

UV+EB Coatings Technology With 1.5-Nanometer Heteroatom Titanates & Zirconates

Presentation Title: **UV+EB Technology With 1.5-Nanometer Heteroatom Titanates & Zirconates**
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Speaker Organization: **Kenrich Petrochemicals, Inc.**
Session: **2020 RADTECH UV+EB TECHNOLOGY & CONFERENCE: Additives**
Date: Monday, **March 9, 2020**
Presentation Time: **11:45 AM - 12:15 PM**

Abstract



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 on "Ti/Zr Coupling Agents" – and their resultant commercial applications.

Polymeric and coating compositions are often filled or reinforced with inorganic and organic fillers, pigments, fibers – some nano-sized. Many are non-silane reactive as noted in "Silane Coupling Agents" by Edwin P. Plueddemann on page 114: "... Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite and boron. Only slight improvement was imparted to asbestine, hydroxy-apatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$), titanium dioxide, and zinc oxide." 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 CaCO_3 , ZnO , TiO_2 , hydroxyapatite, metal powders, carbon black, CNTs, barium sulfide, Portland cement, boron nitride, azodicarbonamide, nitramines, etc. via proton coordination – absent the need for hydrolysis of surface hydroxyls as with silanes. Their use results in: complete deagglomeration/dispersion/lower viscosity; hydrophobicity; organophilicity; increased mechanical properties; greater electron or thermal transfer efficiency; optimized sensitivity; and age-resistant compositions devoid of air and moisture. Ti/Zr chemical reactions via catalysis and compatibilization mechanisms at 0.3 wt. % dosage increase polymer flow and flexibility and appear super-plasticized with zero VOC. Flexibility is independent of filler content or any curative or crosslink mechanisms – thus "tougher" functional polymeric compositions with greater adhesion to a variety of non-polar (such as fluoropolymers) and polar substrates (such as automotive tin plate) are possible.

Among effects to be shown: phosphorus-based heteroatom organometallics add the phosphatizing effect of anti-corrosion or nano-intumescent flame retardance; recycled addition and condensation polymers can be made compatible, copolymerized and regenerated; the water to Portland cement ratio is reduced 31% to equivalent flow; a method for preparing graphene UV-curing adhesive and its application of composite heat-emitting glass; etc. Bi-polar layers of dissimilar zirconates produce transparent antistatic film when dosed at 3% by weight of polymer.

Biographical Note: Salvatore J. Monte, President of Kenrich Petrochemicals, Inc.; B.C.E. Manhattan College; M.S.-Polymeric Materials, NYU Tandon School of Engineering; Society Plastics Engineers Fellow & Honored Service Member; Licensed P.E.; Plastics Industry Association Recycle Subcommittee-Compatibilizers; Board of Governors, Plastics Pioneers Association-MTS Newsletter Chair; 31-U.S. Patents; Lectured Worldwide on Titanate & Zirconate Coupling agents; 450-American Chemical Society CAS Abstracts of published "Works by S.J. Monte"; Classified Top Secret for Solid Rocket Fuel and Energetic Composites Patents for the Insensitive Munitions Program; Lifetime member of the National Defense Industrial Association; Lifetime Member of the BOD-SPE ThermoPlastics Materials & Foams

Division; External Advisory Committee-UCF NanoScience Technology Center; former Chairman of the NYRG-ACS Rubber Division; former President of the SPE P-NJ Section; Testified several times before Congress on Trade and IP Protection; Business Man of the Year 2015-Bayonne Chamber of Commerce; Federated Society Coatings Technology C. Homer Flynn Award for Technical Excellence; Recipient of the Albert Nelson Marquis Lifetime Achievement Award; Rotary Paul Harris Fellow; UA Million Miler; Member PIA, SPE, ACS, ASCE, AIChE, SAMPE, the GRAPHENE COUNCIL.

Primer UV/EB Technology – See link:

https://www.radtech-europe.com/sites/default/files/rte_uveb_brochure_2018_0.pdf

Curing technologies:

1. Free radical cure of mainly acrylic resins but also vinyl and unsaturated polyesters. The reaction is started by a UV initiator (producing a radical under UV light). The radical initiates polymerization of the acrylic double bonds to form a crosslinked polymeric network.
2. Cationic cure of mainly epoxide or other cyclic ether ring opening curing reactions triggered by a UV cationic photo initiator (producing a super acid under UV light).
3. In EB cure there is no photo initiator, the electron beam creates radicals direct in the coated film that start the polymerization reaction. The vast majority of applications use acrylic functional resins cured with a UV photo initiator.

UV/EB Resin types:

1. Acrylic (and vinyl) UV Resins using oligomers and monomers (or diluents). The monomers are low viscous materials, most commonly esters of acrylic acid and simple multifunctional or monofunctional polyols.
 - a) Monomers generally can have from 1 to 6 UV curable groups, and the amount of functional groups will determine the properties of the UV formulation. The monomers are mainly used for: Viscosity and rheology control (dilution); Control of system reactivity (higher functionality cures faster); Increase crosslink density (enhance hardness and chemical resistance); Improve adhesion (penetrate the substrate). Disadvantage of monomers: High shrink on polymerization (can cause adhesion issues).
 - b) UV Curable Oligomers are higher molecular weight and higher viscosity and have various chemical structures such as polyester acrylates, epoxy acrylates, urethane acrylates and acrylic acrylates.
2. Epoxy acrylates are the most common used UV/EB oligomers. Epoxy acrylates are used in all kinds of applications, from primers to topcoats in coatings for all types of substrates and in almost all types of printing inks.
 - a) Advantages are: fast curing; hard; very good chemical resistance; high gloss; and relatively low cost.
 - b) Disadvantages are: yellowing (poor outdoor performance) and very high viscosity.
3. Urethane acrylates are a very versatile performance class of UV materials. They are generally used in applications where high performance is needed, like plastic coatings, wood topcoats, special primers on difficult substrates and high performance inks and adhesives. Known for their toughness, urethanes can be from very soft and flexible to extremely hard and scratch resistant with moderate to excellent chemical resistance. Aromatic and aliphatic urethane acrylates differ in that aliphatic types are very low yellowing and can have excellent outdoor durability, but are the most expensive types.
4. Polyester acrylates have a very broad raw material base which allows for a wide variety of chemical backbone structures and functionalities that can have very hydrophilic to extremely hydrophobic. Polyester acrylates can exhibit low viscosities (close to monomer viscosity) to very high viscosities depending on the molecular weight. Typical useful properties of polyester acrylates include: pigment wetting and dispersion; good water balance for lithographic printing;

adhesion; and generally relative low viscosity compared to epoxy or urethanes. Disadvantage of polyester acrylates are the lower molecular weight byproducts that can be formed in some types.

UV/EB formulations are usually made up from oligomers and monomers about 1-1 ratio depending on the required application viscosity and contain: 1-10% of photo initiator (in case of UV cure); 1-3% of additives to promote flow, leveling, cratering, slip or other properties; and pigments and fillers.

In pigmented coatings or inks with UV cure the photo initiators and lamps may need to be chosen correctly to not overlap too much with the absorption spectrum of the pigments. The main types of UV lamps are:

1. Standard mercury lamps (main peak 240nm);
2. Iron doped mercury lamps (broad emission 240-400nm);
3. Gallium doped mercury lamps (main peak 350-400nm), and;
4. LED lamps (single peak 360-400nm).

The emission spectra of these lamps are different, so depending on the absorption of the pigment the best lamp can be chosen. Also many different types of photo initiators exist, also with different absorption spectra, which can be chosen to match with the lamps and not overlap with the pigment absorption. In pigmented films it is important to consider the layer thickness because if the layer is too thick and UV light cannot penetrate to the bottom of the film, no cure will take place. With EB there are no issues to cure pigmented films or even multiple layers of pigmented films at once.

Introduction to 1.5-Nanometer Heteroatom Titanates & Zirconates

See Table 1 for nomenclature and alpha-numeric codes often used throughout the paper for the sake of brevity.

References, ACS CAS Abstracts and Web Links: A substantial body of literature [Ref. 1 to 240 (general coverage from 1973 to 2008)] has been developed which collectively demonstrates the efficacy of organotitanate and zirconate coupling agents as adhesion promoters, dispersants and alternatives to conventional heavy metal based anti-corrosive pigments in high performance anti-corrosion organic coatings and polymeric composites such as hydraulic and fuel hoses made of aramid reinforced silicone [240]. The author's efforts are references 1-8, 29, 111, 112, 116, 174, 175, 179, 183, 185-187, 213-216, and 239-240. This work plus other references 9 through 110 respectively have variously demonstrated the utility of these organometallic additive as anti-corrosives in vehicles ranging from alkyds through acrylics, epoxies, polyamides, polyurethanes, in both aqueous and solvent based vehicles, applied to metals such as aluminum, copper, carbon and stainless steel, tin plate and zinc, as well as substrates as varied as thermoset polyester and carbon fiber. Applications have varied from enhanced scrubability of latex flat wall paint to less-resistive EMI shielding coatings.

Throughout the paper, we will insert relevant ACS CAS Abstracts to help teach the art of the use of titanate and zirconate coupling agents for more efficient use of raw materials – the essence of Sustainability. For example, the following are some recent UV/EB Abstracts – in addition to those provided in the discussion of Function 5 of the heteroatom titanate/zirconate molecule - that are instructive:

TI Ultraviolet-shielding transparent resin molding and manufacturing method of the same

IN Takeshi, Chonan; Kobayashi, Hiroshi

PA Sumitomo Metal Mining Co., Ltd., Japan

SO Eur. Pat. Appl., 22pp. CODEN: EPXXDW

PI EP 2113528 A2 20091104 EP 2009-157908 20090415

EP 2113528 A3 20091118 EP 2113528 B1 20130619

R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LI, LT, LU, LV, MC, MK,

MT, NL, NO, PL, PT, RO, SE, SI, SK, TR

JP 2009269946 A 20091119 JP 2008-119124 20080430 JP 4655105 B2 20110323

US 20090274896 A1 20091105 US 2009-385354 20090406

CN 101570641 A 20091104 CN 2009-10138108 20090430

CN 101570641 B 20130320

PRAI JP 2008-119124 A 20080430

AB To provide an UV light shielding transparent resin molding using an inorg. UV light absorber and a manufacturing method of the same, having sufficient shielding characteristics of UV light having a wavelength of 375nm close to a visible light, and capable of exhibiting both high UV light shielding and a low haze value. There is provided the UV light shielding transparent resin molding and the manufacturing method of the same, with zinc oxide fine particles dispersed in a transparent resin, each sp. surface area set at 25m²/g or more and 55m²/g or less, average particle size set at 19nm or more and 41 nm or less, half value width of a (101) peak in an x-ray diffraction measurement set at 0.5 or less, and crystallite diameter set at 15nm or more and 20nm or less. An UV-shielding transparent resin molding was prepared from zinc oxide filled poly(ethylene terephthalate).

IT [65380-84-9](#), KR 44 [80481-35-2](#), Plenact AL-M

Author's Note: See Figure 22. KR® TTS was invented by me in 1973 in order to achieve an 85% French Process ZnO in a Naphthenic Oil base to for Neoprene rubber and is now in 680 EU-REACH registered facial cosmetic formulas based on ZnO, TiO₂ and other pigments.

TI Printing ink containing ultraviolet-infrared curable resins for thermoformed plastics

IN Yang, Lizhen; Zhou, Zhen; Hao, Yanping; Jia, Jingru

PA Beijing Institute of Graphic Communication, Peop. Rep. China

SO Faming Zhuanli Shenqing Gongkai Shuomingshu, 9pp. CODEN: CNXXEV

PI CN 1970656 A 20070530 CN 2006-10114766 20061123

CN 100535064 C 20090902 PRAI CN 2006-10114766 20061123

AB The title printing ink comprises (by wt. parts): prepolymer and UV curable resin 100-300, active monomer 50-200, photoinitiator 10-150, IR curable resin 20-200, pigment 70-150, antifoaming agent, leveling agent and polymerization inhibitor. The IR curable resin can be cured under IR of a certain wavelength, and has good compatibility with the UV curable resin. The printing ink can be used for manufacturing plastic products through vacuum-thermoform method, and improving the quality and the yield. The printing ink has simple manufacturing process, wide application range, safe usage and no pollution.

IT [65345-34-8](#), KR 12

TI Ultraviolet shielding antistatic composite coating and preparation method thereof

IN Duan, Xubin; Yin, Yuetao; Wang, Wenqi; Xu, Linying; Yang, Sanfei; Shi, Yiwei

PA Jinjiang City Zhongxin Microfiber Technology Co., Ltd., Peop. Rep. China;

China Leather and Footwear Industry Research Institute (Jinjiang) Co., Ltd.

SO Faming Zhuanli Shenqing, 5pp.

PI CN 105602433 A 20160525 CN 2016-10190063 20160330

PRAI CN 2016-10190063 20160330

AB The method includes subjecting graphite oxide/alc. soln. to centrifugation and ultrasonic treatment, adding titanate coupling agent, carrying out modification, reducing modified graphene oxide with sodium borohydride, centrifugally washing, freeze-drying to obtain organic modified graphene; ultrasonically treating nanometer titanium oxide in anhydrous alc., modifying nano titanium oxide with modifier, after completion of reaction, washing with anhydrous ethanol, drying, and obtaining organic modified nano titanium dioxide; ultrasonic blending organic modified graphene and organic modified nano titanium dioxide for uniformly dispersing them in polyurethane to obtain UV shielding antistatic composite coating. The invention utilizes antistatic and UV shielding performance of graphene and nano TiO₂, with 'bridged bond' effect between organic group on modified nano particle surface and polyurethane resin matrix, increases dispersion of inorg. nano-particles in organic system.

IT [61417-49-0](#), KR TTS

Author's Note: The above abstract teaches the use of subject organometallics in nano-TiO₂ and Graphene PU resin systems – materials of use in new and novel UV/EB coatings,

TI Activated carbon modified by titanate coupling agent for supercapacitor

AU Cai, Ke-Di; Mu, Wei-Fang

CS Institute of Liaoxi Ecological Environment Science, Bohai University,
Jinzhou, 121013, Peop. Rep. China

SO Advanced Materials Research (Durnten-Zurich, Switzerland) (2012), 347-353(Pt. 7, Renewable and Sustainable Energy), 3649-3652 CODEN: AMREFI; ISSN: 1022-6680

PB Trans Tech Publications Ltd.

AB A novel and simple strategy by introducing a titanate coupling agent into the electrode to improve the supercapacitor performance has been developed in this study. The surface modification of the activated carbon material are conducted under neutral conditions. The improved electrodes are characterized by mech. tests and electrochem. measurements. The obtained results reveal that the treated activated carbon electrode retains good mech. properties with decreased binder content. The electrode prepared using activated carbon treated with the Titanate coupling agent and a binder mass content of 8.0 % shows the best electrochem. performance. The specific capacitance reaches 376.2 F·g⁻¹, whereas the internal resistance is 0.91 Ω.

IT [62180-92-1](#) See link for CAS # 62180-92-1:

https://www.google.com/search?rlz=1C1VFKB_enUS643&biw=1522&bih=704&tbm=isch&sxsrf=ACYBGNTkwH69cSljaN0BWEss_9v3ro-flw%3A1578024598569&sa=1&ei=lr4OXpOAIOWD5wKd7YXAAQ&q=CAS+62180-92-1+titanate&oq=CAS+62180-92-1+titanate&gs_l=img.3...13891.17401..18104...0.0.0.81.646.11.....0...1..gws-wiz-img.....35i39.tGwtUaxP9lo&ved=0ahUKEwiTo5Hdx-bmAhXlwVkkHZ12ARgQ4dUDCAc&uact=5

TI Display panel using particles containing pigment

IN Ouchi, Takao; Anzai, Hiroyuki; Hagino, Akihide; Chiba, Masataka

PA Bridgestone Corp., Japan; Nippon Zeon Co., Ltd.

SO Jpn. Kokai Tokkyo Koho, 15pp. CODEN: JKXXAF

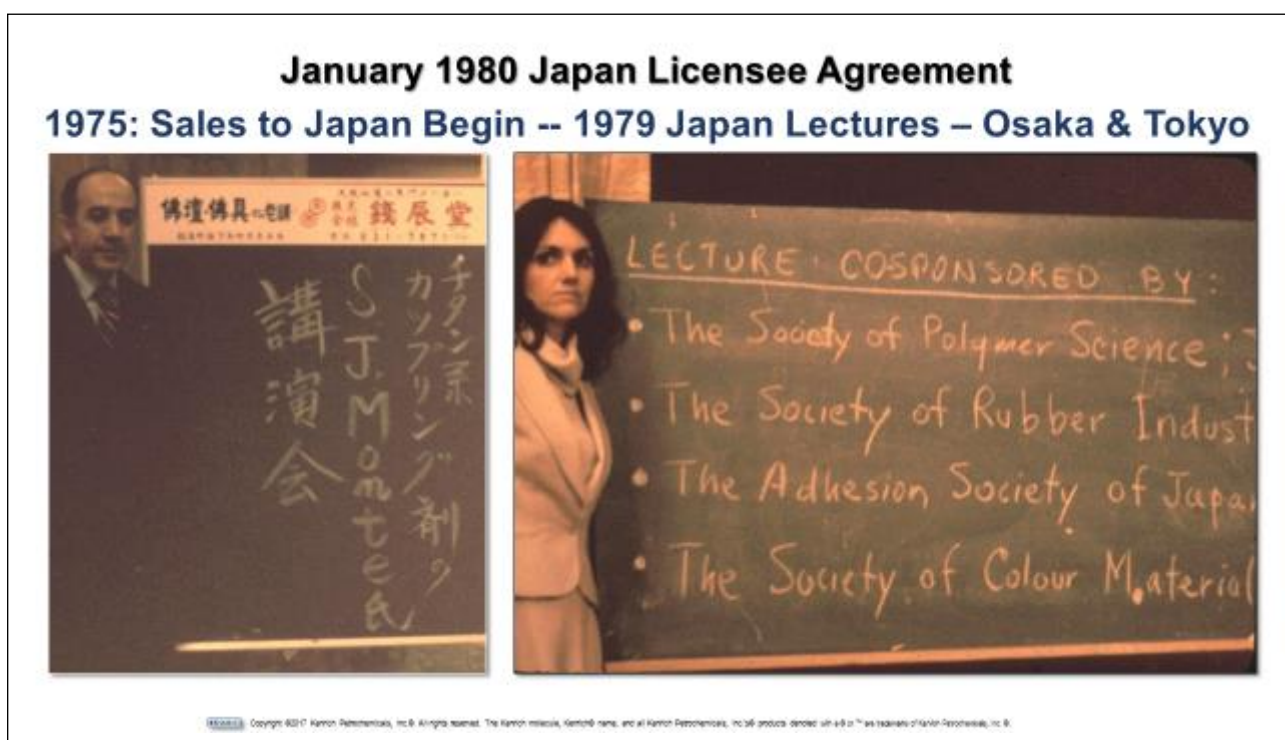
PI JP 2010224484 A 20101007 JP 2009-74578 20090325

PRAI JP 2009-74578 20090325

AB The display comprises display medium contg. particles sandwiched a pair of substrates (≥ 1 of which is transparent), and image is formed by moving the particle by elec. field application. The particle is spherical particle containing pigment and (meth)acrylic compound-hydrocarbon copolymer prepared from polyfunctional monomer(s). The particle satisfies $0.3 \leq D \leq 0.6$ [$D = \text{pigment orientation index determined by } D = \frac{\sum[(A_i \times |X_i^2 + Y_i^2|)}{(\sum A_i \times R^2)}$]; $A_i = \text{particle area}$; $R = \text{particle diameter}$; $(X_i, Y_i) = \text{pigment position coordinates based on particle center of gravity}$]. The particle shows good coloring and charging properties, and the display is useful for re-writable paper.

