molded FR appliance parts and as burn rate and burn rate exponent control agents for propellants for tank rounds and solid rocket fuel for smart bombs. Non-toxic thermoplastic FR compounds will be shown to be possible with: high flexibility having high levels of filler with good processability and impact strength; lower levels of plasticizer that are not extractable; low temperature flexibility with little or no plasticizer; higher production rates at lower temperatures using less energy; synergistic FR effects; and improved mechanical properties of extruded, molded and foamed parts. There are over 355 ACS CAS abstracted "Works by S.J. Monte" (search key words) in the literature and several will be referenced.

INTRODUCTION

The successful application of titanates in flame retarded compositions depends upon understanding organometallic chemistry and physics – and why it is different from silanes and other additives such as lubricants, lecithin, surfactants, metal stearates, impact modifiers, plasticizers, etc. Old mindsets based on prior art silane and other additive thinking can often cause misapplication of titanates and lead to missed opportunities. Titanates "work" by their Six Functions (see Figure 1) when correctly applied as is attested to by several billion dollars worth of commercial finished goods using them in everything from cosmetics and magnetic recording media to propellants for smart bombs. There are over 355 ACS CAS abstracted "Works by S.J. Monte" (key words) in the literature. Subject titanates and zirconates are referred to necessarily by their type and alpha numeric code as shown in Table 1 due to their complex CAS Chemical Names and Structures. It is the focus of the paper and PowerPoint presentation to establish new thinking in FR polymer additives art based on the organometallic heteroatom molecule's *Six Functions*: Function 1-*Coupling*; Function 2-*Catalysis/Repolymerization*; Function 3-*Intumescence*; Function 4-*Polarity/Compatibility*; Function 5-*UV and Free Radical Reactivity*; and Function 6-*Hybrid Multifunctionality*.

DISCUSSION

Ti or Zr coupling agents chemically bridge two dissimilar species at the interface, such as between an inorganic filler/nanoparticulate/fiber and an organic polymer, via proton coordination on non-silane reactive substrates such as CaCO₃ and carbon without needing water of condensation as with silanes.

A discussion of the “Six Functions” of some 60 TSCA CAS registered titanates/zirconates as invented by the author as compared to di-functional silanes is useful to explain their performance differences and may be represented as follows:

<u>Titanate</u>	<u>Silane</u>
(1) (2) (3)(4)(5)(6)	1) (5)
RO-)_n-Ti(-O X R' Y)_{4-n}	RO-)₃Si(-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, carbon black, boron nitride, graphite, aramid or other organic derived fibers. Plueddemann stated [1]: “...Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron”.

Figure 2 shows titanate deagglomeration of CaCO₃ dispersed in paraffinic oil. The coupling effect of the monolayer of titanate to disperse CaCO₃ electrochemically, rather than just mechanically, is apparent.

In its simplest terms, the titanate function (1) mechanism may be termed proton (H⁺) reactive via solvolysis (monoalkoxy) or coordination (neoalkoxy) without the need of water of condensation while the silane function (1) mechanism may be termed hydroxyl (OH⁻) reactive via a silanol-siloxane mechanism requiring water of condensation.

“Coupling” (Function 1) creates a shift in the CPVC (Critical Pigment Concentration Point) resulting in reduced resin demand and an exponential increase in functional pigment performance for conductance of: electrons, heat, cold, light and magnetic forces.

The coupling of the titanate to the inorganic/organic substrate in atomic monolayers allows for elimination of air voids, hydrophobicity, and a complete continuous phase for stress/strain transfer. The silane’s function 1 silanol-siloxane water of condensation mechanism limits its reactions to temperature environments below 100 °C thereby eliminating the possibility of in situ reaction in the thermoplastic or elastomer melt above 100 °C as is possible with subject titanates.

“Coupling” provides atomic monolayer phosphato-titanium intumescent capability to both the inorganic and organic so as to control burn rate and burn rate exponent of flame retardant compositions such as FR thermoplastics and energetics such as ammunition propellant, solid rocket fuel and pyrotechnics.

(2) Catalysis Function (Ti, Zr) = tetravalent titanium, zirconium or non-catalytic silicon (**Si**). The Ti-O (or Zr-O) bond is capable of disassociation allowing transesterification, transalkylation and other catalysis mechanisms such as “Repolymerization” while the Si-C bond is more stable and thus unreactive.