IT [61417-49-0](#), Plenact KR TTS

Author's Note: Plenact is a trademark of Ajinomoto Fine Chemicals Co., Ltd. operating as a licensee under a 1980 license agreement with licensor Kenrich Petrochemicals, Inc. KR[®] is an international trademark owned by Kenrich Petrochemicals, Inc. The author lectured in 1979 for 5-hours in Osaka and Tokyo, Japan to several Japanese polymer societies – Photo: (left) S. J. Monte (right) E. G. Monte:



TI Cationically photopolymerizable adhesive composition for optical elements

IN Ogawa, Hiroshi; Suwa, Tatsuhiro; Song, Cheong Hun

PA Cheil Industries, Inc., S. Korea

SO PCT Int. Appl., 39pp. CODEN: PIXXD2

PI WO 2010047386 A1 20100429 WO 2009-JP68265 20091023

W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

KR 2011079573 A 20110707 KR 2010-7025873 20091023

EP 2348081 A1 20110727 EP 2009-822083 20091023

R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LI, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR, AL, BA, RS

CN 102197101 A 20110921 CN 2009-80142291 20091023

US 20110195249 A1 20110811 US 2011-92627 20110422

US 8236872 B2 20120807

PRAI JP 2008-274705 A 20081024

WO 2009-JP68265 W 20091023

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT

OS MARPAT 152:502783

AB Disclosed is an adhesive compn. having excellent adhesiveness and durability. This cationic photopolymerizable adhesive composition includes (a) 75-99.8 parts of at least one of the following: an aliphatic epoxy compound, an alicyclic epoxy compound, an oxetane, and a vinyl ether; (b) 0.1-5 parts of a titanate coupling agent; and (c) 0.1-20 parts of a photopolymn. initiator (where the total mass of (a), (b), and (c) equals 100 parts). The adhesive is useful in making optical elements, such as an optical polarizing plate.

IT [61417-49-0](#), Plenact KR-TTS [65460-52-8](#), Plenact KR 41B

TI Pressure-sensitive adhesive compositions for optical films, optical films having adhesive layers therefrom, and imaging devices equipped with same optical films

IN Inoue, Shinichi; Yasui, Atsushi; Toyama, Yusuke; Hosokawa, Toshitsugu

PA Nitto Denko Corp., Japan

SO Jpn. Kokai Tokkyo Koho, 18pp. CODEN: JKXXAF

PI JP 2010065102 A 20100325 JP 2008-231160 20080909

PRAI JP 2008-231160 20080909

AB The title adhesive compns. contain 100 parts base polymers and 0.001-50 parts titanium-containing coupling agents and/or zirconium-containing coupling agents. The compns. may further contain 0.005-5 parts crosslinking agents. The title adhesive layers show durable adhesion without foaming and delamination in heat moist conditions. Thus, an adhesive layer, formed from a composition containing 99:1 Bu acrylate-4-hydroxybutyl acrylate copolymer 100, trimethylolpropane tolylene diisocyanate adduct (3:1) (Coronate L) 0.4, and titanium coupling agent (Plenact KR TTS) 0.5 parts, on a release film, was bonded to an optical sheet polarizer to give an adherent optical film, which was bonded to a glass, showing no foaming and delamination after 500 h aging in atmospheric with 95% relative humidity at 80°.

IT [61417-49-0](#), KR TTS [153590-16-0](#), NZ 33

TI Transparent acrylic polymer compositions with good heat resistance, their manufacture, and their moldings

IN Takahashi, Kazuyo; Arimoto, Kikuo; Oki, Hiroyuki

PA Kuraray Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 25pp. CODEN: JKXXAF

PI JP 2008174613 A 20080731 JP 2007-7989 20070117

JP 4990638 B2 20120801

AB Title compns., showing total light transmittance $\geq 85\%$ in UV regions and haze $\leq 1.5\%$ after melt molding, comprise (A) 100 parts acrylic polymers and (B) 1-50 parts colloidal SiO₂ with average particle size ≤ 50 nm. The compns. are manufactured by mixing acrylic polymers and colloidal SiO₂ treated with surface-treating agents with absolute value of difference in solubility parameter (SP) to the acrylic polymers < 1.2 before, in, and/or after polymerization of radically polymerizable monomers containing $\geq 50\%$ (meth)acrylic acid esters to give dielec. constant ≥ 3.9 . Moldings obtained from the compns. are useful for electronic materials, lenses, and building materials. Thus, 100 parts Me acrylate-Me methacrylate copolymer (SP 9.3) was mixed with 5.2 parts IPA-ST-S (colloidal SiO₂) surface-treated with Plenact KR 138S (titanate, PS 9.2), melt kneaded, and press molded to give a test piece showing UV transmittance 88%, haze 1.5%, flexural modulus 4100 MPa, and bending strength 128 MPa. IT [65460-52-8](#), Plenact KR 41B [67729-57-1](#), Plenact KR 138S

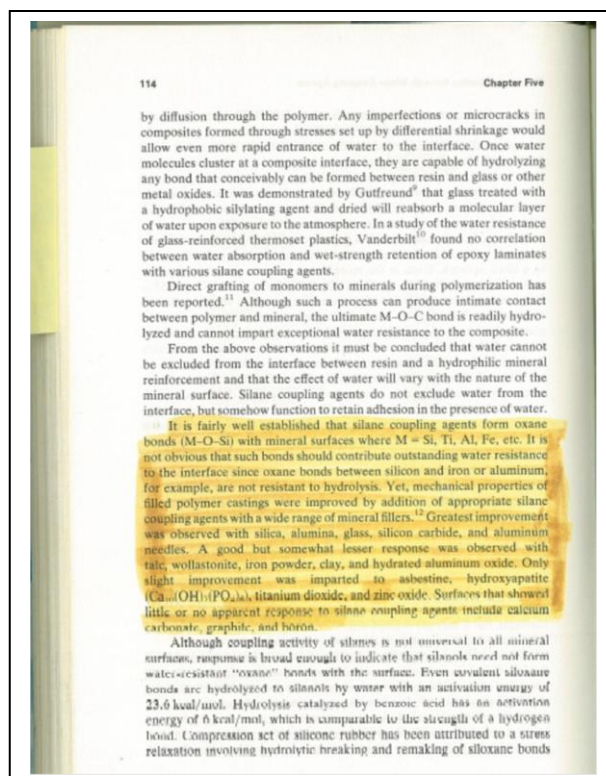
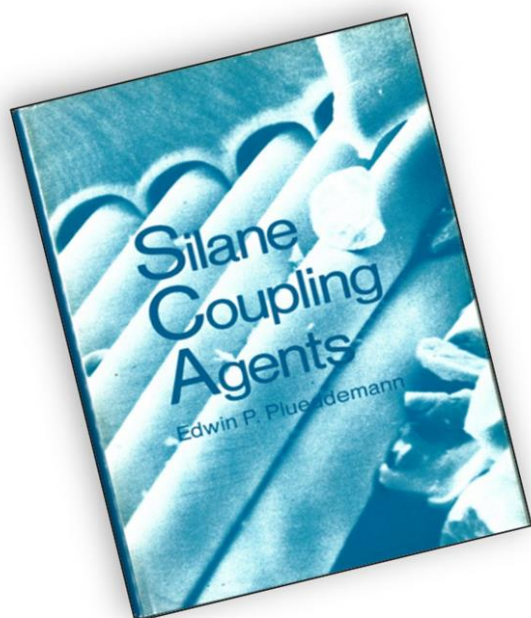
The mechanism(s) by which these materials provide the indicated benefits are incompletely known. However, various attributions have been contributory to understanding how these materials work. They are summarized and referenced as follows: improvements in coating to substrate and coating to internal particulate adhesion [9-30]; anti-corrosive participation by the additive as a consequence of surface pacification [1-63]; and catalytic modification of resin matrix chemistry through repolymerization and/or cross-link not normally associated with conventional esterification and/or adhesion promoters [101-109]. Common to the bulk of the cited references are that the organic resin derived and pigmented coatings discussed have thermal limitations in excess of approximately 300°C. Their application to inorganic resin coatings has only infrequently appeared in the literature [59, 61 and 63]. In reference 58, usage of organotitanates in conjunction with borosilane and borosiloxane formulations were shown to provide substantial improvement in adhesion and moisture resistance, whereas in references 59 and 61, usage of organotitanates were shown to drastically improve salt spray resistance in zinc rich sodium silicate based coatings. Organometallic mechanisms of coupling, catalysis, crosslinking, metallocene catalysis, repolymerization and copolymerization will be discussed according to the Six Functions of the titanate/zirconate molecule to attempt to explain the multi-functional effects referenced in the literature.

Additional links are provided:

- [Technical Literature](#)
- [4-Page Brief Overview – Titanates & Zirconates in Thermoplastic & Thermoset Compounds](#)
- [Why Titanates & Zirconates May Be Better Adhesion Promoters Than Silanes For Silica & Carbon Reinforced Polymeric Composition](#)
- [Why Titanates & Zirconates May Be Better Adhesion Promoters Than Silanes](#)
- [The Use of Titanates and Zirconates In Flame Retarded Compositions](#)
- [Catalyst Designed for Multi-Polymer Compatibilization & Regeneration of PCR\(Post Consumer Recycle\)](#)
- [New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle \(PCR\)](#)
- [Processing and Molding Polymers with 1.5-Nanometer Titanates Zirconates In Pellet Form Nov 2018](#)
- [Ti and Zr Catalysts in the Macromolecular Melt Regenerate Unfilled and Filled Virgin Re grind and Recycled Plastics](#)
- [A New 1.5-Nanometer Titanium Treated Portland Cement](#)

Since the 1970's, coupling agents have been a dynamic arena for dramatic composite performance improvement often causing a new paradigm in polymer applications technology with over 4,000 ACS CAS abstracted works by "Others". In the 70's, it was Japan dominating with applications in microelectronics, magnetic recording media, OLED's and digital copier toner and in the 21st Century into 2020 – China is dominant in applications R&D with my invention titanates and zirconates. Table 2 lists – ACS CAS ABSTRACTS FOR NANOCOMPOSITES USING TITANATE OR ZIRCONATE FOR THE 9-MONTH PERIOD SEPT. 3, 2005 TO MAY 31, 2006.

Nanotechnology, Graphene and Sustainability are topical in 2020, but materials science often fails to deliver on its promises because investigators fail to consider the importance of the interface – the nature and amount of the surface modifiers used on the nanoparticulates as received for formulating – and using application and testing techniques that do not take into account that one is operating at a thickness of less than 2-nanometer – the length your fingernail grows in a second. Factors such as: solubility parameters; dosage; sequence of addition; rheology and specific energy input; shifts in Critical Pigment Volume Concentration points requiring less monomer or solvent; prewash of surfaces for small batches; a non-silane mindset in that hydrolysis is not needed to effect “coupling”; interfaces are not limited to hydroxyl-bearing materials; and in situ reactions can occur with almost every inorganic or organic in a formulation; catalysis can be used to plasticize; and other factors discussed herein



Also, a silane mindset says that non-hydroxyl bearing inorganic interfaces and organic interfaces such as CaCO₃, carbon and aramid are not able to be coupled – which they are – with subject organometallics. Why? Plueddemann, the Father of Silane Chemistry, stated [113]: *"It is fairly well established that silane coupling agents form oxane bonds (M-O-Si) with mineral surfaces where M = Si, Ti, Al, Fe, etc. It is not obvious that such bonds should contribute outstanding water resistance to the interface since oxane bonds between silicon and iron or aluminum, for example, are not resistant to hydrolysis. Yet, mechanical properties of filled polymer castings were improved by addition of appropriate silane coupling agents with a wide range of mineral fillers. Greatest improvement was observed with silica, alumina, glass, silicon carbide, and aluminum needles. A good but somewhat lesser response was observed with talc, Wollastonite, iron powder, clay, and hydrated aluminum oxide. Only slight improvement was imparted to asbestine, hydroxyapatite (Ca₁₀(OH)₂(PO₄)₆), titanium dioxide, and zinc oxide. Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron."*

Plueddemann also states [113]: *"... From the above observations it must be concluded that water cannot be excluded from the interface of resin and a hydrophilic mineral reinforcement and that 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."

By-product *Water of Condensation* at the interface as a result of the silane hydrolysis mechanism is a source of long term aging failure – particularly if the nano-interface goes above the boiling point of water – a condition that does not exist with neoalkoxy heteroatom titanates and zirconates as borne out in 10% salt water boil tests aged 240-hours on fiberglass, graphite and aramid reinforced epoxy, vinyl ester, polyester and urethane thermoset composites wherein the silane systems loss significant original mechanical properties while titanates and zirconates are virtually unchanged – see Table 3 in Reference [3] for long and short fiber reinforced epoxy data.

Another coupling agent mindset that exists because of the success of silane art in thermosets is that the best coupling agent is one whose organofunctionality matches that of the polymer or is reactive with the polymer's curative. For example, it would be assumed that an amino silane would be superior to a pyrophosphato titanate in an amine cured epoxy. Logical, but the mindset does not always reflect what happens in practice. For example, investigators from Osaka University concluded [114]: *"The effects of different coupling agents on the mechanical properties of the TiO₂ coated with a silane (A-1100 amino–cf. Table 1 in [114]) coupling agent were compared with composites prepared by dispersing titanate (KR 38S pyrophosphato–cf. Table 1 in [114]) coupling agent-coated TiO₂ in epoxy. Young's modulus and flexural strength of the titanate coupling agent-treated composites were significantly better than those of the silane coupling agent-treated composites. Apparently, a strong interfacial bonding between the filler and the matrix existed when the titanate coupling agent was used."*

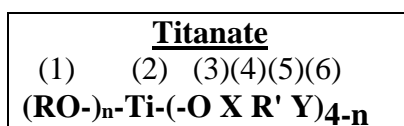
This paper will show that small amounts of subject organometallics will not only effectively exfoliate the particulate (pigment, filler, carbon) but also functionalize its surface with favorable metallocene-like Ti or Zr repolymerization catalysis capabilities resulting in improved flow and mechanical properties while also providing atomic phosphorus intumescence for flame retardance or anti-corrosion when phosphato or pyrophosphato organometallics are selected.

Keep in mind that Table 3 reviews titanate, zirconate and silane effects in graphite, aramid (neither of which are silane reactive) and glass fiber reinforced epoxy [183]. The author is of the opinion that the effect of subject coupling agents on materials used in “non-coatings compositions” such as shown in Table 3 are applicable to UV/EB coatings. For example, if a given titanate can reduce the viscosity of TiO₂ in mineral oil, it will do the same in an alkyd, polyester, acrylic or just about any thermoplastic and thermoset monomer, oligomer or polymer system.

The unifying concept of the “Six Functions” of the titanate molecule will often be used to attempt to explain or understand the “why?” behind the data on fillers, fibers and pigments and compositions to be discussed. Some conventional – and not so conventional – filled, unfilled, catalyzed and flame retarded compositions are shown so that the potential efficacy of subject titanates and zirconates in filled, fiber reinforced non-nano and nano coatings and compositions is appreciated and better understood.

DISCUSSION

Six Functions of the Titanate (Zirconate) Molecule – A discussion of the “Six Functions” of some 60 titanates/zirconates as invented by the author is useful to explain their performance differences and may be represented as follows:



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. Figure 1 depicts the theoretical atomic monolayer of a less than 2-nanometer on the interface of any inorganic/organic particulate or fiber of any size.

Figure 2 shows titanate deagglomeration of (silane-inert) CaCO₃ in non-polar paraffin liquid. The coupling effect of the monolayer of titanate to disperse CaCO₃ electrochemically, rather than just mechanically, is apparent. Typically, 0.5 to 0.7% pyrophosphato titanate reduces the viscosity of 70% 3-micron CaCO₃ in non-polar mineral oil from 2,080,000 cps without titanate to 12,800 cps with titanate (see Figure 3). The author has compounded 70% untreated and 0.5% KR TTS titanate treated CaCO₃ (OMYA 3) filled (silane-inert) PP homopolymer and then injection molded the compounds into dumbbell shaped test specimens. The untreated specimen snapped at the slightest attempt at bending while the titanate containing specimen could be bent 180° - or twisted 360° as if it were rubber - with no white stress cracking at the bend (cf. Figure 4) indicating Function 1 coupling of the two silane-inert interfaces (CaCO₃ and PP) and an obvious mechanical property maintenance – and a not so obvious inducement of stress/strain strength via Function 2 catalysis. Improved mandrel bend of a CaCO₃ filled coating is an obvious extension of the effect shown in Figure 4. See recent abstract next:

TI Effects of filler treatments on the mechanical, flow, thermal, and morphological properties of talc and calcium carbonate filled polypropylene hybrid composites

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SO Journal of Applied Polymer Science (2005), 98(1), 413-426 CODEN: JAPNAB; ISSN: 0021-8995

PB John Wiley & Sons, Inc.

AB Com. available [neoalkoxytitanate \(LICA 12\)](#) and organosilane (3-aminopropyltriethoxysilane) coupling agents were used to treat talc and calcium carbonate (CaCO₃) to compare their effects with those of untreated fillers upon their incorporation into polypropylene (PP). Com. stearic acid treated CaCO₃ was also used to widen the scope of the study. Single-filler PP composites (containing either talc or CaCO₃) and hybrid-filler composites (containing a mixture of talc and CaCO₃) were compounded on a twin-screw extruder and subsequently injection-molded into dumbbells. The silane and titanate treatments dramatically increased the elongation at break for both the single-filler and hybrid-filler composites, whereas stearic acid did not. There was also a moderate improvement in the impact strength of the composites, particularly those treated with LICA 12. The hybrid composites, through the synergistic coalescence of pos. characteristics from talc and CaCO₃, had exceptionally good impact properties, more so with the aid of the coupling agents. [For example, the impact strength value of a LICA 12 treated hybrid composite was the greatest for all the composites studied](#), overshadowing the superiority of the CaCO₃-filled PP composites, which predominantly had the highest impact properties. Further investigations of the thermal and morphol. properties were also conducted to facilitate the determination of the coupling mechanisms and their interesting effects on the hybrid composites.

IT 919-30-2, Z6011 103850-22-2, LICA 12

IT 57-11-4, Stearic acid, uses 471-34-1, Omyacarb 3-SA, uses 14807-96-6,

Figures 1, 2 and 3 would lead one to assume that the effect in Figure 4 is due to filler dispersion when in fact we have begun to understand that the major factor may be in Function 2 Catalysis – independent of Function 1 filler coupling. Since the acrylic moiety is a major player in monomers and oligomers, we took an unfilled acrylic macromolecule as shown in Table 4 and with two to three parts per thousand of a neoalkoxy titanate or zirconate, we increased the *Tensile Yield Strength* by 25% and the *Elongation @ Break* by five to six-fold while increasing polymer flow rates 20 to 40%. Since a film's *Toughness* can be defined as the *Area under the Plot of Stress (Tensile) vs. Strain (Elongation)*, it is apparent that tougher UV/EB coatings can be produced by using higher molecular weight oligomers of Epoxy acrylates or less monomers as diluents to equivalent rheology.

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. Coupling or exfoliation can be done in-situ in any thermoset, thermoplastic, solvent, monomer, oligomer, or water phase without filler or fiber pretreatment.

Since almost all 3-dimensional particulates and species have surface protons, titanates have been shown to be reactive with aramids, polyamids, polyesters, carbonates, sulfur, sulfur donors, sulphates,

nitrides, nitrates, nitramines, carbon, boron, metal powders, azodicarbonamide, sodium bicarbonate and many other reinforcing or functional submicron/nano inorganic – organic fillers/particulates/fibers used in polymer compositions [1–240].

For example, Philip D. Bourgeois [197] used subject organometallics not only to exfoliate nanoclay to transparency in the barrier resin, but primarily as an adhesion promoter between the barrier resin (PA) and the polyester (PET) inner and outer layers: “*A plastic container or preform includes a multilayer wall having at least one layer of polyester resin, at least one layer of barrier resin, and an adhesion-promoting material blended with the barrier resin and/or the polyester resin to promote bonding between the barrier and polyester layers. The adhesion-promoting material includes an organometallic coupling agent based upon Ti, Zr or Al. The organometallic coupling agent preferably has an amino end group with an affinity for carboxylic end groups in the polyester, and preferably is selected from the group consisting of neopentyl(diallyl)oxy, tri(N-ethylenediamino) Et titanate, zirconate and aluminate. Coupling agents based upon titanium and zirconium are particularly preferred for containers and preforms having a clear (non-colored) wall.*”

In general, 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. When phosphato, phosphito or pyrophosphato titanates are used, they provide atomic monolayer phosphato-titanium intumescent capability to both the inorganic/organic substrate so as to control burn rate and burn rate exponent of flame retardant compositions or phosphato-Ti/Zr anti-corrosion protection.

(2) Catalysis Function (Ti, Zr) = tetravalent titanium, zirconium. The Ti-O (or Zr-O) bond is capable of disassociation allowing transesterification, transalkylation and other catalysis mechanisms such as post-reactor *Repolymerization* or *Copolymerization* or *Regeneration* of recycle or regrind. Silane Si-C bonds are thermally stable and inert. Organic titanates (and zirconates) are well known catalysts [115,116] used in the manufacture of: polyolefins [117,118]; polyesters [119-125]; PBT [126]; polyurethanes [127-132]; polycarbonates [133-134]; polysiloxanes [135-142]; PET [198].

For example, reference [126] refers to U.S. Patent 5,237,042 dated August 17, 1993 issued to the Korea Institute of Science and Technology (KIST) entitled "Process for the Preparation of Polybutylene Terephthalate (PBT) Based Polymer". It disclosed the use of a complex catalyst consisting of antimony and titanium (KR 41B) compounds to produce a PBT polymer "having excellent color, a small amount of side-product and a high degree of polymerization within a short time". Additionally, Cho et al. [210] developed a process for preparing polyethylene naphthalate-based polymers by using composite catalysts comprising titanium compounds (KR 41B) and aromatic phosphites. Lee et al. [211] used barium sulfate, titanated (with KR 138S), silylated (with 3-(trimethoxysilyl)propyl methacrylate) in the transesterification of filled PBT/PET blends. Kitani et al. [212] developed an ether reaction production method for an alkylene oxide addition product which uses catalyst for alkoxy conversion.

Titanates (and zirconates) are also able to cross-link or cure a variety of polymers: polyolefins [143]; polybutadienes [144,145]; styrene-butadiene copolymers [146]; polystyrene [147]; polysiloxanes [148,137,149-152]; epoxy [153-158]; fluorocarbon resins [159-162]; acrylic and methacrylic resins [163-172]; polyvinyl alcohol [173].

The author claims that much of the flexibility that a single-site Ti or Zr coupling agent induces to a polymer is analogous to metallocene catalysis effects [1]. Metallocenes are single site catalysts based on titanium (titanocene) and zirconium (zirconocene) chemistry providing a new generation of polymers exhibiting increased flow (process rheology) and improved mechanical properties when compared to analog polymers catalyzed from mixed metal (Ziegler-Natta type) catalysts. Metallocene catalysts are designed for use in the polymerization phase of polymer manufacturing. They are expensive organometallic complexes not designed for in-situ "addition-to" or "residence-in" the finished polymer used next by coatings formulators. Table 4 shows the metallocene-like catalytic effect of six neoalkoxy titanates and six neoalkoxy zirconates on an injection molded unfilled acrylic resin. Examination of Table 4 shows of the addition of 0.2 parts of a phosphato titanate (0.3 phr CAPOW L 12/H) to the acrylic

increases: tensile yield by 42%, elongation by 620% and flexural strength by 53%. Again, since polymer toughness is defined as the area under the curve created by the plot of stress vs. strain, it is clear that a tougher acrylic film or coating can be made.

Titanate and zirconate coupling agents, particularly the neoalkoxy type, are thermally stable, single site catalytic organometallic esters designed to be used as additives in a polymer used next by coatings, ink and adhesive formulators, compounders, processors and recyclers. They remain as ever-present catalysts in the polymer exposed to repeat thermal mix cycles during recycling. The patented [174] effect on a polymer (macromolecule) is called "Repolymerization." Repolymerization affects all polymers to some degree and has been shown to provide improved original/aged mechanical properties – particularly strain strength, which is important to mandrel bend coatings performance as will be shown later in discussing Figure 28.

Coating compositions requiring high heat performance are usually made of cured thermoset resins rather than uncured thermoplastic polymers. But whether the polymer is cured or uncured, the aromatic (e.g. styrene) or aliphatic (e.g. ethylene, propylene, butadiene) backbones which typically make up the resin or thermoplastic are functions (2) to (4) reactive with titanate (or zirconate) independent of function (5) curative reaction mechanisms. Thus, the monolayered, organometallic-coupled particulate and/or fiber becomes a catalyst support bed for single site, *in-situ*, and metallocene-like repolymerization of the surrounding polymer. Repolymerization appears to effect the isothermal recrystallization time, chain branching and morphology of the polymer chains surrounding the coupled particulate pigment, extender or fiber. The metallocene-like benefits thus derived such as easier polymer processing and better mechanical properties are apparent.

For example, a dodecylbenzenesulfonyl titanate (LICA 09 – cf. Table 1) at 2 parts per thousand parts of unfilled and 40% CaCO₃ filled polypropylene reduced injection mold cycle times by 42 and 35.5% respectively and reduced process temperatures from 184°C to 163°C and 180°C to 141°C respectively indicating polymer flow effects were independent of filler content. Similarly with the same amount of LICA 09, the time and temperature to fill a mold of a flame retarded acrylonitrile-butadiene styrene (ABS) to form a computer fascia was reduced from 77 to 60 seconds and from 208 to 181°C respectively. The mechanical stress-strain properties of a like amount of LICA 09 in unfilled ABS showed a 75% increase in flexural strength and 37% increase in elongation [174-175]. Similarly, a dodecylbenzenesulfonic titanate (KR 9S – cf. Table 1) increased significantly the Pencil Hardness of an alkyd white enamel coating (cf. [116] – Table 352).

For example, a modified polyphenylene sulphide resin containing titanium organometallic compound (LICA 09) and molten polyphenylene sulphide (PPS) resin was prepared without any particulate or fiber content. The isothermal crystallization time (at 250°C) of the PPS was substantially decreased from 175 secs to 106 secs, and the crystallization temperature was increased by 8°C, with the addition of titanium organometallic compound [176].

Geoffrey Holden, the inventor of Kraton[®] suggested [177] LICA 09 as a coupling and hydrophobic agent for a TiO₂, precipitated CaCO₃ filled, solvated styrene-butadiene block copolymer architectural type sealant.

When an aliphatic amino titanate (LICA 44) is used at 0.66 parts, the viscosity of 33 parts of XC-72R conductive black dispersed in 100 parts of a TDI based urethane cut with 300 parts of methylene chloride is reduced from 55,000 to 600 cps while 0.65 parts a pyrophosphato titanate (KR 38S) will drop the Mooney viscosity, ML (1 + 4) @ 100°C of a 50 phr HAF Black filled SBR 1500 from 64 to 28.

Powder coatings based on epoxy resin have shown significant improvement in adhesion, flow and anticorrosion using CAPOW[®] L38/H (65% active LICA 38 Coupling Agent POWder masterbatch on silica carrier). Similarly, CAPOW KR 55/H is used in polyester powder coatings. This is consistent with effects previously reported in liquid epoxy and polyester systems [116].

Thomas S. Kohm reported the elimination of 'pink ring', 'post hole failure', and low Z-axis thermal expansion for multi-layered copper/fiberglass/filler reinforced epoxy printed circuit boards [178]. Kohm stated, "*It has been found that printed wiring boards on base materials containing titanate or zirconate*

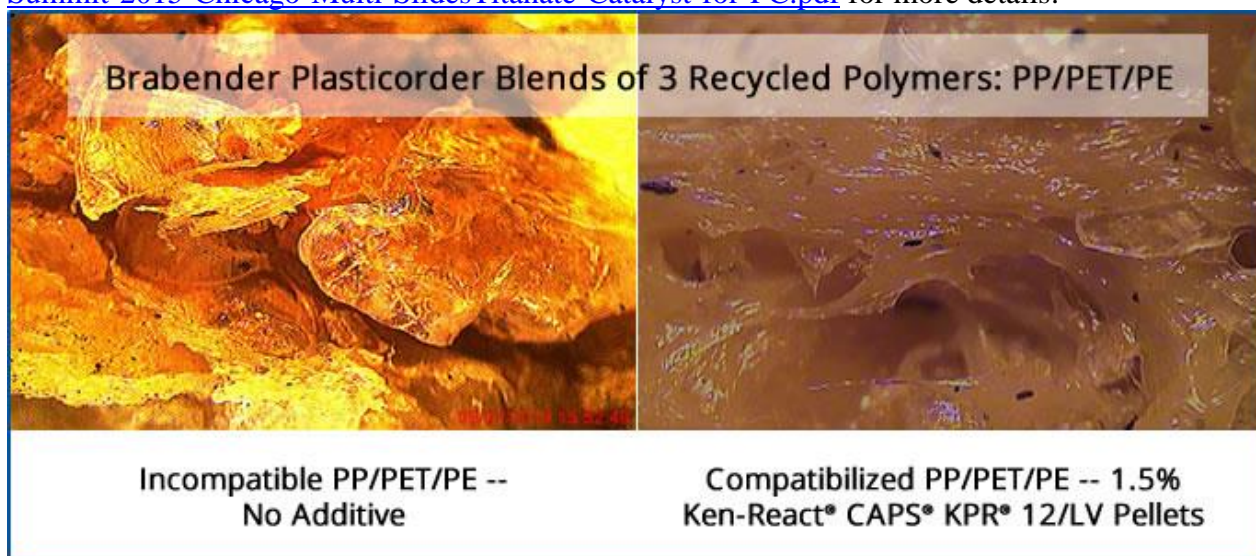
coupling agents are more resistant to thermal cycling failure than when silane coupling agents are used. It has also been found that silane coupling agents are attacked by alkaline solutions such as electroless copper deposition solutions more rapidly than organotitanate and organozirconate coupling agents".

Titanate and zirconate coupling agents may also act catalytically as compatibilizers via copolymerization or activation of both addition and condensation polymers [179]. When the activation occurs to more than one polymer simultaneously, in the absence or presence of filler or reinforcement (both inorganic and organic), or peroxide, said activation may result in repolymerization, or copolymerization (i.e. intermolecular rearrangement), or grafting, or other molecular modifications resulting in some other form of "alloying" as follows:

1. Rapid equilibration of molecular weights to produce near thermodynamic equilibrium distribution irrespective of starting compositions.
2. Randomization of most block copolymers except some aliphatic polyethers.
3. Reduction in polydispersity of molecular weight resulting in a narrower molecular weight distribution curve.
4. Controlled introduction of organofunctional groups for bonding enhancement.
5. Catalysis of a wide variety of reactions.
6. The compatibilization of Addition and Condensation polymers.

Some referenced examples of subject organometallic effects on polymer blends are:

- a) Acetal/Acrylic [180] showing that the use of LICA 44 at a level of 0.2 parts by weight of a blend of 80 parts of acetal and 20 parts of acrylic results in a increase in the Gardner impact from 12 to 265 inch/pounds. Coatings Impact strength improvement is implied;
- b) Recycled PET/Recycled PC wherein A. Maupome reported [181] results with 0.2% LICA 12 showing a ten-fold increase in elongation at break and a doubling of tensile modulus. Similar effects in polyester coatings is implied;
- c) PP/LCP and HDPE/LCP Blends wherein R. Holsti-Miettinen overcame the difficulties of blending liquid crystalline polymer (LCP) with non-polar polyolefins using neoalkoxy titanates and zirconates [182].
- d) See link: <https://4kenrich.com/wp-content/uploads/2018/02/Ken-React-KPR-Global-Plastics-Summit-2015-Chicago-Multi-SlidesTitanate-Catalyst-for-PC.pdf> for more details:



The catalysis effect of titanate on a non-polar copolymer such as EPR is to produce in-situ a metallocene-like polymer that has greater flow and flexibility. For example, illustrated in Figure 5 is an unfilled EPR rubber that has been sheeted off a 2-roll mill and placed on the SS cutting table. The EPR sheet (left) displays the characteristic "nerve". The EPR sheet (right) has been compounded with 0.3 phr of a 65% active monoalkoxy phosphato titanate (KR 12) and is completely denerved. Flexibilization is achieved without plasticizer. PVC plastisols can be formulated to equal flexibility with 18% less

plasticizer. In solvent borne coatings, less solvent is needed. In fact, Cowles mixing with titanates should involve solvent-starving to maintain Specific Energy Input – i.e. maintain shear for optimal dispersion. In UV/EB coatings, less monomer is needed producing films with greater strength due to the average higher molecular weight of the cured macromolecule. The titanate catalytic effect on unfilled rubber is important to understand because it changes the way we view “coupling agents” in polymeric compositions.

A major mindset that must be overcome in dealing with titanate effects on polymer coatings and compounds is to understand that changes in compound behavior are not only the result of filler dispersion, or filler to polymer bridging called coupling – but of Function (2) organometallic catalysis. The de-nerving of the EPR with just 0.2 phr titanate is an indication that a catalytic event has occurred because there is no filler – and such a low level of additive was used that it is not lubrication. Also, titanates are not surfactants – they are catalysts that couple, phosphatize and compatibilize at the nano-interface. This mindset change is necessary so that the rubber compounder or paint or UV/EB formulator understands the data that is obtained with titanate. For example, a rubber compounder might misinterpret a large increase in elongation with titanate as a retardation of cure when in effect it is the result of the compound now having too much plasticizer as compared to a control without titanate. The paint formulator should formulate with less diluent or solvent to obtain film flexibility with higher strength and higher reverse impact. In my mind, the effect shown in Figure 4 – and the ability to make rubber moldings with low eluted components as shown in the abstract below – points to the opportunity that a small amount of titanate is a means to reduce VOC in a coatings, the amount of low molecular weight monomer in UV/EB formulations, or in a thermoset formulation such as MEKP cured unsaturated polyester.

TI Rubber moldings with low eluted components

IN Kuzawa, Naoya

PA Nichias Corp., Japan

SO Jpn. Kokai Tokkyo Koho, 6 pp. CODEN: JKXXAF

PI JP 2005298671 A2 20051027

AB Title moldings contain 100 parts rubbers contg. $\leq 1.5\%$ components (A) with weight-average mol. weight of ≤ 104 , 50-100 parts carbon black, 0.5-3.0 parts titanate couplers, and crosslinkers. A composition containing Keltan 6640B (containing 1.1% A component) 100, carbon black 70, TMPT 2, Percumyl D 2, and Ken-React KR TTS 2 parts was vulcanized and molded at 170° for 20 min to form a test piece with no eluted material after 200 h in 150° water.

IT Carbon black, uses Titanates

IT 61417-49-0, Ken-React KR TTS

(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. For example, the dynamic TGA in Figure 6 shows the intumescent FR protection afforded by use of a chelated phosphato titanate for graphite reinforced epoxy. The control loses 70% of its integrity at 300°C while the phosphato titanate (KR 212) only loses 10% at 700°C.

When an atomic 1.5 nanometer monolayer of pyrophosphato titanate such as KR 38S is coupled to silica, an anticorrosive pigment is created. For example, a study was made with the objective to determine the corrosion resistance of an epoxy-polyamide coating in which a pyrophosphato titanate (KR 38S) plus silica is used in place of basic lead silico chromate, BLSC M-50. An anti-corrosive primer formulation based upon BLSC M-50 in an epoxy-polyamide binder was prepared. Two additional formulations were then prepared. One containing untreated silica with no BLSC M-50 or KR 38S and another containing 0.5% KR 38S based upon the weight of the silica. The BLSC M-50 was replaced with untreated silica or silica plus KR 38S to an equivalent systems viscosity. Because of the higher oil absorption of the silica, the control formulation having no KR 38S resulted in a product having a lower PVC and a reduced paint yield. However, the silica plus KR 38S formulation allowed a higher level of silica to be used resulting in a primer with a PVC and paint yield higher than that of the BLSC M-50 control. The ingredients were added in the order shown in Table 5. The primers were applied to cold rolled steel panels at a dry film thickness of 1.5—2.0 mils and dried for 7 days at 25°C and 50% relative

humidity. They were then exposed (without top coats) to the following environments: Salt Fog 500—1,000 hours (cf. [116] – Figures 66 & 67) and humidity (100%)—500 hours (See Figures 7 & 8). The test indicated that the titanate must be added to the formulation prior to the incorporation of any pigments in order to maximize its effectiveness. The test results were positive as can be seen from the figures and are shown in the next Table. In as much as some observations are necessarily subjective, they have been reported using the following scoring scheme:

<u>Score</u>	<u>Performance</u>	<u>or Effect</u>
10	Excellent	No Change
9		Trace
8	Very Good	Very slight
6	Good	Slight
4	Fair	Moderate
2	Poor	Considerable
0	Very Poor	Severe

See abstract next:

TI Corrosion prevention of edges of surface-treated steel sheets by forming anticorrosive films, and coating solutions for forming same films

IN Fujisawa, Kazuhisa; Yanagisawa, Kasumi; Owaki, Takeshi; Iwai, Masatoshi

PA Kobe Steel, Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 13 pp. CODEN: JKXXAF

PI JP 2005254106 A2 20050922

AB In forming the anticorrosive films, coating solns. contg. titanate coupling agents bearing ≥ 3 C ≥ 5 hydrophobic groups are applied on surface-treated steel sheets. The coating solns. contain 0.5-20 weight% of the coupling agents. The formed anticorrosive films show high performance and high adhesion with the surface-treated steel sheets (e.g., galvanized steel sheets).

IT Coupling agents

(titanate; corrosion prevention of metal-plated steel sheet by forming titanate coupling agent anticorrosive film)

IT 61417-49-0, KRTTS 65460-53-9, KR-46B 67691-13-8, KR38S 90959-84-5, KR9SA

(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 as determined by polarity of the polymer or substrate. Adhesion is largely effected by matching polarities. A coupling agent allows a bridging of dissimilar polarities. Anyone familiar with solvents or plasticizers knows that dispersion is effected by polarity with aromatic>naphthenic>aliphatic (paraffinic). Table 226 taken from reference [116] shows that a titanate can make a straight chain aliphatic mineral oil disperse more effectively than an aromatic oil.