“Catalysis” (Function 2) with titanates creates new & novel “Repolymerization” and “Copolymerization” of polymers independent of thermoset crosslink mechanisms (Function 5) at dosages as little as 2 parts per thousand. The metallocene-like catalysis analogy of “titanate/titanocene” and “zirconate/zirconocene” is claimed by the author.

The “Catalysis” aspect of organometallics as coupling agents adds a new dimension of capabilities and properties to uncured thermoplastics and cured thermosets such as: increased flexibility and toughness (defined as the area under the plot of stress vs. strain); finer, more uniform cell structure because foamed polymer bubble breakage is reduced; “Repolymerization” and “Copolymerization” of the macromolecule in the melt allowing regrind to be regenerated to virgin properties and improving the properties of polymer blends; reduced recrystallization time and increased polymer flow at lower temperatures resulting in faster extrusion, blow and injection mold cycle times and better quality parts as measured by strength, impact, aging, acid and salt spray resistance, appearance, weld line elimination and clearance tolerances.

(3) Hetero Atom Function (X) = Binder functional groups such as phosphato, pyrophosphato, sulfonyl, carboxyl, etc. impart intumescence, burn rate control, anticorrosion, quaternization sites, disassociation rate/electron transfer control, etc.

(4) Thermoplastic Function (R') = thermoplastic functional groups such as: aliphatic and non-polar isopropyl, butyl, octyl, isostearoyl groups; naphthenic and mildly polar dodecylbenzyl groups; or aromatic benzyl, cumyl phenyl groups optimize bonding.

(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 a titanate containing 1-mole of an aliphatic isostearoyl ligand (function 4) and 2-moles of acryl ligands (function 5).

Flame Retardance via 2-Nanometer Atomic Phosphorus Intumescence

Titanate multifunctional coupling reduces the viscosity and increases flexibility of all manner of filled polymeric compositions. For example, Table 2 shows typically that 0.5% pyrophosphato titanate reduces the viscosity of 50% CWC (Excel) Nanocor CWC Nano Clay in mineral oil from 416,000 to 4,800 cps.

Table 3 shows 3.0% pyrophosphato titanate reduces the viscosity of 45% Cloisite Na⁺ MMT Clay in mineral oil from 416,000 to 4,800 cps.

Table 4 shows 0.7% pyrophosphato titanate reduces the viscosity of 60% Mg(OH)₂ in mineral oil from 1,120,000 to 12,800 cps, while Table 5 shows 50% ATH viscosity reduced from 500,000 to 4,800 cps.

Figure 3 shows the hydrophobicity imparted by titanate to a compressed slab of hydrophilic CaCO₃.

Figure 4 shows the exfoliation of 20-nanometer silica using 2.4% LICA 38J quat. The author suggests that the current ammonium quats used to exfoliate MMT are poor interfacial agents for most non-Nitrogen bearing polymers.

Figure 5 is a KEVEX analysis showing the Function 3 Phosphorus and Function 2 Titanium elements have been deposited via Function 1 on the surface of Cu metal by use of a pyrophosphato titanate (KR 238S).

Figure 6 shows 0.7% LICA 38 pretreatment allows 60% Mg(OH)₂ filled LLDPE.

Figure 7 shows 60% ATH (Polyfill 402)/40% Mineral Oil – (left) No Titanate – 800,000 cps, (right) 0.7% LICA 38 Titanate added *in situ* – 9,600 cps. Table 6 shows the relative improvements in 50% ATH filled PP w. titanate.

Figure 8 – 70% 3 μ CaCO₃ filled Polypropylene homopolymer, wherein 0.5% KR TTS titanate treatment by weight of CaCO₃ allows 180° bend of tensile bar with no white stress cracking.

Figure 9 shows that 3% LICA 38 pretreatment of CaCO₃ produces a 44% CaCO₃ filled FR polyolefin.