Table 226

VISCOSITY EFFECTS OF KR TTS AND KR 38 TITANATES ON CaCO₃ INITIAL AND AGED 7 DAYS IN VARIOUS OILS (PLASTICIZERS)

Formulation	Brookfield Viscosity, CPS @ 25C								
	Oil (As Shown)	- 40.00g	Control No Titanate	Titanate Dispersion	- KR TTS Oil		Titanate Dispersion	- KR 38S Oil	
					Initial	Aged 7 Days		Initial	Aged 7 Days
Oils (Plasticizers)			Initial	Initial	Aged 7 Days	Aged 7 Days	Initial	Aged 7 Days	Aged 7 Days
Ester (DOP)			432,000	7,326	16,650	11,655	3,499	4,165	3,749
Mineral Oil (Prorex 907)			400,000	3,332	1,992	2,988	2,075	3,519	2,749
Paraffinic Oil (Sunpar 2150)			560,000	11,988	17,490	26,660	46,100	59,400	69,972
Paraffinic Oil (Sunpar 2280)			576,000	16,650	17,985	24,990	79,680	47,481	33,320
Naphthenic Oil (Circosol 415)			480,000	1,665	2,310	7,462	2,249	4,165	2,832
Aromatic Oil (Sundex 790)			9,600	9,628	15,770	9,960	4,998	6,560	6,240

A major advantage of Function 4 is the compatibilization effect of the pigment with the binder and reduction in the amount of solvent, diluent or plasticizer needed – usually about 15% reduction or more.

Although it is useful to assign a specific function as the principle reason why a coupling agent effect occurs, it is usually a symphony of the Six Functions that causes a titanate or zirconate to outperform a silane of similar polarity, such as comparing an aliphatic amino zirconate (NZ 44) with an aliphatic amino silane (A-1100). First we'll look at the CaCO₃ interface and then the fiberglass interface where silanes made the fiberglass industry and the first “plastic” car a reality as embodied in the Corvette automobile.

TI The interactions of silane and zirconate coupling agents with calcium carbonate

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SO International Journal of Polymeric Materials (2007), 56(3), 227-246 CODEN: IJPMCS; ISSN: 0091-4037

PB Taylor & Francis, Inc.

AB The structure and form of the deposit on calcium carbonate were studied for two types of silane coupling agents and a zirconate one. The structure of the deposited layers as well as their interactions with the filler were investigated by means of Fourier Transform Infra-Red Spectroscopy. The extent of the recovery was determined using the dissoln. method, which allowed measurement of the adsorbed quantity and to estimate the mol. area occupied by each coupling agent as well as the orientation of the mols. on the surface of CaCO₃. The structure of the aminosilane layers deposited on calcium carbonate appeared to be greatly influenced by the initial conditions of treatments. These include the pH, the concentration of the aqueous bath of impregnation, duration, and method of application. The results showed the formation of polymerized structures of the silanes on the surface of CaCO₃ and the deposit was composed of monomers and oligomers that were both physisorbed and chemisorbed. The study of the chemical structure of the zirconate agent that was deposited on the surface of CaCO₃ showed that a monomol. layer was chemical adsorbed. The physisorbed part of the zirconate was mainly constituted of monomers that were soluble in the solvent used for the extraction

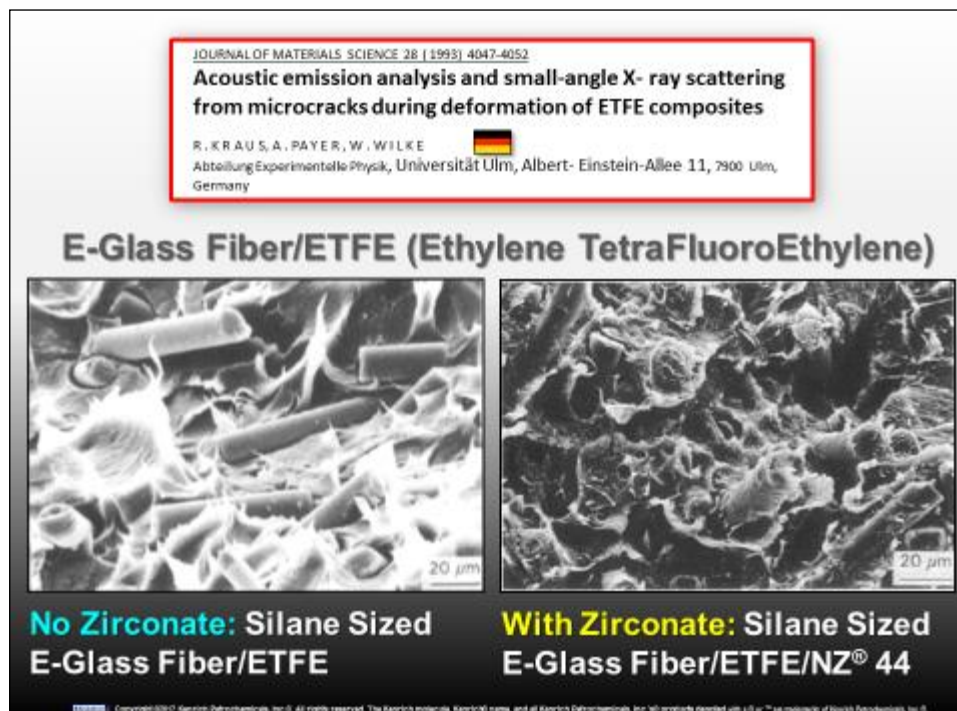
IT Coupling agents

(interactions of silane and zirconate coupling agents with calcium carbonate and structures of deposited coupling agents)

IT 471-34-1, Alcal UF-5, processes 919-30-2, A-1100 1760-24-3, Z-6020 103373-95-1, NZ 44

RL: PEP (Physical, engineering or chemical process); PROC (Process)

(interactions of silane and zirconate coupling agents with calcium carbonate and structures of deposited coupling agents)



TI Acoustic emission analysis and small-angle x-ray scattering from microcracks during deformation of ETFE composites

AU Kraus, R.; Payer, A.; Wilke, W.

CS Abt. Exp. Phys., Univ. Ulm, Ulm, 7900, Germany

SO Journal of Materials Science (1993), 28(15), 4047-52 CODEN: JMSTAS; ISSN: 0022-2461

AB During the deformation of unfilled and glass fiber-reinforced ethylene-tetrafluoroethylene copolymer (ETFE), microcracking was observed by small-angle x-ray scattering (SAXS). The fibers induce local stress maximum and increase the formation of microcracks. Fiber delamination processes were monitored by acoustic emission anal. The use of coupling agents improves the fiber-matrix adhesion and increases the mech. yield stress and decreases the delamination processes.

IT [103373-95-1](#), LZ 44 (coupling agents, for improved glass fiber adhesion in fluoropolymer composites)

Author's Note: Lubrizol purchased the LZ[®] (Liquid Zirconate) trademark from Kenrich Petrochemicals, Inc. and registered the NZ[®] (Neoalkoxy Zirconate) trademark – so, LZ 44 = NZ 44.

(5) Thermoset Function (Y) = thermoset functional groups such as acryl, methacryl, mercapto, amino, etc. react with various curatives to increase x-link network density or provide a UV/EB function. In the 1970's, the author theorized that if a trimethylolpropane trimethacrylate (CAS 3290-92-4) could be used a co-agent in free radical peroxide cured thermoset to increase the degree of crosslink – then why not put the trimethacrylate Function (5) on a Ti or Zr center, which will provide the same degree of reaction with free radicals to densify the cure, but also add Function (1) Coupling, Function (2) Titanium Catalysis, Function (3) carboxyl groups, and Function (4) interfacial compatibility between dissimilar substrates – and KR 33 and KR 39 titanates were invented with a Function (1) isopropoxy group, followed later by NZ 33 and NZ 39 zirconates with a Function (1) neoalkoxy group. It was theorized that the neoalkoxy group (neopentyl diallyl oxy) – as compared to the isopropoxy group – would provide the additional interfacial benefits of:

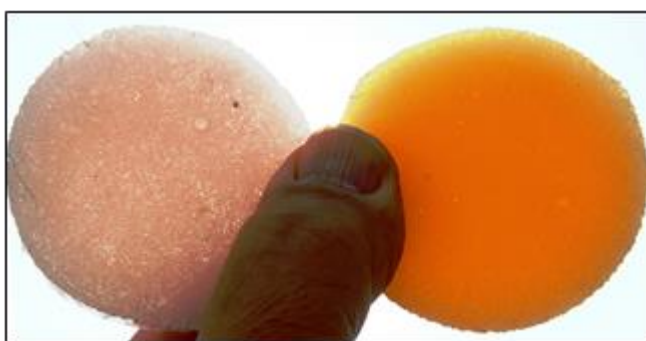
1. A neopositioned quaternary carbon for greater thermal stability;
2. Diallyl groups for secondary free radical crosslinking;
3. Proton coordination with surface hydrogens to deposit monolayers of Ti/Zr functionality without any leaving groups as occurs with silane hydrolysis and monoalkoxy titanate solvolysis.

In addition, Zirconium was selected over titanium because polymer compositions requiring acrylates or methacrylates would require the better transparency as compared to Titanium. Tetrafunctional organo-metallic compounds based on titanium (Ti), silicone (Si) and Zirconium (Zr) make useful coupling agents because the central metal's tetravalency is conducive to electron sharing. Titanium ester derived coupling agents have an advantage in their relative ease of manufacture and molecule building, thus providing specific function for a wide scope of composite applications as indicated in the selection tables in this manual. However, all materials have inherent natural limitations. For example, when coupling to metal substrate (M) the hydrolytic stability and strength of the Ti-O-M bond is superior to the Si-O-M bond. However, when coupling to silica, the extra strength of the Si-O-Si bond is often preferable to the Ti-O-Si bond-particularly in thermosets systems where dispersion requirements are non-critical.

Also, Titanium acts as an oxidizing agent in the presence of peroxide. Peroxide free radicals are thereby eliminated and cure efficiency is retarded – but, can be accelerated with heat thus surpassing cobalt naphthanate as a cure time accelerator. The Titanium effect can be used to eliminate the heat of exotherm in MEKP cured unsaturated polyesters, thus eliminating micro-bubbles and the need for topcoats.

Polyester Castings (2¼" x ¼" discs) – the control disc (left) cured in 40-min. shows aeration bubbles caused by cure exotherm of 282°F (138°C) while the CP-03B titanate disc (right) is free of bubbles. The hybrid titanate took 7-hrs to cure with no exotherm in the first 5.5-hours, then exotherm rises slowly from 77°F (25°C) to 90°F (32°C) at the 6-hr. point, then to 94°F (34°C) @ 6.5 hrs., then to 96°F (35.5°C) @ 7 hrs., and then cools to 77°F (25°C). The discs show (left) aeration bubbles caused by cure exotherm 282°F (138°C) while the titanate disc (right) is free of bubbles as is made apparent by holding the discs to

the light suggesting a significantly reduced need for a gel coat and better transfer of stress/strain. Drop impact of the polyester castings (2¼" x ¼" discs) from a 6' height is shown. The control disc (left) was dropped once and shattered and pieced together for the photo. The titanate disc (right) bounced on the 1st drop and did not break and broke on the 2nd drop and was pieced together as shown.



Aged Silane Sized Fiberglass Windmill Blades Headed to Landfill Due to Intefacial Failure

Zirconium is an activator for peroxide resulting in a desirable acceleration of peroxide and air-based cures – the basis for many thermoset and coatings systems – and perhaps more effective in UV/EB cures.

Titanates offer the possibility of undesirable color formation experienced when they come in contact with additives containing phenolic functionality. Phenolic functionality is encountered in the form of: heat and light stabilizers (antioxidants) used in thermoplastic vinyl and polyolefin systems, alkyds and urethanes. Phenolics are also used as chain stops in polyester systems, urethanes, alkyds and acrylics. In common with virtually all Titanium IV derivatives, titanate based coupling agents (including neoalkoxy and acetylacetonate) produce colored pigments on contact with phenolic containing free hydroxy groups. The color intensity developed is proportional to the increasing concentration and conjugation of the phenolic hydroxyl from yellow through orange to red and burgundy.

Zirconates in general are not color body producers in contact with phenols other than nitrophenols. Subject organotitanate and organozirconate coupling agents do not interact with hindered amines (light stabilizers and/or antioxidants-HALS) under common operating conditions. In unfilled plastics, the zirconates often provide superior UV stability when compared to the titanates. Zirconium chemistry provides a functional equivalent alternative to silanes and titanates in these instances. Neoalkoxy zirconates also provide novel opportunities for the adhesion of fluorinated polymers to metal substrates because the introduction of a zirconate at the interface results in a metal oxygen zirconium VI organo fluoride.

Some work by others is next shown based on Function (5) effects:

TI Surface functionalization of pigments and/or dyes for radiation curable ink printing and coating applications

IN Wang, Zhikai; Wu, Bin

PA UCB, S.A., Belg.

SO U.S. Pat. Appl. Publ., 7 pp., Cont.-in-part of U.S. Ser. No. 736,129,

PI US 20040050299 A1 20040318 US 2003-450270 20031017

US 6913639 B2 20050705

WO 2002048272 A1 20020620 WO 2001-US47241 20011210

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW

RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, CH,

CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR,

BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

US 20050155522 A1 20050721 US 2005-42077 20050126

PRAI US 2000-736129 B2 20001215

WO 2001-US47241 W 20011210

US 2003-450270 A3 20031017

AB Functionalized pigment compns. are produced by reacting a radiation-reactive organometallic coupling agent with a pigment/dye. A composition contained Uvecoat 2000 and RX-05613 (zirconium acrylate-functionalized TiO₂).

IT [146987-99-7](#), NZ 39

TI Production of inorganic/organic hybrid nanocomposites using ultrasonic agitation

IN Wang, Zhikai

PA UCB, S.A., Belg.

SO PCT Int. Appl., 25 pp. CODEN: PIXXD2

PI WO 2003055939 A1 20030710 WO 2002-EP14545 20021219

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN,

CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,

LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH,

PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ,

UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,

KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES,

FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR, BF, BJ,
 CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
 US 20030148042 A1 20030807 US 2001-28735 20011228
 CA 2468956 A1 20030710 CA 2002-2468956 20021219
 AU 2002356776 A1 20030715 AU 2002-356776 20021219
 EP 1461380 A1 20040929 EP 2002-805762 20021219
 R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
 IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK
 CN 1602332 A 20050330 CN 2002-824326 20021219
 JP 2005512809 T 20050512 JP 2003-556464 20021219
 US 20050084607 A1 20050421 US 2004-497782 20040607
 MX 2004006268 A 20040927 MX 2004-6268 20040624
 PRAI US 2001-28735 A 20011228
 WO 2002-EP14545 W 20021219

AB A method for producing an org./inorg. hybrid nanocomposite comprises (a) subjecting a dispersion of inorg. particles to ultrasonic agitation to produce a dispersion of nanosized inorg. particles having at least one linear dimension of a mean size from 0.1 to 250 nm, and (b) reacting the nanosized inorg. particles with an organic coupling agent to modify the surface of the particles to inhibit agglomeration of the particles. Thus, alumina C nanoparticles having an average size of 121 nm were produced by ultrasonic and mech. agitation in methanol for 1 h, mech. agitation only produced alumina particles having an average size of 15-20 μ m. The alumina nanoparticles were surface modified with 1-5%-methanol solution of NZ 39, and the dispersions were homogeneously mixed with an organic resin producing a UV curable nanocomposite comprising alumina nanoparticles (10.0), NZ 39 surface modifier (0.05), Z 6030 adhesion promoter (0.48), Ebecryl 8402-tripropylene glycol diacrylate 50/50 mixture (91.03), and Irgacure 184 photoinitiator (3.64 parts).

IT [146987-99-7](#), NZ 39

TI Reactive and gel-free compositions for making hybrid composites

IN Wang, Zhikai; Black, Carol; Qiao, Jun

PA UCB, S.A., USA

SO U.S. Pat. Appl. Publ., 7 pp. CODEN: USXXCO

PI US 20040044095 A1 20040304 US 2002-231137 20020830

US 6838536 B2 20050104

CA 2496457 A1 20040311 CA 2003-2496457 20030828

WO 2004020485 A1 20040311 WO 2003-EP9533 20030828

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN,
 CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
 GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
 LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM,
 PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN,
 TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,

KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES,

FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR,

BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

AU 2003264119 A1 20040319 AU 2003-264119 20030828

EP 1539833 A1 20050615 EP 2003-790930 20030828

EP 1539833 B1 20070523

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,

IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK

CN 1678642 A 20051005 CN 2003-820670 20030828

CN 100386348 C 20080507

JP 2005536617 T 20051202 JP 2004-532129 20030828

AT 362944 T 20070615 AT 2003-790930 20030828

MX 2005001916 A 20050829 MX 2005-1916 20050217

PRAI US 2002-231137 A 20020830

WO 2003-EP9533 W 20030828

AB A substantially reactive and gel-free compn. which comprises: (A) particles capable of reaction with a radiation curable resin (e.g., MA-ST-S); (B) a coupling agent for modification of the surface of the particles (e.g., Ken-React NZ 39); (C) a radiation curable resin (e.g., Ebecryl 1290); and (D) a radiation curable salt capable of inhibiting gel

formation in the composition (e.g., calcium acrylate dihydrate). Upon radiation cure of the composition, composites with excellent mech. properties are obtained.

IT [146987-99-7](#), Ken-React NZ 39

TI Laser stereolithography of ZrO₂ toughened Al₂O₃

AU Licciulli, A.; Esposito Corcione, C.; Greco, A.; Amicarelli, V.; Maffezzoli, A.

CS Dipartimento di Ingegneria dell'Innovazione, Università degli Studi di Lecce, Lecce, 73100, Italy

SO Journal of the European Ceramic Society (2005), 25(9), 1581-1589 CODEN: JECSEJ; ISSN: 0955-2219

PB Elsevier B.V.

AB Ceramic laser stereolithog. is a manufg. process suitable candidate for the production of complex shape tech. ceramics. The green ceramic is produced layer by layer through laser polymerization of UV curable ceramic suspensions. A number of critical issues deserve attention: high solid loading and low viscosity of the suspensions, high UV reactivity, prevention of interlayer delamination in the green and in the sintered body, good mech. performance. In this work, ZrO₂ reinforced Al₂O₃ components have been obtained from an acrylic modified zircon loaded with alumina powders. The zircon compound is effective as organic photoactivated resin and allows the dispersion of a high volume fraction of Al₂O₃ powder (up to 50 volume%) while keeping viscosity at reasonable low values. The zircon compound also represents a liquid ceramic precursor that converts to oxide after burning out of the binder. Thanks to the good dispersion of the alumina powder in the zircon acrylate, a uniform dispersion of ZrO₂ submicron particles is obtained after pyrolysis. These are located at the grain boundaries between alumina grains. Formation of both monoclinic and tetragonal ZrO₂ occurs as evidenced by XRD. No delamination occurs in bending tests as evidenced by SEM fractog., satisfactory modulus and strength values were concurrently found.

IT [146987-99-7](#), Ken-React NZ 39

TI Compositions containing crosslinking agents suitable as optical fiber coatings

IN Fabian, Michelle D.

PA Corning Incorporated, USA

SO PCT Int. Appl., 36 pp. CODEN: PIXXD2

PI WO 2002094730 A2 20021128 WO 2001-US51005 20011024

WO 2002094730 A3 20030227

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW

RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR

US 20030053781 A1 20030320 US 2000-726002 20001129

US 6553169 B2 20030422

AU 2001297838 A1 20021203 AU 2001-297838 20011024

EP 1337490 A2 20030827 EP 2001-274044 20011024

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR

JP 2004536758 T 20041209 JP 2002-591407 20011024

PRAI US 2000-726002 A 20001129

WO 2001-US51005 W 20011024

AB The compn. for optical fiber coatings includes a coupling agent devoid of any Si containing compound and has, after curing, a Young's modulus of ≥ 50 MPa. The coupling agent is capable of bonding to an organic compound and comprises ≥ 1 compound selected from titanate-containing compds., zirconate-containing compds. and mixts. thereof. It is preferred that the coupling agent is included in an optical fiber layer that is not $< 5 \mu$ away from an outer surface of the glass fiber. The coupling agent-containing composition is applied non-directly to the optical fiber surface.

IT [64157-14-8P](#), Ken-React KR 55

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(Ken-React KR 55, coupling agent for optical fiber coating; compns. containing crosslinking agents suitable as optical fiber coatings)

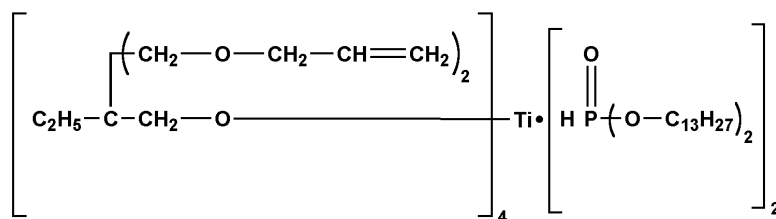
IT [146987-99-7P](#), NZ 39

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(NZ 39, coupling agent for optical fiber coating; compns. containing crosslinking agents suitable as optical fiber coatings)

IT **153590-16-0P**, NZ 33

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(coupling agent for optical fiber coating; compns. containing crosslinking agents suitable as optical fiber coatings)

Author's note: Apparently Fabian considered the tetradiallyl groups of KR 55 as a suitable unsaturated crosslink site candidate as shown in its structure next:



TI Surface functionalization of pigments and/or dyes for radiation-curable printing inks and coatings and their preparation

IN Wang, Zhikai; Wu, Bin

PA UCB, S.A., Belg.

SO PCT Int. Appl., 18 pp. CODEN: PIXXD2

PI WO 2002048272 A1 20020620 WO 2001-US47241 20011210

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW

RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

CA 2431410 A1 20020620 CA 2001-2431410 20011210

AU 2002026022 A 20020624 AU 2002-26022 20011210

EP 1358282 A1 20031105 EP 2001-995444 20011210

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR

JP 2004537609 T 20041216 JP 2002-549793 20011210

CN 1220736 C 20050928 CN 2001-821865 20011210

MX 2003005349 A 20040420 MX 2003-5349 20030613

US 20040050299 A1 20040318 US 2003-450270 20031017

US 6913639 B2 20050705

PRAI US 2000-736129 A2 20001215

WO 2001-US47241 W 20011210

AB The functionalized pigment is prep'd. by reaction a pigment and/or a dye with a radiation-reactive organometallic coupling agent (RO)_mM(OXR'Y)_n (M = metal atom from IIa, IIIb, IVb, Vb, VIb, VIIb, VIII, Ib, IIb, and IIIa; R = (un)substituted C1-8 alkyl; X = organic functional group; R' = organic group; Y = radiation curable functional group; m, n = 1-3). Thus, a UV-curable powder coating composition comprising Uvecoat 2000 (UV-curable powder coating resin) 72.1, Irgacure 819 (photoinitiator) 3.5, TiO₂ 20.0, RX 05613 [NZ 39 (neopentyl(diallyl)oxytriacyl zirconate)]-treated TiO₂ 4.0 and degassing agent 0.4 parts showed gloss (60°) 99.0%, Haze 40.0 and pencil hardness (scratch) 3H.

IT **146987-99-7**, Ken-React NZ 39

TI FT-IR microscopic studies on coupling agents: treated natural fibres

AU Singh, B.; Gupta, M.; Verma, Anchal; Tyagi, O. S.

CS Central Building Research Institute, Roorkee, 247667, India

SO Polymer International (2000), 49(11), 1444-1451 CODEN: PLYIEI; ISSN: 0959-8103

PB John Wiley & Sons Ltd.

AB Natural fibers (sisal) were treated with various coupling agents such as organosilane, zirconate, titanate and N-substituted methacrylamide. The nature of the adsorbed chemical species on the fiber surface was analyzed by

Fourier transform IR microscopy (FT-IR). The presence of precipitated oligomers on the surface was confirmed by the appearance of hydrogen-bonded carbonyl group and unsatn. bands. The results showed an irregular physisorption/chemisorption of coupling agents, their penetration beyond the surface, and a decrease in the hydrophilicity of fibers. SEM and dynamic contact angle studies on the fibers supported these findings. FT-IR microscopy in its reflectance mode was more effective in ascertaining the chemical nature and structure of adsorbed layers onto sisal fiber surfaces compared with DRIFT and transmission spectroscopy. The difference in the properties of untreated and chemical treated fibers has also been verified in the polymer composites.

IT [103432-54-8](#), LICA 38 [146987-99-7](#), NZ 39

TI Influence of fiber surface treatment on the properties of sisal-polyester composites

AU Singh, B.; Gupta, M.; Verma, Anchal

CS Central Building Res. Inst., Roorkee, 247 667, India

SO Polymer Composites (1996), 17(6), 910-918 CODEN: PCOMDI; ISSN: 0272-8397

PB Society of Plastics Engineers

AB The effect of several chem. treatments, viz. organotitanate, zirconate, silane, and N-substituted methacrylamide, on the properties of sisal fibers used as reinforcement in unsatd. polyester resin (.apprx.50 vol%) was investigated. An improvement in the properties was observed when sisal fibers were modified with surface treatments. Under humid conditions, a decrease of 30 to 44% in tensile and 50 to 70% in flexural strength has been noted. The strength retention of surface-treated composites (except silane) is high compared with untreated composites. It is observed that n-substituted methacrylamide-treated sisal composites exhibited better properties under dry as well as wet conditions. Fractog. evidence such as fiber breakage/splitting and matrix adherence on the pulled-out fiber surface explains such behavior.

IT [146987-99-7](#), NZ 39 [103432-54-8](#), LICA 38

TI Process for the surface modification of particles

IN Nelson, James M.; Archibald, Matthew N.; Thompson, Wendy L.; Tiefenbruck, Grant F.

PA 3M Innovative Properties Company, USA

SO PCT Int. Appl., 29 pp. CODEN: PIXXD2

PI WO 2009131910 A2 20091029 WO 2009-US40947 20090417

WO 2009131910 A3 20100114

W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AP, EA, EP, OA

EP 2283081 A2 20110216 EP 2009-733720 20090417

R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LI, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR, AL, BA, RS

KR 2011015572 A 20110216 KR 2010-7026319 20090417

CN 102015913 A 20110413 CN 2009-80114749 20090417

JP 2011518919 T 20110630 JP 2011-506371 20090417

US 20110048923 A1 20110303 US 2010-988092 20101116

US 8318120 B2 20121127

PRAI US 2008-47849P P 20080425

WO 2009-US40947 W 20090417

AB A method for the prepn. of functionalized particles includes providing a feedstock made of particles, a surface treatment agent reactive with the particles, and solvent. The feedstock is exposed to microwave radiation to heat the feedstock and react the particles with the surface treatment agent to provide the functionalized particles in .ltorsim.60 min.

IT [103406-74-2](#), Lica 09 [103432-54-8](#), Lica 38 [146987-99-7](#), Ken-React NZ 39

IT [146987-99-7DP](#), Ken-React NZ 39, silica surface-modified with

IT [103432-54-8DP](#), Lica 38, reaction products with ultramarine blue 690 pigment

TI Pressure-sensitive adhesive compositions for optical films, optical films having adhesive layers therefrom, and imaging devices equipped with same optical films

IN Inoue, Shinichi; Yasui, Atsushi; Toyama, Yusuke; Hosokawa, Toshitsugu

PA Nitto Denko Corp., Japan

SO Jpn. Kokai Tokkyo Koho, 18pp. CODEN: JKXXAF

PI JP 2010065102 A 20100325 JP 2008-231160 20080909

PRAI JP 2008-231160 20080909

AB The title adhesive compns. contain 100 parts base polymers and 0.001-50 parts titanium-containing coupling agents and/or zirconium-containing coupling agents. The compns. may further contain 0.005-5 parts crosslinking agents. The title adhesive layers show durable adhesion without foaming and delamination in heat moist conditions. Thus, an adhesive layer, formed from a composition containing 99:1 Bu acrylate-4-hydroxybutyl acrylate copolymer 100, trimethylolpropane tolylene diisocyanate adduct (3:1) (Coronate L) 0.4, and titanium coupling agent (Plenact KR TTS) 0.5 parts, on a release film, was bonded to an optical sheet polarizer to give an adherent optical film, which was bonded to a glass, showing no foaming and delamination after 500 h aging in atmospheric with 95% relative humidity at 80°C.

IT [61417-49-0](#) [153590-16-0](#), NZ 33

TI Pretreatment agent containing zirconium coupling agent for adhesion of metal oxide ceramics

IN Morosawa, Yusuke; Kimura, Mikio

PA Tokuyama Dental Corp., Japan

SO Jpn. Kokai Tokkyo Koho, 12pp. CODEN: JKXXAF

PI JP 2009209109 A 20090917 JP 2008-55465 20080305

JP 5164614 B2 20130321

PRAI JP 2008-55465 20080305

AB The invention relates to a pretreatment agent (primer agent) for applying on the surface of metal oxide ceramic, especially a dental ceramic material, for improving the adhesiveness of the ceramic material with polymerizable composition, especially dental resin cement, wherein the pretreatment agent contains a zirconium coupling agent in an organic solution. A kit for adhesion of a metal oxide ceramic-based dental prosthesis material to dentin, including the pretreatment agent and a dental resin cement is also disclosed. For example, a zirconium coupling agent (NZ 33) 5 g was dissolved in ethanol 99.5 g to give a pretreatment agent. The pretreatment agent was applied on a polished and dried zirconium oxide, and attached a stainless steel stick with an adhesive resin cement (Bistite II) to examine the adhesion property.

IT [117753-51-2](#), KZ 55 [121543-39-3](#), KZ TPP [153590-16-0](#), NZ 33

RL: THU (Therapeutic use); BIOL (Biological study); USES (Uses)

(pretreatment agent containing zirconium coupling agent for adhesion of metal oxide ceramics)

TI Radiation-curable hybrid composition with high refractive index for coating and its production

IN Wang, Zhikai; Tweedy, Harrell

PA Cytec Surface Specialties, S.A., Belg.

SO PCT Int. Appl., 35pp. CODEN: PIXXD2

PI WO 2008058849 A1 20080522 WO 2007-EP61770 20071031

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

EP 2084216 A1 20090805 EP 2007-822117 20071031

R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR

KR 2009088370 A 20090819 KR 2009-7009912 20071031

JP 2010509476 T 20100325 JP 2009-536695 20071031

IN 2009DN01852 A 20090529 IN 2009-DN1852 20090320

CN 101535391 A 20090916 CN 2007-80042247 20090513

US 20100075062 A1 20100325 US 2009-514632 20090602
PRAI US 2006-858942P P 20061115
US 2007-929646P P 20070706
WO 2007-EP61770 W 20071031

AB The process for prep. a hybrid org.-inorg. nanocomposite used to prep. high refractive index ($n_D \geq 1.52$) protective coatings for brightness enhancers for LCDs, comprises (a) diluting an aqueous solution of inorg. nanoparticles (such as ZrO_2) with a first solvent (such as acetic acid or Me Et ketone) to form a dispersion; (b) adding surface modifiers (such as 1-benzoyl acetone, di-Ph acetic acid, di-Ph phosphonic acid, ethylene methacrylate phosphate; 2,2,6,6-tetramethyl-3,5-heptanedione or neopentyl(diallyl)oxy trimethacryl zirconate); (c) removing the first solvent to enhance the interactions between the surface modifier and nanoparticles; (d) washing the resultant slurry of surface modified lipophilic nanoparticles by repeated dilution with an azeotropic solvent mixture (such as Et acetate, toluene and water) and distillation to remove low RI impurities and/or OH groups, (e) adding a radiation curable polymer precursor (such as an optionally brominated epoxy acrylate to the mixture opt with a photo initiator (PI); and (f) removing the remaining solvent to form a solid composite comprising an intimate mixture of surface modified inorg. nanoparticles and uncured polymer precursor.

IT [153590-16-0](#), NZ 33

TI Electrical devices having an oxygen barrier coating

IN Galla, Matthew P.

PA Tyco Electronics Corporation, USA

SO Eur. Pat. Appl., 17 pp. CODEN: EPXXDW

PI EP 1632960 A1 20060308 EP 2005-108043 20050902

EP 1632960 B1 20101229

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, PL, SK,
BA, HR, IS, YU

US 20060051588 A1 20060309 US 2004-934349 20040903

US 7371459 B2 20080513

CN 1744792 A 20060308 CN 2005-10099690 20050902

CN 1744792 B 20110831

JP 2006121049 A 20060511 JP 2005-254692 20050902

JP 4942318 B2 20120530

US 20080187649 A1 20080807 US 2008-80657 20080402

US 7632373 B2 20091215

JP 2012015553 A 20120119 JP 2011-226116 20111013

PRAI US 2004-934349 A 20040903

JP 2005-254692 A3 20050902

AB An elec. device includes two electrodes and a conductive polymer layer, containing a mixture of a polymer and a conductive filler, separating the electrodes. An O barrier material containing a thermosetting polymer component is present on the exposed surface of the conductive polymer layer that is not in contact with the laminar electrodes. The O barrier material may be a polyamine-polyepoxide material, and may provide for acceptable barrier properties over a wide range of humidity levels.

IT [153590-16-0](#), NZ 33

TI Inverse gas chromatography in the examination of modified fillers

AU Voelkel, Adam

CS Faculty of Chemical Technology, Institute of Chemical Technology and Engineering, Poznan University of Technology, Poznan, 60-965, Pol.

SO Macromolecular Symposia (2003), 194(Eurofillers'01 Conference, 2001), 27-37 CODEN: MSYMEC; ISSN: 1022-1360

PB Wiley-VCH Verlag GmbH & Co. KGaA

AB Dispersive and sp. surface properties of silica modified with titanium and zirconium coupling agents were characterized by means of inverse gas chromatog. This method was also successfully applied in the examination of raw and modified silicates.

IT [61417-49-0](#), KR TTS [61417-55-8](#), KR 9S [61417-56-9](#), KR 26S [61548-33-2](#) [103373-95-1](#), NZ 44

[109766-35-0](#) [146987-99-7](#) [153590-16-0](#), NZ 33

TI Effects of coupling agents on mechanical properties of metal oxide-polymethacrylate composites

AU Yoshida, K.; Greener, E. H.

CS Dent. Sch., Northwestern Univ., Chicago, IL, 60611, USA

SO Journal of Dentistry (1994), 22(1), 57-62 CODEN: JDENAB; ISSN: 0300-5712

AB The effects of several coupling agents on the mech. properties of metal oxide-polymethacrylate composites reinforced with titanium dioxide (TiO₂), aluminum oxide (Al₂O₃), silica (SiO₂) and zirconium dioxide (ZrO₂), as fillers for opaque resins were assessed. The prepared composites consist of 24.75 weight% triethyleneglycol dimethacrylate (TEGDMA), 24.75 weight% 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA), 0.5 weight% benzoyl peroxide (BPO) and 50 weight% metal oxide filler. Three methacrylate coupling agents--methoxydiethyleneglycol trimethacryloyl titanate, 3-trimethoxysilylpropyl methacrylate and 2,2-di(allyloxymethyl)butyl trimethacryloyl zirconate--were used for surface treatment of TiO₂, SiO₂ and ZrO₂, resp., while Al₂O₃ was treated with 4-methacryloxyethyl trimellitate anhydride (4-META). 4-META was also adopted as a coupler for TiO₂, SiO₂ and ZrO₂ powders. Compressive and transverse strength specimens were prepared with the use of coupled or untreated filler and heat cured at 110°C and 0.5 MPa for 30 min. All coupled metal oxide composites had significantly higher compressive and transverse strengths than did untreated composites after 1 mo's immersion in 37°C water. SEM of fractured TiO₂ composite surfaces after storage in water for 1 mo showed an interface failure between TiO₂ filler and matrix resin for untreated TiO₂ composite and cohesive failures within the resin for treated specimen. Similar results were observed with silanated SiO₂ composite. However, cohesive and interface failures were seen in zirconated ZrO₂- and 4-META-coupled Al₂O₃ composites. Thus, titanated TiO₂-polymethacrylate composite may be useful as a composite pigment for opaque resin materials.

IT [153590-16-0](#), NZ 33

Why not surface modify ordinary Portland cement and enhance its nano-reaction with water to reduce the water:cement ratio by 31% to equivalent slump (flow) ...

or compatibilize ordinary P

Portland Cement	
Oxide	% content
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	0.4–1.3
SO ₃	1.3–3.0

Oil Soaked Sea Water Sand Filled Water / Portland Cement

(45) Date of publication and mention of the grant of the patent: 12.04.2017 Bulletin 2017/15

15 No Titanate 18 With Titanate

TI Reinforcing of synthetic rubber with waste cement dust modified by coupling agents

AU Krysztafkievicz, Andrzej; Jesionowski, Teofil; Rager, Bozena

CS Institute of Technology and Chemical Engineering, Poznan University of Technology, Poznan, 60-965, Pol.