The author has demonstrated in: Ammunition and Explosives – the ability to control the flame spread of nitramine explosive (85% RDX/15% CAB) in spalls of burning LOVA ammunition propellant with LICA 12 [2]. The patent [2] was filed February 18, 1986 and held under Pentagon Secrecy Orders for National Security until released and issued to Monte 15-years later on March 6, 2001; reduce the burn rate and burn rate exponent of AP/Al/HTPB PU solid rocket fuel with LICA 38 [3]. The patent [3] was filed Feb. 20, 1986 and held under Pentagon Secrecy Order until May 19, 1998; and render CaCO₃ filled LLDPE flame retardant with LICA 38 [4].

Flame retardant 3-micron CaCO₃ was prepared by Henschel pretreatment with 3% LICA 38 using a low speed setting (1800 rpm's). LICA 38 was added dropwise to the center of the CaCO₃ vortex over a 1-minute period followed by a 50-second postmix. The thus treated filler and untreated filler were then incorporated at 44% by weight into a 20-melt LLDPE on a 2-roll mill, sheeted off, pressed, and cut into uniform strips. Alternately, the pyrophosphato titanate could have been incorporated into the polymer followed by addition of untreated CaCO₃ using reactive compounding techniques. As can be seen, after 2-min.:8-secs., the pyrophosphato titanate treated CaCO₃ filled LLDPE extinguished itself leaving about one-third of the composition unburned while the control continued to burn to completion. It is possible that the titanate alone as a 2-nano pyrophosphato titanium moiety could create the same FR effect thus eliminating completely the negative effect caused by any solid particulate added to a polymeric composition.

It is therefore obvious to me, and should be to those skilled in the art, that synergism can be obtained by use of phosphato and pyrophosphato organometallics in all manner of flame retardant compositions. Some work by other investigators is offered next to provide corroboration of the teachings.

ATH and Mg(OH)₂ Non-Toxic Flame Retarded Thermoplastics – Phosphato and pyrophosphato functionality provides intumescent synergism and high loadings of non-toxic ATH [5] and Mg(OH)₂ [6]. Typically, greater than 60% ATH loading by weight is needed in PP to obtain a UL94 V₀ rating. For example, Robert Andy stated [ref. 5 – page Add-9] in U.S. 4,525,494 concerning the use of a phosphato titanate (KR 12) treated ATH: *“The present invention provides a polypropylene composition containing (64%) hydrated alumina which has high izod impact strength, increased flow, increased elongation, increased deflection and increased Gardner impact values compared with the original polypropylene, without loss of tensile strength. The practice of this invention will give flame retardance to any polypropylene system while enhancing the strength of the product. For example, the practice of this invention has produced polypropylene products that have impact strengths which are increased four times and flow rates increased seven times over the starting material without loss of tensile or any other critical property”*.

Eichler et. al. of Alusuisse Martinswerk GMBH claim [7]: *“The invention relates to surface modified filling material compositions for thermoplastic, duroplastic or elastomeric materials which comprise a halogen-free, flame-retardant filling material. Said filling material is surface-treated with organotitanates and/or with organozirconates and with a siloxane derivative.”*

Masaharu Kato et. al [8] made similar observations as to which additives produced new and novel non-toxic flame retardant compositions.

ATH Filled Polyolefin Compositions – Braga et. al of Basell used ATH treated with LICA 12 to obtain “Flame-proof polyolefin compositions” [9]. The abstract states: *“Invention concerns polyolefin compns. with high flame resistance. The compns. comprise (A) 20-60% a heterophasic olefin polymer compn. comprising a cryst. olefin polymer (a) and an elastomeric olefin polymer (b), the compn. (A) being optionally modified with at least one functional monomer in an amt. 0.005-0.6% with respect to the total wt. of the total compn.; (B) 15-40% one or at least one inorg. hydrated fillers; (C) 12-40% one or at least one org. flame retardants contg. nitrogen in the mol.; (D)0-40% one or at least one inorg. anhyd. fillers. Possible applications include the use as insulating material in elec. wires and cables and the use as waterproofing sheets for roofs and tunnels.”*

Mg(OH)₂, Tetrabromobisphenol A, Antimony Trioxide Flame Retardant PP, ABS and Acrylic Acid-Propylene Graft Copolymer – Wen-Yen et. al. studied the effects of maleic anhydride-styrene graft copolymer compatibilizer, LICA 38, NZ 38 and LICA 44 as approaches to interfacial modification for flame retardant polymeric materials [10].