SO Journal of Adhesion Science and Technology (1997), 11(4), 507-517 CODEN: JATEE8; ISSN: 0169-4243

PB VSP

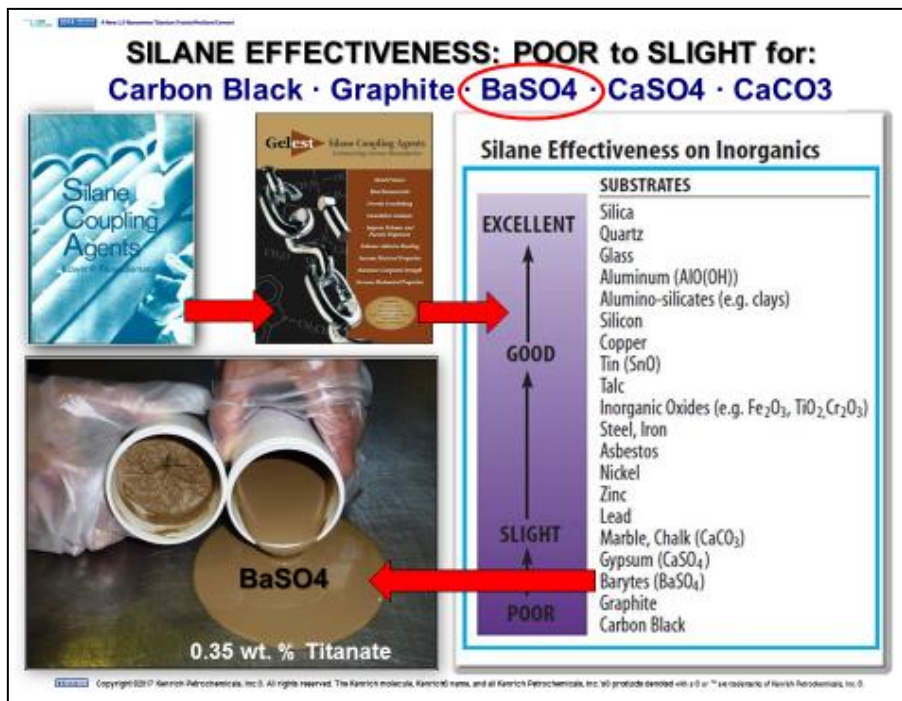
AB A method for utilizing waste cement dusts as fillers for styrene-butadiene rubber (SBR) is presented. Such fillers were introduced into the elastomer system together with the waste silica (post-HF silica). The surfaces of both fillers were modified using pro-adhesion compds. (silane and titanate coupling agents). The modified fillers

evidently increased strength parameters of the studied vulcanizates. This was attributed to the hydrophobization of their surfaces and to the introduction to the surfaces of functional groups with chemical affinity to the polymer.
 IT [61417-49-0](#), KR TTS [61436-48-4](#), KR 33CS

TI Modified waste cement dust-fillers for rubber mixtures

AU Krysztalkiewicz, Andrzej; Maik, Marek; Rager, Bożena
CS Inst. Technol. Inżynierii Chem., Politechnika Poznańska, Poznań, 60-965, Pol.
SO Fizykochemiczne Problemy Mineralurgii (1995), 29, 169-81 CODEN: FPMIDB; ISSN: 0137-1282
PB Wydawnictwo Politechniki Wrocławskiej

AB The dust surface was modified with silane and titanate coupling agents and the physicochem. properties of the resulting waste cement dust were determined. The effect of the modifier type and its amount on the strength of Ker 1500 butadiene-styrene rubber was investigated.
 IT [61417-49-0](#), KR TTS [61436-48-4](#), KR 33CS



TI The effect of surface modification on physicochemical properties of precipitated silica

AU Krysztalkiewicz, A.; Rager, B.; Jesionowski, T.
CS Inst. of Technology and Chemical Engineering, Poznań University of Technology, Poznań, 60-965, Pol.
SO Journal of Materials Science (1997), 32(5), 1333-1339 CODEN: JMTSAS; ISSN: 0022-2461

PB Chapman & Hall

AB The main goal of this study was to obtain hydrophobic silica whose properties would allow their application as plasto- and elastomer fillers. Thus, hydrated silica was modified by silane and titanate coupling agents. The modification procedure and appropriate modification apparatus were developed. The degree of silica surface modification was evaluated by different methods. As grounds for this evaluation, changes in the physicochem. properties, brought about by the condensation reaction of surface silanol groups with alkoxy or hydroxyl groups of the mols. of coupling agents, were used. The degree of hydrophobicity of the silica surface was determined on the basis of the heat of immersion of this surface, and silanol groups were identified by the IR spectroscopy. Moreover, changes in the tendency to form agglomerates and aggregates of mols. were studied by microscopy, it was found that modification with silane and titanate coupling agents leads to an increase in silica activity. Application of these agents results in the change of the hydrophilic character to the hydrophobic one.

IT [61417-49-0](#), KR TTS [61436-48-4](#), KR 33CS

TI Surface modification of highly dispersed rubber fillers and pigments by titanate proadhesive and hydrophobic compounds

AU Krysztalkiewicz, A.; Rager, B.; Maik, M.

CS Institute Technology Chemical Engineering, Technical University Poznan, Poznan, Pol.

SO Colloid and Polymer Science (1994), 272(12), 1547-59 CODEN: CPMSB6; ISSN: 0303-402X

PB Steinkopff

AB A method of modifying silicate and carbonate fillers with titanate coupling agents and proadhesive agents was worked out. The modification aimed at hydrophobization of filler surface by introduction to the surface of functional groups with chemical affinity to polymers. Optimum amts. of modifying substances and appropriate conditions for performing the modification process were established. The obtained fillers showed a high degree of hydrophobicity. The modified fillers were applied in rubber mixts. based on butadiene-styrene rubber or natural rubber, in polyurethanes, in PVC, and as pigments in oil dyes of high corrosive resistance.

IT [61436-48-4](#), Isopropyltrimethacryl titanate, [61417-49-0](#), KR TTS

TI Moisture-resistant insulating mica tape containing monoalkoxy titanate

IN Roberts, Jonathan W.

PA Essex Group, Inc., USA

SO U.S., 8 pp. CODEN: USXXAM

PI US 4374892 A 19830222 US 1981-270174 19810603
CA 1171349 A1 19840724 CA 1982-403430 19820520
AU 8284433 A 19821209 AU 1982-84433 19820603
AU 546966 B2 19850926
PRAI US 1981-270174 A 19810603

AB A moisture-resistant elec. insulation tape having a good dielec. dissipation factor comprises a sheet of mica paper impregnated with a B-staged polybutadiene (I) [9003-17-2] resin and 0.1-0.35% (based on mica weight) of a monoalkoxy titanate containing long saturated chains or reactive functional groups, a woven glass scrim next to the mica paper, and a rubber sealing layer next to the glass scrim and (optionally) next to the mica paper. Thus, a tape was constructed using a 0.0036-cm thick poly(ethylene terephthalate) [25038-59-9] mat, a 0.015-cm thick mica layer, and a 0.005-cm thick glass scrim. I containing isopropyl trimethacryloyl titanate (KR 33CS)(II) [61436-48-4](#) was applied with a brush, and the resin passed through the glass scrim into the mica paper. This was followed by coating with Kraton 1107 rubber in the same manner. After immersion in H₂O for 10 min, the tapes showed an average H₂O absorption of 0.44%, as compared to 21.8% for a similar tape containing no II. After heat aging for .apprx.491.25 h at 180°, the dielec. dissipation factor at 155° was 0.0049 at 10 V/mil, 0.0049 at 20 V/mil, 0.0049 at 30 V/mil, 0.0050 at 40 V/mil, 0.0050 at 50 V/mil, 0.0051 at 60 V/mil, and 0.0051 at 70 V/mil, as compared to 0.0051, 0.0052, 0.0052, 0.0053, 0.0053, 0.0055, and 0.007, resp., for the tape containing no II.

IT [61436-48-4](#) KR 33DS, [67691-13-8](#) KR 38S

(6) **Hybrid Function -R'Y**_{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).

Suggested Titanate and Zirconate Anticorrosion Mechanisms for Coatings on Metal According to the Six Functions – Four anticorrosion mechanisms are offered:

1. Substrate - reduce anodic activity by chelating and/or bonding to metal surface according to Function 1 by solvolysis, chelation or proton coordination depending on the chemical structure of the titanate or zirconate used.
2. Interface - reduce cathodic activity by hydrophobic ligands (Function 4) that minimize concentrations of H⁺ and/or H₂O at the metal surface and in the voids or on the surface of the pigments and extenders. Figure 9 depicts a monolayer of phosphato titanate to create a “Phosphatized” (Function 3) substrate. Figure 10 is a KEVEX analysis showing the Function 1 atomic deposition of Function 2 Ti (Titanium) and Function 3 P (Phosphorous) on a Cu (Copper) metal substrate by use of pyrophosphato titanate (KR 238S – cf. Table 1). Figure 11 shows the oxidative protection afforded to brass powder by deposition of 0.35% LICA 38 (cf. Table 1) in a 25% brass/xylene slurry followed by forced air oven drying @ 200°C for 24-hours..
3. Barrier Film - improve barrier film adhesion via coupling of the film to the metal, which maintains blocking properties to ions, O₂ and H₂O.
4. Barrier Film Pigments and Extenders - improve barrier film properties with respect to ions, O₂ and H₂O by enhancing the uniformity and impermeability of the film via optimum dispersion of pigments and extenders in the barrier film to create a void-free, true continuous phase. Figure 12 shows the hydrophobicity created by a 1.5 nanometer atomic monolayer of KR TTS on pure CaCO₃ slabs. For example, Table 5 – Figures 7 and 8 demonstrated that silica containing 0.5% KR 38S titanate can replace basic lead silico chromate in an epoxy polyamide coating on steel.

Application Principles – Two principles govern coupling agent applications are: *uniform distribution* of the coupling agent in the liquid phase or before or during the polymer melt (powder coatings, plastics, elastomers) for uniform coupling/catalysis of the next to be added filler/fiber interfaces and *high specific energy input during* the liquid polymer dispersive mix or melt phase for maximum shear/work energy for optimal dispersion so that coupling at the filler/fiber interface and catalysis in the polymer interphase are made complete. The typical practice for a coatings formulator – after checking for coupling agent solubility in the medium to be used – should be to add the coupling agent early in the grind with polymer/monomer/oligomer/solvent/water – disperse – and then add pigments and extenders and other additives under high shear. The titanate or zirconate must be completely soluble in the organic phase or soluble, co-solvated or well emulsified in the water phase (see later discussion of Table 22) to form atomic monomolecular layers on the interface. Small laboratory test batches require a titanate wash of the mixing bowls, weigh out dishes and utensils, and all surfaces of the dispersion equipment before the first test batch. The wash solution should be 0.25% titanate in 99.75% of solvent or water.

Uniform Distribution – In the Polymer Melt Phase Before Pigment/Filler Contact for Uniform Coupling and Catalysis – Coupling in atomic monolayers may take place on the surface of a particulate in both the organic and water phase. But, in order to effect atomic monomolecular coupling (less than 2-nm), the titanate or zirconate must be solubilized in the organic (solvent, plasticizer, polymer) phase or finely emulsified into the water followed by addition of the particulate or reinforcing fiber. For example, Figure 13 shows that ceramic powder mixed in solvated PTFE (left jar) is incompatible and not wetted out exhibiting phase separation. The center jar had a neoalkoxy phosphato titanate (NZ 12) dispersed into water/PTFE followed by addition of ceramic. Since the NZ 12 is insoluble in water – as are most zirconates – the ceramic is unwetted, phase separated and the zirconate gave no benefit. The right jar had the organosoluble NZ 12 added to a solvent/PTFE at RT followed by ceramic to create a stable and homogenous mixture. Figures 14 and 15 show the wetting of recycled flax fibers and recycled kraft fibers in water using 2 wt.% of an emulsifiable 25% active isostearyl titanate (KR TTS WE25) that has been rendered emulsifiable by the addition of 3-parts of a non-ionic surfactant. As a rule, any emulsified titanate should provide a clear or uniform milky solution with no precipitate in water at 5% dosage. If the emulsified titanate produces a turbid solution the titanate is unable to work at the atomic level and is not effective.

If the organic phase has a high molecular weight, then sufficient shear and high mixing torque is needed to assure titanate distribution at the atomic level – before the addition of fillers or fibers to be next coupled. If solubility cannot be achieved in the organic phase at room temperature or below the flashpoint of initial boiling point of the coupling agent, then powder or pellet masterbatches are often useful to assure atomic reaction.

Subject organometallics work on a catalytic principle at stoichiometric levels of 0.1 to 0.6 parts additive per thousand parts polymer and 0.5 to 0.7% by weight of most fillers and 2 to 6% for some fine carbon blacks, fumed silicas and nano-particulates. For example, Figure 16 shows 0.7 wt. % pyrophosphato titanate reduces the viscosity of 40% calcined clay in mineral oil from >2,000,000 cps to 19,200 cps.

In room temperature liquid water based systems such as in the water slurry exfoliation of MMT clay or in high solids polymer systems epoxy, it is best practice to add the coupling agent into the liquid phase just prior to addition of the filler or particulate to be coupled. For example, since titanates are transesterification catalysts and are used as catalysts in the synthesis of esters such as PET [126] and PBT [198], it is best practice when using ester plasticizers to dissolve them into the plasticizer just prior to use so as to keep residence time minimized to avoid side reactions that diminish effectiveness.

In polyurethane systems, subject organometallics can behave as catalysts – as do tin catalysts – depending on their chemical structure. Table 271 – one of ~400-Tables and 376-Figures from Reference [116] show the different gel times of various titanates in a 2-K PU system compared to DBTDL:

Table 271
GEL TIMES OF VARIOUS TITANATE AND OTHER CATALYSTS IN A TWO COMPONENT URETHANE


Catalyst	Time	Catalyst	Time
KR 44	0'20"	KR 238S	6'40"
KR 44U	0'35"	KR 62ES	6'40"
Sym Amine Ti	0'55"	Dibutyl Tin Dilaurate	7'12"
KR 77U	1'20"	KR 210S	7'20"
KR 41B	1'30"	KR 58FS	7'25"
KR 46B	2'00"	KR 112	8'00"
KR 9S	2'20"	KR 262ES	8'05"
KR 55	3'30"	KR 212	9'15"
KR TTS	4'25"	KR 12	10'00"
KR 34S	4'50"	KR 38S	10'00"
KR 158FS	5'55"	Trifunctional	
KR 138S	6'30"	Aluminum	No Gel

The concern with localization and physiabsorption of the coupling agent forming more than a nano atomic monolayer on the filler or fiber is that it results in whole segments of uncoupled particulate surfaces, as well as over and under catalysis of the polymer. And physiabsorbed titanate or zirconate in multiple layers on a filler interface cannot be post spread into atomic monolayers with excessive mixing energy because of the strong capillary attraction forces. So it is critical to get the small amount of titanate distributed in atomic monolayers, which is the perennial nanoscience challenge. This problem is largely overcome by dilution & using masterbatches of the coupling agent. A simple rule is to use like coupling agent form to like polymer physical form, i.e. liquid to liquid, powder to powder and pellet to pellet.


High Specific Energy Input During the Polymer Melt Phase – Once the titanate dissolves into the polymer liquid or dissolves as the polymer begins to melt, work energy through mechanical shear creates

the required reactive compounding conditions for intimate titanate coupling and catalysis. In extrusion compounding or liquid systems requiring high heat, it's important to keep the initial mixing temperature of the polymer below the Initial Boiling Point of the titanate until it has worked into the heat sink of the polymer – and then the temperature can be raised to the conventional art requirement. The area under the power curve formed by a plot of torque vs. time is a measurement of the work energy or shear on the polymer/catalyst matrix. The most efficient polymer mix cycles generate peak torque (AMPS) in a short time. Torque is controlled by temperature, rpm's and backpressure or plasticizer/solvent/water letdown. High torque creates high polymer shear rates, which are necessary for exfoliation in nanocomposites. Polymers are non-Newtonian in flow and their melt viscosity decreases asymptotically with increasing shear. Under high shear rates, polymers exhibit the lowest viscosity with the least amount of rheological variation as compared to greater polymer viscosity variation at lower shear rates - i.e. high shear rates give reproducible results.

Even though subject organometallics achieve complete pigment dispersion in various coatings formulations in a shorter period of time (see slide next), it is advisable to solvent starve, reduce monomer, increase oligomer in a coatings formulation during mixing to achieve complete deagglomeration and a continuous film devoid of air and water to assure a more ageless coating.



The 33rd Biennial Western Coatings Symposium and Show
 Paris Las Vegas Hotel and Convention Centre
 Las Vegas, NV – October 15-18, 2017



Energy & Mix Time Savings Ball Mill Grinds

Coatings System	% Titanate Used	Energy Cost (\$/100 gal)		Mix Time (hr./100 gal)	
		Control	Titanate	Control	Titanate
Alkyd	0.5 KR 138S	9.4	1.7	23.1	4.2
Acrylic WB	1.0 KR 46B	1.0	0.4	2.6	1.6
Epoxy	0.5 KR 38S	11.3	1.9	22.1	3.7
Epoxy Ester	1.2 KR 138S	25.5	6.4	47.8	11.9
Chlor. Rubber	2.0 KR 46B	1.9	0.2	1.5	0.2
PVC Plastisol	0.5 LICA 38	0.6	0.4	0.5	0.5

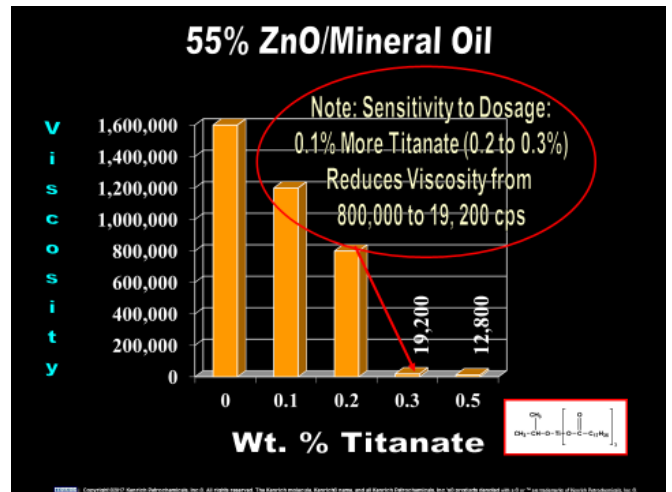
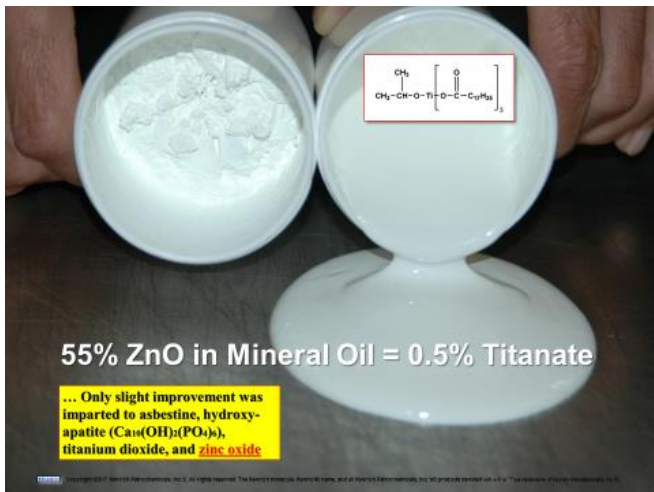
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Dosage Determination Principles Based on Polymer and Filler Types – Optimum dosage is determined by the materials used in the compound. An obvious statement, but, then why do so many investigators choose 1.0% or 1 phr coupling agent dosage as a single data point to determine titanate efficacy? Most of the titanate literature points to an optimum dosage of 0.2 to 0.6% by total weight of the polymer composite – including the weight of the pigment, extender filler or fiber.