References

- [1] Plueddemann, Edwin P., *"Silane Coupling Agents"*, Pg. 114, 1982 Plenum Press.
- [2] Monte, S. J.; Sugerman, G; Kenrich Petrochemicals, Inc., U.S. 6,197,135 dated March 6, 2001, *"Enhanced Energetic Composites"*.
- [3] Monte, S.J.; Sugerman, Kenrich Petrochemicals, Inc.; G; Dixon, Scott J. USAF Contractor, U.S. 5,753,853 dated May 19, 1998, *"Solid Propellant with Titanate Bonding Agent"*.
- [4] Monte, S.J., *"Regeneration in the Melt of Recycle and Re grind Thermoplastics Using Neoalkoxy Titanates and Zirconates"*, SPE-GPEC 2003, Feb 26-27, 2004, Detroit, MI.
- [5] Monte, S.J., Kenrich Petrochemicals, Inc., *"Ken-React Reference Manual - Titanate, Zirconate and Aluminate Coupling Agents"*, March 1995, 340 pgs.
- [6] Mitsubishi Cable Ind., US 4,769,179 - 9/6/88.
- [7] Eichler, Hans-Jürgen; Palmer Michael; Herbiet, René, ALUSUISSE MARTINSWERK GMBH, WO 00015710 dated 14. September 1999, *"Surface-Modified Filling Material Composition"*.
- [8] Kato, Masaharu; Omoto, Masanobu; Ishimatsu, Hirofumi; Madalle, James; Kratzer, Jeff A.; EP 0 708 143 A1 dated 24.04.1996, *"Polyvinyl Chloride Based Resin Composition and Products Derived Therefrom"*.
- [9] Braga, Vittorio; Goberti, Paolo; Zucchelli, Ugo; Marchini, Roberta, Basell Technology Company Bv, Neth., WO 2001048075, EP 1155080 dated 2001-11-21, *"Flame-proof polyolefin compositions"*.
- [10] Chiang, Wen-Yen; Hu, Chia-Hao, Department of Chemical Engineering, Tatung Univ., Taipei, 104, Taiwan, Composites, Part A (2001), 32A(3-4), 517-524, CODEN: CASMFJ; ISSN: 1359-835X, Elsevier Science Ltd., *"Approaches of interfacial modification for flame retardant polymeric materials"*.

TABLE 1-PYROPHOSPHATO, PHOSPHATO AND PHOSPHITO TITANATES AND ZIRCONATES

Type	Chemical Structure	Code
Mono-alkoxy Titanates		KR 38S
Oxyacetate Chelate Titanates		KR 138S
A,B Ethylene Chelate Titanates		KR 238S
Quat Titanates		KR 238J LICA 38J NZ 38J
Coordinate Titanates & Zirconates		KR 55 KZ 55
Neoalkoxy Titanates		LICA 38
Neoalkoxy Titanates		LICA 12
Cyclo-heteroatom Titanates & Zirconates		KR TPP KZ TPP
Neoalkoxy Zirconates		NZ 38

TABLE 2 –LICA 38 – VISCOSITY OF 50% NANOCOR® CWC CLAY IN MINERAL OIL

Additive, % by Weight of Clay	Nano Clay	Mineral Oil	Viscosity Cps
Control	50	50	416,000
LICA 38, 0.3%	50	50	89,600
LICA 38, 0.5%	50	50	4,800
LICA 38, 1.0%	50	50	4,800
LICA 38, 2.0%	50	50	4,800

TABLE 3 –LICA 38 – VISCOSITY OF CLOISITE Na⁺ NANOCCLAY (MMT-Southern Clay) IN MINERAL OIL

Cloisite Na ⁺ Nanoclay	Mineral Oil	LICA 38 Dosage, % Wgt. of Clay	Brookfield (HBT) Viscosity, cps @ 25°C
45	55	0	720,000
45	55	0.5	400,000
45	55	1.5	144,000
45	55	3.0	57,600
45	55	6.0	51,200