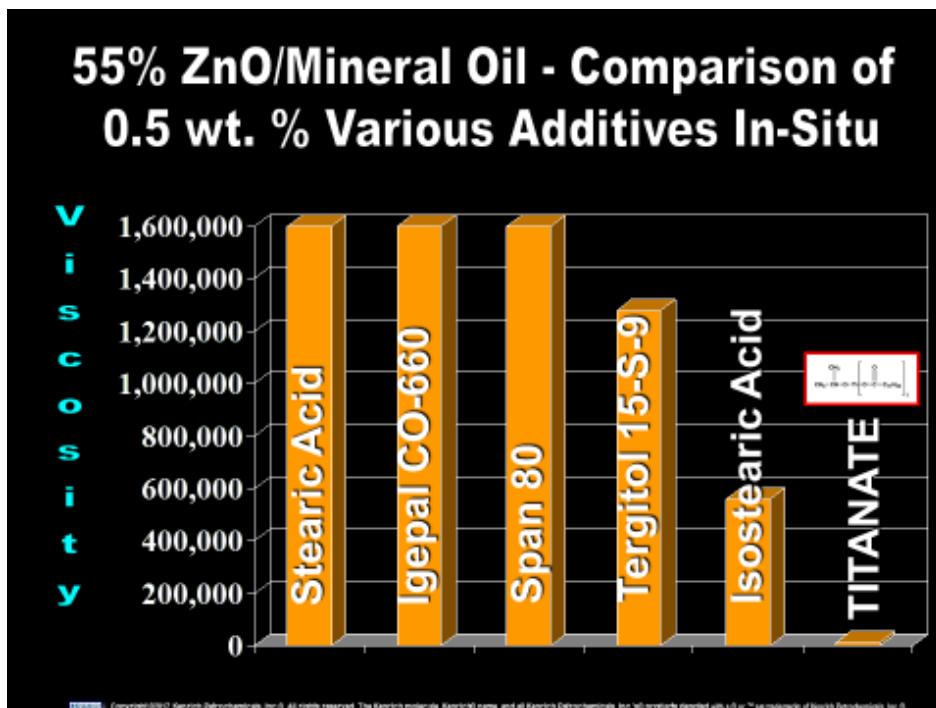
Even some nanoclays and fine surface area silicas and carbon blacks show some significant dispersion improvement at 0.5% dosage. For example, 0.5% LICA 38 by weight of nanoclay appears to be the optimum dosage when added early in the grind before addition of the nanoclay in a 50% Nanocor® CWC filled mineral oil. The viscosity of the mix will be reduced from 416,000 to 4,800 cps – while 0.3% LICA 38 yields 89,600 cps – and 1 and 2% LICA 38 do not reduce the viscosity any lower than 4,800 cps. See Table 6. Note the LICA 97 in Table 6 had no effect because it is insoluble in mineral oil. But, certain nanoclays such as Southern Clay's Cloisite Na⁺ may require up to 6 weight % LICA 38 as shown

in Table 7. Also, a fine particle size carbon black may require a 0.75-1.25 to as high as 3.6 weight % dose. Materials such as graphene oxides require ~4.0 wt. % titanate or zirconate.

Therefore, a 3-data point ladder study is most useful to vector into the optimal dosage. See ZnO next:



Note, the attachment of isostearic acid to titanium changes it from an isostearic acid surfactant to a triisostearoyl titanate coupling agent (IT 61417-49-0, KR TTS) – and the wetting effect is analogous to the difference between light and laser:



Since nano filler levels are used in the range of 2 to 10% - and since they have much higher surface area, 2 to 6 wt % titanate dosage is suggested. At 6 wt % titanate, 3% nano filler results in 0.18% titanate by weight of polymer, which is close o the 0.2 to 0.6% ideal dosage for Function (2) Repolymerization catalysis of an unfilled polymer, as will be discussed.

Dosage Effectiveness as Determined by Applications Technique – The physics of mixing, as well as the chemistry of the interface, dictate the uniformity of subject coupling results. Mg(OH)₂ presents a

particular challenge to obtaining uniform coupling in the dry powder state. Figure 17 shows that 0.7 wt. % of a pyrophosphato titanate, when added in-situ to the mineral oil, reduces the viscosity at 50% Mg(OH)₂ loading from 640,000 cps to 12,800 cps. Other inorganics such as ATH are not quite as demanding. In fact, in-situ treatment is a good benchmark standard to use to measure dry powder pretreatment effectiveness. For example, Magnifin H 5 Mg(OH)₂ and Martinal OL-104/LE Al(OH)₃ (Martinswerke AG, Germany) were treated with KR 38S and LICA 38 pyrophosphato titanates (see Tables 8 and 9) and the following conclusions were drawn:

Magnesium Hydroxide

- Table 8-Tests 2 & 5 – The in-situ technique provides a benchmark viscosity reduction from 1,152,000 to 6,400 cps for both monoalkoxy and neoalkoxy pyrophosphato titanates.
- Tests 3 & 6 – Pretreatment: neat (no dilution) monoalkoxy and neoalkoxy pyrophosphato titanates added dropwise over 1-minute to a fluidized bed of the Mg(OH)₂ created by a Henschel operating at low speed (1800 rpm) reduce the viscosity to only 192,000 cps when added to mineral oil as compared to 6,400 cps for in-situ, thus indicating a “localization” of the titanate and non-uniform coating.
- Tests 4 & 7 – Pretreatment: diluted titanate blended 1:3 with KP 140 [Tri-Butoxyethyl Phosphate plasticizer (CAS 78-51-3)] and pretreated at 2.8% (0.7:2.1) of the blend by weight of Magnifin H 5 Mg(OH)₂ in the same manner as Tests 3 & 6 provides a viscosity reduction of 6,400 cps – the same as in-situ. The method is predictive of a pretreated grade of Magnifin H 5 that will incorporate into olefins at the 60% filler level to provide smooth, flexible plastic sheets with good mechanical properties, color and appearance as previously reported with Mg(OH)₂ [1] – and enhanced flame retardance by virtue of monolayer pyrophosphato intumescence. But mineral producers resist applying any additive such as a titanate because it creates another grade to market. Using a plasticizer as a diluent further limits the markets in which the Mg(OH)₂ can be used. The only reason why the plasticizer was used was because we did not have access to an airless spray gun for the tests. So, we did the next best thing and slowed the dropwise addition from 1-minute to 5-minutes in Test 8.
- Test 8 – Pretreatment: slowing down the rate of addition of the undiluted titanate overcomes “localization” and a 6,400 cps viscosity is produced that is comparable to the in-situ and dilution methods.

Aluminum Trihydrate

In Table 9, we worked with only the monoalkoxy KR 38S (REACH EU EINECS Phase-In Substance) on the ATH because the interest for this work emanated from the EU (Germany). The results with LICA 38 should be similar. Differences between LICA 38 and KR 38S may show up in the processed thermoplastic, but pretreatment minimizes the differences between monoalkoxy and neoalkoxy functions because the monoalkoxy group had been spent via solvolysis in the mineral pretreatment step. In any case, neat KR 38S, pretreated at 0.7% of the blend by weight of Martinal OL-104/LE ATH by simple 1-minute dropwise addition to the Henschel fluidized bed as in Table 8 – Tests 3 & 6 and then again diluted as in Table 8 – Tests 4 & 7 produced end viscosities in mineral oil similar to the in-situ control. The ATH, thus treated, should incorporate into olefins at the 64% filler level (ATH amount needed to provide UL 94V₀ FR rating) to provide smooth, flexible plastic sheets with good mechanical properties and enhanced flame retardance by virtue of monolayer pyrophosphato intumescence.

Dosage Determination by Viscosity Response with Various Pigments and Fillers – Since 1973, the author has found viscosity response of all manner of inorganics and organics in mineral oil containing varying amounts of titanate or zirconate at high pigment to binder ratios to be predictive of organometallic efficacy as a coupling agent for that inorganic or inorganic in polymers. Mineral oil, if the titanate or zirconate is soluble in it, is useful because of its low viscosity at room temperature and its non-polarity, which does not contribute significantly to “wetting” the pigment thus isolating the effect of the titanate on the particulate interface independent of the vehicle. A high pigment to binder ratio that produces a Brookfield viscosity at 25°C of at least 50,000 cps – or a ratio that is at slightly below the

CPVC (Critical Pigment Volume Concentration Point – the point at which pigment oil absorption demand exceeds available resin) – is useful because it “sensitizes” the system being tested for viscosity response data. So, if one plots the viscosity data points on a y-axis from a ladder of dosages on the x-axis, a log curve usually results. When the tangent of that resultant curve approaches parallel to the x-axis, the intercept point dropped to the x-axis usually determines the optimal dosage. Some examples of dosage determination and pigment dispersion are next provided.

Pigments – TiO₂, Red Iron Oxide, Yellow 763ED (PbChromate), Ultramarine Blue 51-51 (Sodium Alumino Sulphosilicate), Green F5687 (Co(Al,Cr)₂O₄), Thermax Black, DayGlo Z-15-3 Blaze Orange and ZnO Filled Mineral Oil and DOP Ester: Table 10 is a study of the viscosity response of various pigments to coupling agent in mineral oil and DOP. Most pigments respond at 0.5 wt. % dosage and LICA 38 appears to be a more superior dispersant than LICA 12 – independent of polymer considerations. However, for Function 2 polymer “repolymerization” considerations, selection would be based on polymer considerations as well as pigment interface. In any case, many of the in situ viscosity reduction effects achieved, such as the reduction of 55% Ultramarine Blue in DOP from 2,080,000 cps without titanate to 19,200 cps with 0.5% LICA 38 (see Figure 18), are significant. Figures 19, 20 and 21 show the effects on PbChromate Yellow, Red Iron Oxide and Co(Al,Cr)₂O₄ Green pigments. Figure 22 shows (left) 55% 0.3 μ ZnO in mineral Oil has viscosity of 1,600,000 cps, while (right) 0.5% titanate by weight of ZnO is added in-situ to mineral oil followed by ZnO has viscosity of 12,800 cps. Figure 23 from Table 10 is a pictorial representation of the data points in Table 10 for 60% TiO₂ in mineral oil with LICA 38. Figure 24 shows cosmetic products (680 cosmetic formulations are EU REACH registered) using titanate for pigment dispersion.

Ferrite Powders for Magnetic Media: Most γ -ferric oxide based copier toners and magnetic recording media (see Figure 25) contain a titanate as invented by the author as indicated in U.S. patents by Sony (US 4,330,600)[184], Fuji (US 4,444,850)[185] and TDK (US 4,425,630)[186]. In confirmation, a recent example of the efficacy of the pyrophosphato titanate as a pigment dispersant or exfoliant for difficult to disperse materials such as Co₂Z ferrite powders is delineated clearly in the following abstract:

TI Dispersion of nonaqueous Co₂Z ferrite powders with titanate coupling agent and poly(vinyl butyral)

AU Hsiang, Hsing-I.; Chen, Chih-Cheng; Tsai, Jaw-Yue

CS Department of Resources Engineering, National Cheng-Kung University, Taichung, Tainan, Taiwan

SO Applied Surface Science (2005), 245(1-4), 252-259 CODEN: ASUSEE; ISSN: 0169-4332

AB Co₂Z ferrite powders with the chem. compn. 3Ba0.5Sr0.5O₂CoO.cntdot .12Fe₂O₃ have superior high frequency magnetic properties. However, Co₂Z ferrite powders are difficult to apply to practical processes because of agglomeration induced by the strong magnetic attraction between particles. In this study, Co₂Z ferrite powders pretreatment using a titanate coupling agent - neopentyl(diallyl)oxy tri(dioctyl)pyrophosphate titanate (LICA 38) on the sedimentation and rheol. behavior is investigated. The bonding mechanisms between ferrite powder, LICA 38, and poly(vinyl butyral) (PVB) are studied using diffuse reflectance Fourier transform IR spectroscopy to explain the difference in the rheol. and sedimentation behaviors of untreated and titanate coupling agent-modified ferrite powders. The affinity of Co₂Z ferrite and PVB could be substantially enhanced by coating a titanate coupling agent onto the ferrite surface. The coated layer could prevent particles from agglomeration induced by the magnetic interaction.

Carbon Black: Figure 26 shows the improved appearance and smoothness of 11% carbon black filled 20-melt LLDPE. The sheet containing 11% untreated carbon black (left) pulled off a two roll mill is rough with poor appearance while the sheet (right) using the same concentration of 0.75% LICA 38 pretreated carbon black is smoother.

Carbon in its many forms as reinforcing, pigments, and conductive carbon black, graphite, graphite fiber, graphene, graphene oxide, CNTs, etc. are all reactable with subject organometallics. As a result of three ACS CAS SEARCHES using the key words: **GRAPHENE – GRAPHITE – CARBON NANOTUBES** (Carbon Black Not Included) – 130 abstracts were obtained. My company is a member of the Graphene Council and these searches proved useful in setting up NDA’s with various groups.

We will show some relevant abstracts from the following three ACS CAS Searches:



Science IP Order: 3189677 TI/ZR COUPLING AGENTS



Science IP Order: 3140835

Ti/Zr Coupling Agents - Modified Update of Science IP Order



3069078

5=> d a3069078rns/a ;d query

A3069078RNS/A

RNS OF KENRICH CHEMICALS

It is clear China is past the copycat phase of material science development. In 2017, I gave a talk to the Plastic Industries Association's 28th Annual Compounders Conference of the Flexible Vinyl Compounders Division entitled, "Is China Cleaning Our R&D Clocks in PVC Compatibilization and Nanotechnology While We Combat Prop 65 and Regs". You be the judge given the abstracts next offered based on my invention products and teachings:

TI Method for preparing graphene UV-curing adhesive and its application of composite heat-emitting glass

IN Hou, Shuting; Zhang, Ruijun; Shen, Haibin

PA Wuxi Yunting Graphene Technology Co., Ltd., Peop. Rep. China

SO Faming Zhuanli Shenqing, 12pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 107090252	A	20170825	CN 2017-10256665	20170419
PRAI	CN 2017-10256665		20170419		
OS	CASREACT 168:61720				

AB The title graphene UV curing adhesive comprises UV resin B, graphene, surfactant, and leveling agent. The method comprises the steps of: coating one surface of glass with graphene UV curing adhesive, combining the two pieces of glass, irradiating with UV light, curing to form graphene UV-cured adhesive membrane, forming a glass-membrane-glass integrity, adding an electrode and applying voltage on the graphene adhesive membrane between two layers of glass, and generating heat to reach 50-75°C in 1-3s. The invention uses the characteristics of large sp. surface area and two-dimensional nanostructure of the graphene to form a uniform elec. conductive and thermally conductive passage capable of rapidly heating up by applying voltage. The invention has high drying speed, and is eco-friendly. The resulting heatable glass has important application in automobile front windshield and house snow removal.

IT [61417-49-0](#), KR TTS

TI Ultraviolet shielding antistatic composite coating and preparation method thereof

IN Duan, Xubin; Yin, Yuetao; Wang, Wenqi; Xu, Linying; Yang, Sanfei; Shi, Yiwei

PA Jinjiang City Zhongxin Microfiber Technology Co., Ltd., Peop. Rep. China; China Leather & Footwear Industry Research Institute (Jinjiang) Co.,Ltd.

SO Faming Zhuanli Shenqing, 5pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 105602433	A	20160525	CN 2016-10190063	20160330
PRAI	CN 2016-10190063		20160330		

AB The method includes subjecting graphite oxide/alc. soln. to centrifugation and ultrasonic treatment, adding titanate coupling agent, carrying out modification, reducing modified graphene oxide with sodium borohydride, centrifugally washing, freeze-drying to obtain organic modified graphene; ultrasonically treating nanometer titanium oxide in anhydrous alc., modifying nano titanium oxide with modifier, after completion of reaction, washing with anhydrous ethanol, drying, and obtaining organic modified nano titanium dioxide; ultrasonic blending organic modified graphene and organic modified nano titanium dioxide for uniformly dispersing them in polyurethane to obtain UV shielding antistatic composite coating. The invention utilizes antistatic and UV shielding performance of graphene and nano TiO₂, with 'bridged bond' effect between organic group on modified nano particle surface and polyurethane resin matrix, increases dispersion of inorg. nano-particles in organic system.

IT [61417-49-0](#), KR TTS

TI Thermally conductive flame-retardant control cable

IN Li, Zhengxiang; Wang, Zhaolan; Liu, Qin

PA Anhui Land Group Co., Ltd., Peop. Rep. China

SO Faming Zhuanli Shenqing, 7pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	CN 105199225	A	20151230	CN 2015-10634469	20150929
PRAI	CN 2015-10634469		20150929		

AB Title cable includes a cable core, an insulation layer, a shielding layer and a sheath layer; the insulation layer is coated on the cable core, the shielding layer is coated on the insulation layer, and the sheath layer is coated on the shielding layer; wherein the insulation layer is made of low-smoke halogen-free polyolefin composition including polypropylene, Me vinyl silicone rubber, EVA, tetrapropylbenzenesulfonyl, iso-Pr tri(isostearoyl) titanate, caprolactam, magnesia, 2,5-dimethyl-2,5-di-t-butylperoxy-3-hexyne, alkylated diphenylamine, 2-mercaptobenzimidazole zinc salt, dicyclohexyl phthalate, kaolin, ceria, polyacrylonitrile fiber, anti-aging agent and antioxidant. The polyacrylonitrile fiber is prepared by adding graphene oxide 20-50, N,N-dimethylformamide 80-100, acrylonitrile monomer 10-20, and modified Mg hydroxide in a reactor, adding ammonium persulfate in nitrogen, heating to 60-80 °C for 20-40 h, precipitating, filtering, rinsing and drying, then adding N-methylpyrrolidone 50-80 parts, ultrasonic processing at 40-70 °C for 20-25 h, extruding through spinning capillary, solidifying in diethylene glycol for 2-10 s, standing in hydrobromic acid for 20-50 min, rinsing and drying. The modified Mg hydroxide is prepared by mixing Mg hydroxide with natural coconut fibers and NaOH solution with concentration of 0.5-0.7 mol/L, sealing at room temperature for 1-2 days, adding fatty alc. sodium sulfate, zinc borate, phosphorus oxide, tri-Ph phosphate, triisopropylphenyl phosphate, ultrasonic dispersing for 10-30 min, adding Na lignosulfonate and bentonite, ultrasonic dispersing for 20-50 min at 50-80 °C, filtering, rinsing and drying. The present invention has good thermal conductivity and excellent flame retardant property.

IT [61417-49-0](#), Iso-propyl tri(isostearoyl) titanate, KR TTS

TI EPDM-based conductive rubber and its preparation method

IN Yang, Fuhe; Chen, Tianan; Zhao, Renli

PA Shenzhen Debang Interface Material Co., Ltd., Peop. Rep. China

SO Faming Zhuanli Shenqing, 6pp.

CODEN: CNXXEV

DT Patent
LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 102585385	A	20120718	CN 2012-10038416	20120220
PRAI	CN 2012-10038416		20120220		

AB The title product includes EPDM rubber 15-20, titanate coupling agent 0.005-1, vulcanizer 0.6-1.2, activator 4-6 and conductive powder 71.8-80.4 wt%. The EPDM rubber is ethyldenenorbornene third monomer-containing EPDM or dicyclopentadiene third monomer-containing EPDM. The titanate coupling agent is KR-138. The vulcanizer is organic peroxide (boron phosphide, 2,4-dichlorobenzoyl peroxide, diisopropylbenzene peroxide or/and 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane). The conductive powder is pure silver conductive powder, pure nickel conductive powder, Ni-coated graphite conductive powder, Ag-coated Al conductive powder, Ag-coated Cu conductive powder, Ag-coated Ni conductive powder or/and Ag-coated glass conductive powder. The conductive powder includes powder with its particle size of 50-100 μm and powder with its particle size of 20-50 μm at a weight ratio of 10: 1. The method includes the following steps of (1) baking conductive powder, mixing different particle sizes powders to obtain conductive powder; (2) adding titanate coupling agent, wet method treating to obtain titanate-coated conductive powder; and (3) plasticizing EPDM rubber for 5-15 min, adding the above titanate-coated conductive powder, mixing and plasticizing for 10-20 min, adding vulcanizer and activator, mixing and plasticizing for 10-20 min to obtain title product. The product shows excellent oxidation resistance, ozone resistance, erosion resistance, elec. conductivity, stable resistance time, controllable resistance temperature coefficient, high temperature boundary, etc.