TABLE 4 – LICA 38 – VISCOSITY OF Mg(OH)₂ IN MINERAL OIL

(1) Test	(2) LICA 38 % Wt.	(4) Min. Oil Amt.	(5) Mg(OH) ₂ Powder Amt.	(6) Brookfield Viscosity, cps @ 25C
In Situ	0.0	40.00	60 Untr.	1,120,000
In Situ	0.2	40.00	60 Untr.	400,000
In Situ	0.5	40.00	60 Untr.	32,000
In Situ	0.7	40.00	60 Untr.	12,800
In Situ	1.0	40.00	60 Untr.	8,000
In Situ ^a	2.8	40.00	60 Untr.	12,800
Pretr. ^b	0.7	40.00	60 Pretr.	800,000
Pretr. ^c	2.8	38.74	60 Pretr.	12,800

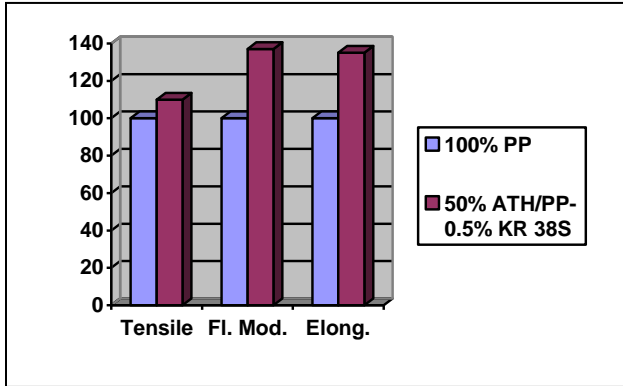
a) Wt. % titanate added in situ in mineral oil followed by Mg(OH)₂.
 b) Wt. % titanate added dropwise to fluidized bed of Mg(OH)₂ in a Henschel.
 c) 0.7% titanate blended with 2.1% FR plasticizer (C.P. Hall KP-140).

TABLE 5 - Al(OH)₃ (Martinal OL-104/LE – Martin Marietta) TREATED WITH 0.7% PYROPHOSPHATO TITANATE

Item	ATH Parts	Min. Oil Parts	Titanate Parts	Visc. cps @ 25C
Control	50	50	-	500,000
KR 38S ¹	50	50	0.35	4,800
KR 38S ²	50	50	0.35	6,400
KR 38S ³	50	50	1.40	6,400

1) In Situ.
 2) Pretreated neat.
 3) Pretreated – CA:FR Plasticizer-1:3

TABLE 6 – THE RELATIVE EFFECT OF 0.5% KR 38S TITANATE ON 50% ATH FILLED PP



Six Functions of Titanate Molecule
(1) Coupling, (2) Catalysis, & (3) Intumescence

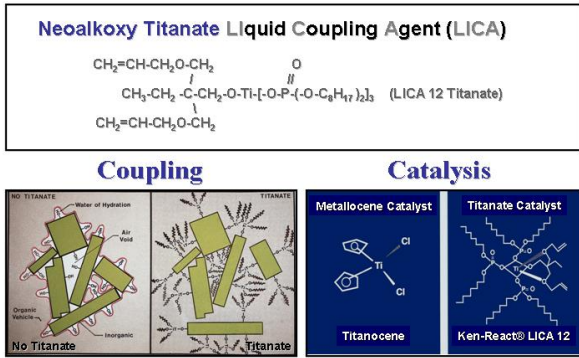


Figure 1 – The Titanate Molecule’s Six Functions: (1) Coupling, (2) Catalysis, (3) Intumescence, (4) Thermoplastic Compatibilization, (5) Thermoset Reactivity (6) Hybrid Multifunctionality.

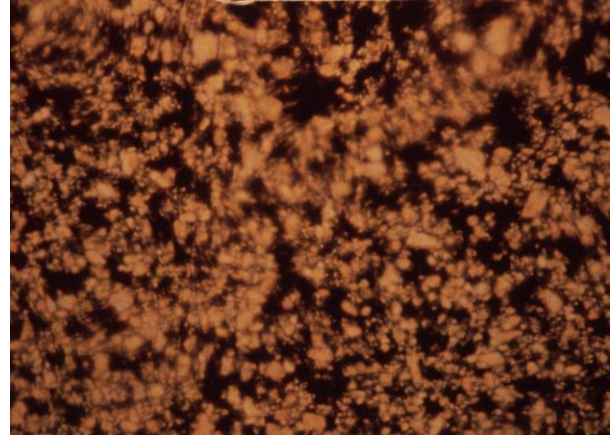
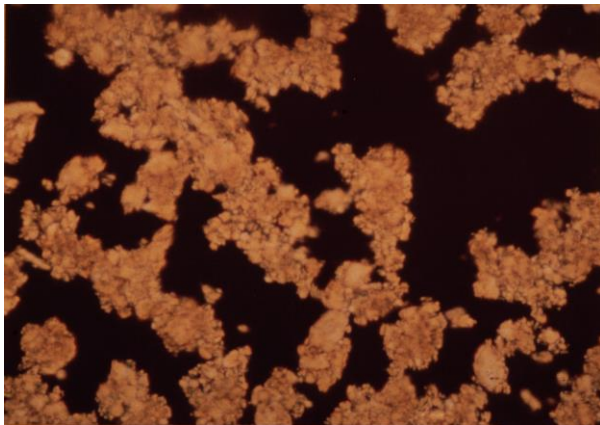


Figure 2 – SEM’s CaCO₃ dispersed in non-polar liquid paraffin – no titanate (1st SEM) & titanate (2nd SEM).

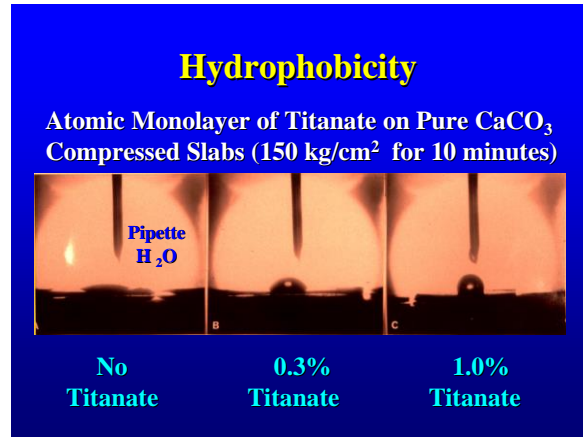


Figure 3 – Titanate effect on contact angle of a water droplet on pure CaCO₃ compressed slabs.



Figure 4 – (Left)-34% 20-nanometer silica sol gel (Nyacol) control with no titanate. (Right)-2.4% LICA 38J exfoliates silica and absorbs the water to form a powder.

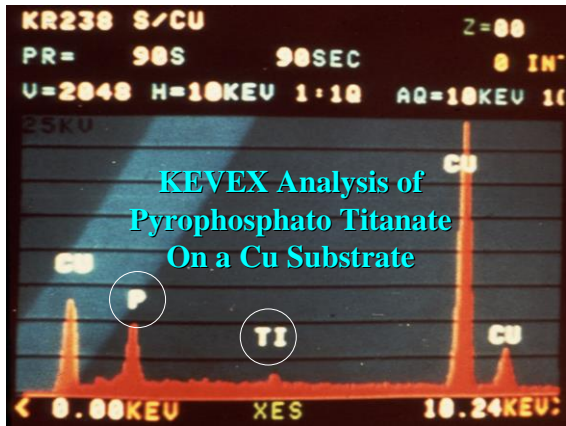


Figure 5 – KeveX analysis of deposition of a monolayer of Phosphorous and Titanium on the surface of Cu via KR 238S pyrophosphato titanate.



Figure 8 – 70% 3 μ CaCO₃ filled Polypropylene homopolymer, wherein 0.5% KR TTS titanate treatment by weight of CaCO₃ allows 180° bend of tensile bar with no white stress cracking.



Figure 6 - (Left) 60% Mg(OH)₂ /LLDPE. (Right) 0.7% LICA 38 treated 60% Mg(OH)₂ /LLDPE.



Figure 7 – 60% ATH (Polyfill 402)/40% Mineral Oil – (left) No Titanate – 800,000 cps, (right) 0.7% LICA 38 Titanate added *in situ* – 9,600 cps.

**Figure 9 –
8 Time
Sequenced
Photographs**

--
**CaCO₃
Made Into
A Flame
Retardant**
--
**Time Lapse
Photos
(0 to 2
minutes:37.53
seconds)**
--

**The
Comparison
of:
44% CaCO₃
Untreated
(left row
specimens)
and
44% CaCO₃-
Treated with
3% LICA 38
(right row
specimens)
filled LLDPE
demonstrat-
ing the flame
retardant
intumescent
effect of the
pyro-
phosphato
titanate.**