IT [67729-57-1](#), KR-138S

TI Room-temperature curable epoxy non-sticky coating for papermaking roller and preparation method thereof

IN Liu, Yan; Duan, Xinguang; Li, Xinping; Bai, Hui
PA Shaanxi University of Science & Technology, Peop. Rep. China
SO Faming Zhuanli Shenqing, 6pp.
CODEN: CNXXEV

DT Patent
LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 102766389	A	20121107	CN 2012-10232872	20120706
PRAI	CN 2012-10232872		20120706		

AB The invention discloses to a room-temp. curable epoxy non-sticky coating for papermaking rollers which is composed of epoxy resin 45-49, acetone 11-13, MoS₂ 4-6, crosslinking agent (titanate crosslinking agent of KR 238S or KR 238 TER50) 0.8-1, dispersing agent (dispersing agent of BYK-P104 or 3100) 1.3-1.5, curing agent (polyamide 651 or diaminodiphenyl methane) 19-23, graphite 4-6, Cr₂O₃ 4-6, polytetrafluoroethylene 3-5, and antifoaming agent (Foamaster 111 or J02000 organic silicone oil) 0.6-0.8 weight%. The preparation process comprises heating epoxy resin in container at 60 °C, adding acetone, stirring to dissolve epoxy resin, resp. adding graphite, MoS₂, Cr₂O₃ and polytetrafluoroethylene, stirring completely, resp. adding crosslinking agent, dispersing agent and antifoaming agent, stirring completely, adding curing agent, stirring at 100 rpm/min for 15 min, and standing to obtain the non-sticky coating. The non-sticky coating has effect of preventing corrosion of papermaking roller and preventing paper pulp, adjuvants or coating adhere to papermaking roller surface.

IT [67729-57-1](#), KR 238S

TI Thermally conductive rubber compositions for heat dissipation of electric parts

IN Hatanaka, Tomokazu; Oshige, Jinya; Okazaki, Nobumitsu

PA Uchiyama Manufacturing Corp., Japan

SO Jpn. Kokai Tokkyo Koho, 3 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	JP 2002003670	A	20020109	JP 2000-187057	20000622
PRAI	JP 2000-187057		20000622		

AB The compns. contain ethylene-propylene type copolymer 100, graphite (av. particle size 10-150 μm) 100-800, titanate-based coupling agents 1-30, and organic peroxides 1-15 parts. Thus, EPDM 100, graphite (average particle size 12 μm) 800, tetraoctylbis(ditridecylphosphite)titanate 7, tert-butylhydroperoxide 7, stearic acid 2, and process oil 120 parts were kneaded to give a composition showing good appearance, thermal conductivity, and hardness.

IT 65460-53-9 KR 46B

TI Graphene-modified cyanate resin and its preparation method

IN Ou, Qiuren; Ji, Peijun; Zhao, Liang

PA Aerospace Research Institute of Special Materials and Processing Technology, Peop. Rep. China

SO Faming Zhuanli Shenqing, 8pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 108165006	A	20180615	CN 2016-11114026	20161207
PRAI	CN 2016-11114026		20161207		

AB Title graphene modified cyanate ester resin comprises cyanate ester resin, graphene and coupling agent, wherein graphene was added into cyanate ester resin in two parts, the first part was mixed with cyanate ester resin and coupling agent, and then the second part was added, graphene was evenly dispersed by non-interventional gravity dispersion process, the total amount of graphene added is 5%~ 20% of the mass of cyanate ester resin, in the first part, the amount of graphene added is 0.5%-1% of the mass of cyanate ester resin, the amount of the coupling agent added is 1%~ 3% of the mass of cyanate ester resin, the amount of the coupling agent added is not less than two times that of the graphene added in the first part.

IT 61417-49-0, TTS

TI Supercritical polymeric polystyrene/graphene 3D printed spherical powder and preparation method thereof

IN Chen, Hekui

PA Wu, Dan, Peop. Rep. China

SO Faming Zhuanli Shenqing, 7pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 108047363	A	20180518	CN 2017-11378116	20171219
PRAI	CN 2017-11378116		20171219		

OS CASREACT 170:5809

AB Title method comprises (1) the graphene is dispersed in a solvent and then the modifier is added and the reaction is continuously stirred at 60-100° for 2-6 h, after the reaction is completed, the solid and liquid are separated and finally dried at 80-120° to obtain a modified graphene; wherein, the ratio of the mass fraction of graphene, modifier and solvent is 100:10-40:300-1000; (3)

the styrene, the modified graphene, the initiator and the liquid carbon dioxide are added into the supercrit. polymerization tank and the mixture is continuously stirred and reacted at 60-100° for 4-12 h to obtain a polystyrene/graphene 3D printed spherical material; wherein the ratio of the mass fraction of styrene, modified graphene, initiator and water is 100:1-100:0.5-1.5:180-300; (3) the reaction system after the completion of the reaction is released to normal temperature and normal pressure, and the liquid carbon dioxide is volatilized to obtain a polystyrene/graphene 3D printed spherical powder.

IT [61417-49-0](#) KR TTS

TI Method for improving dispersibility of graphene in coating by loading graphene in surface-modified pyrophyllite via electrodeposition

IN Chen, Qing; Zan, Hang

PA Chengdu New Keli Chemical Science Co., Ltd., Peop. Rep. China

SO Faming Zhuanli Shenqing, 9pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 107619618	A	20180123	CN 2017-11033149	20171030
	CN 107619618	B	20181106		
PRAI	CN 2017-11033149		20171030		

AB The title method for improving dispersibility of graphene in coating includes surface-modifying pyrophyllite with coupling agent, covering copper foil on surface thereof, soaking in ionic liquid dispersion liquid of graphene oxide, adopting the pyrophyllite as cathode, placing anode, supplying direct-current elec. field, carrying out electrodeposition for firmly loading graphene oxide among the interlayer of the pyrophyllite to obtain composite filler, and feeding the filler in coating. The inventive method has simple operation and low cost, can effectively promote dispersion of graphene in coating, and significantly improve corrosion resistance of coating and mech. performance of coating film.

IT [61417-49-0](#) KR TTS

L5 ANSWER 249 OF 374 CA COPYRIGHT 2019 ACS on STN

AN 167:255933 CA [Full-text](#)

TI Graphene-nano-silver composite material, preparation method and application thereof

IN Wang, Xin; Li, Wenbo

PA Guangzhou Yingdige New Material Technology Co., Ltd., Peop. Rep. China

SO Faming Zhuanli Shenqing, 11pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 106954636	A	20170718	CN 2017-10104125	20170224
PRAI	CN 2017-10104125		20170224		

AB The title composite material comprises (by wt. parts): graphene mixed powders 1-16, and nano-silver antimicrobial powders 1-9. Graphene mixed powders comprise (by weight parts): graphene 0.3-65, graphite carbon 0.2-25, and graphite 0.02-10. Nano-silver antimicrobial powders comprise (by weight parts): silver nitrate 2-5, zirconium phosphate 90-95 and zinc oxide 1-5. The composite material has good antimicrobial effect and stable property. The preparation method has few steps and simple process. In addition, the invention also discloses the antimicrobial fiber prepared from the composite material, preparation method and application thereof in blended yarn. The inhibition ratio of the antimicrobial fibers to Escherichia coli, Staphylococcus aureus and Candida albicans exceeds the national standard

IT [61417-49-0](#), Isopropyl triisostearoyl titanate [61548-33-2](#) KR 7

TI Inorganic surface-treated galvanized steel sheet, preparation method therefor, and aqueous inorganic surface treatment agent thereof
 IN Yang, Jiayun; Zhang, Jianping; Zhang, Wenqi; Dai, Yigang
 PA Baoshan Iron & Steel Co., Ltd., Peop. Rep. China
 SO Faming Zhuanli Shenqing, 34pp.; Chemical Indexing Equivalent to 168:288910 (WO)
 LA Chinese
 FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 107779853	A	20180309	CN 2016-10719583	20160824
	WO 2018036465	A1	20180301	WO 2017-CN98430	20170822
PRAI	CN 2016-10719583	A	20160824		

AB An environmentally-friendly inorg. surface-treated galvanized steel sheet, a preparation method therefor and an aqueous inorg. surface treatment agent thereof, capable of satisfying requirements of rapid deep-drawing treatment of progressive dies in the field of micromotors, and providing excellent red rust resistance performance and excellent surface conductivity for parts and components. An aqueous inorg. surface treatment agent comprising a single organic silane crosslinking agent containing hydrophobic groups, a system crosslinking agent, water-soluble nano sol, surface modified high-d. polyethylene particles, tetra-Et orthosilicate modified oxidized graphene, a water-soluble fluorinated compound, a water-soluble phosphorous compound and a water-soluble metal salt compound are coated and cured on the surface of a galvanized steel sheet; the obtained inorg. surface-treated galvanized steel sheet has excellent red rust resistance performance, excellent surface conductivity, surface lubricating performance and excellent blackening resistance performance, and can satisfy requirements of rapid deep-drawing treatment and bare service of progressive dies, and the inorg. surface-treated galvanized steel sheet is especially applicable to the field of micromotors.

IT [61417-55-8](#) KR 9S

TI A kind of aqueous coating containing graphene/zinc-aluminum hydrotalcite-like compound nanocomposite and preparation method thereof

IN Yu, Dayang; Wen, Shaoguo; Wang, Jihu; Luo, Jian; Wu, Youtong
 PA Shanghai University of Engineering Science, Peop. Rep. China
 SO Faming Zhuanli Shenqing, 19pp.
 LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 106995643	A	20170801	CN 2017-10370434	20170523
PRAI	CN 2017-10370434		20170523		

AB The aq. coating comprises: 30-50 wt. part of aq. resin, 25-40 wt. part of water, 0.1-0.5 weight part of dispersant, 0.1-0.5 weight part of wetting agent, 0.1-0.5 weight part of defoamer, 0.1-0.5 weight part of thickener, 0.1-0.5 weight part of coalescing agent, 0-10 weight parts of curing agent, 25-40 weight parts of titanium dioxide, 0-20 weight parts of calcium carbonate, and 0.1-2.5 weight parts of graphene/zinc-aluminum hydrotalcite-like compound nanocomposite. The invention adds graphene/zinc-aluminum hydrotalcite-like compound nanocomposite into aqueous coating, for significantly improving heat resistance, anti-corrosion, flame retardancy, weatherability, impact resistance, wearability, hardness and barrier property, and enhancing multi-efficiency of aqueous coating.

IT [61417-49-0](#), KR TTS

TI Scratch-resistant and wear-resistant coating material and preparation method thereof

IN You, Bo; Hu, Hang; Li, Bin
 PA Fudan University, Peop. Rep. China
 SO Faming Zhuanli Shenqing, 16pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 106752923	A	20170531	CN 2016-11060357	20161128
PRAI	CN 2016-11060357		20161128		

AB The title method comprises the steps of: modifying the surface of graphene with active groups through chemical modification method to obtain modified graphene, and blending modified graphene with polysiloxane, non-essential blending resin, solvent, non-essential curing agent, non-essential pigment filler and non-essential additive to obtain graphene composite nanoparticles with high scratch resistance and wear resistance. Said polysiloxane has formula as shown, wherein the substituents are defined in the specification. The invention improves the dispersibility of graphene by 140% or higher, and reduces the wear amount by 60% or higher, and has excellent adhesion force, heat resistance, weathering resistance, fire retardancy and corrosion resistance. Graphene/polysiloxane composite coating can be applied to surface protection of various base materials such as metal, plastic, wood, concrete and glass in the fields of automotive paint, photoelec. material, precise instrument, offshore heavy corrosion resistance and building.

IT [61417-49-0](#) KR TTS

TI Flexible resiliently-compressible thermally and electrically conductive gasket composition

IN Yang, Xiaowang; Meng, Zhaokui

PA Dongguan Leizidun Electronic Materials Co., Ltd., Peop. Rep. China

SO Faming Zhuanli Shenqing, 7pp.

LA Chinese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	CN 106675031	A	20170517	CN 2016-11268488	20161231
PRAI	CN 2016-11268488		20161231		

AB The flexible resiliently-compressible thermal and electricity conductive gasket composition is composed of polyetheramine 100 parts, cyclic carbonate 5-125 parts, antioxidant 1010 0.5-5 parts, titanate coupling agent 2-10 parts, elastic micro mist 100-300 parts, electricity conductive and heat-conductive powder 300-900 parts. The cyclic carbonate is a curing agent for polyether amines. The cyclic carbonate compound is a small mol. compound with epoxy group or a polymer synthesized by reaction with carbon dioxide under a predetd. condition. The titanate coupling agent includes isopropoxytrioleoyloxy titanate and isopropoxy tristearate oxo titanate. The thermally conductive conductive powder is used to increase the thermal conductivity of the polymer, including nickel-plated metal powder, nickel-plated metallic copper powder, silver-plated copper powder, silver powder, silver nanowire, graphene microchip; the conductive conductive powder has a particle size of from 0.5 to 80 μm .

IT [61417-49-0](#) KR TTS

TI Graphene ink composition with good heat radiation and electromagnetic wave shielding effect

IN Yang, Seung Jin; Kim, Yun Hyeon

PA Changsung Corp., S. Korea

SO Repub. Korean Kongkae Taeho Kongbo, 17pp.

LA Korean

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	KR 2017035571	A	20170331	KR 2015-134588	20150923
	KR 1783841	B1	20171010		
PRAI	KR 2015-134588		20150923		

AB Title ink comprises (A) a coupling agent 1-15, (B) graphene, 8-12, (C) a solvent 55-75, and (D) a binder 10-25%.

IT 80481-35-2, Al-M

RL: MOA (Modifier or additive use); USES (Uses)
(Plenact AL-M; graphene ink composition with good heat radiation and electromagnetic wave shielding effect)

IT 61417-49-0, TTS

TI **High-strength flame-retardant polycarbonate composite material used for protective window and preparation method thereof**

IN Ruan, Ruiqi

PA Peop. Rep. China

SO Faming Zhuanli Shenqing, 5pp.

LA Chinese

FAN.CNT 1

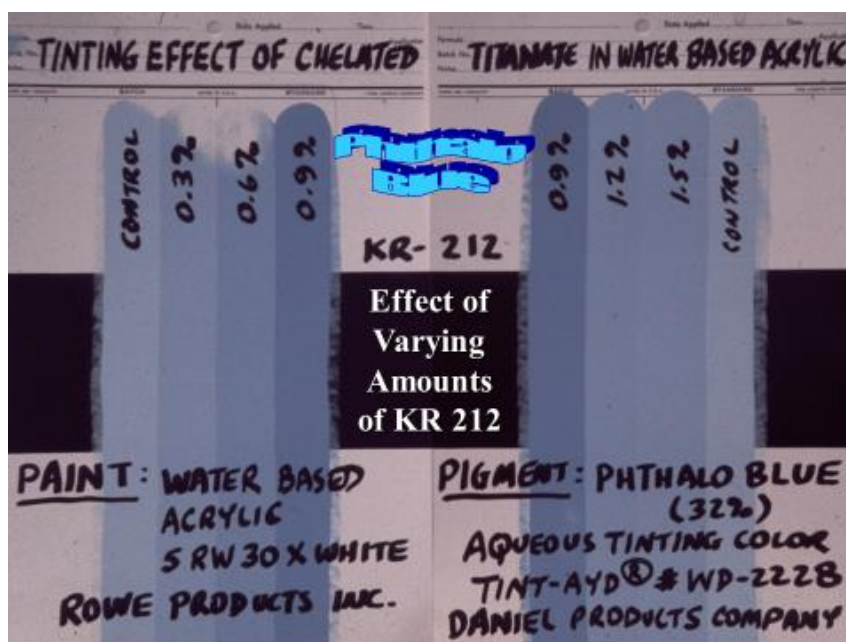
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 106751675	A	20170531	CN 2016-11202936	20161223
PRAI	CN 2016-11202936		20161223		

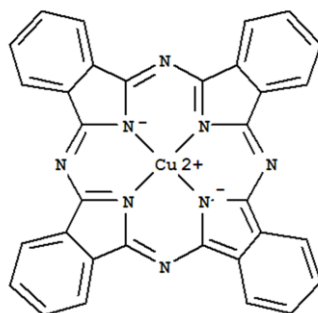
AB The polycarbonate composite material is prepd. from polycarbonate resin 140-160, chlorinated polyvinyl chloride 20-30, hydrogenated styrene-butadiene-styrene block copolymer 10-15, hexaphenoxycyclotriphosphazene 8-10, dibasic lead sulfate 3-5, calcium stearate 4-6, zinc stearate 4-6, antioxidant CA 6-8, tri(2-chloroethyl) phosphate 5-7, titanium triisostearoylisopropoxide 6-8, bromochlorinated paraffin wax 4-5, tert-Bu peroxybenzoate 2-3, antioxidant 626 4-6, light calcium carbonate powder 18-22, halloysite nanotubes 10-14, graphene 10-14, nano hydrotalcite 8-10, magnesium molybdate 6-8, white clay 3-5 and silica 4-6 weight parts. The polycarbonate composite material has high mech. strength and flame retardancy, and is used for protective window.

IT 61417-49-0, Titanium triisostearoylisopropoxide, KR TTS

RL: MOA (Modifier or additive use); USES (Uses)
(preparation of high-strength flame-retardant polycarbonate composite material used for protective window)

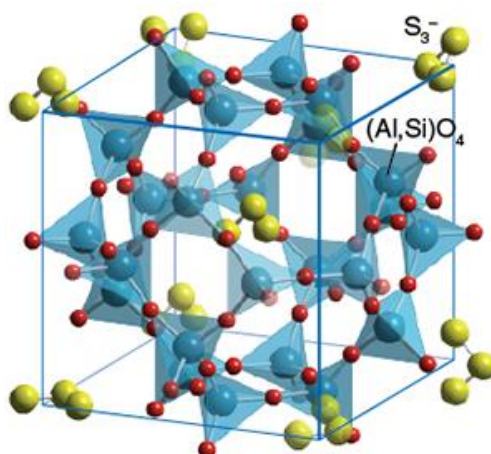
Silane coupling agents are not reactive with carbon. Further discussion follows on the experience learned from working with many different materials such as increasing the intensity of phthalo blue in a waterbased acrylic coating using KR 212, which was also used for the white coating on the Space Shuttle solid fuel rocket boosters.





D1 - C1

Phthalocyanine Blue Pigment



Ultramarine Blue Pigment

Ultramarine Blue (Sodium Alumino Sulphosilicate) Dispersed in Water, Toluene and Mineral Oil – In Situ and Pretreated with a Pyrophosphato Titanate: In the discussion of Table 10, we observed: “*Many of the in situ viscosity reduction effects achieved, such as the reduction of 55% Ultramarine Blue in DOP from 2,080,000 cps without titanate to 19,200 cps with 0.5% LICA 38, are significant*”. So we explored further. Tables 11 to 16 show and discuss the in situ treatment and dry pretreatment of two ultramarine blue pigments having surface areas of 1.2m²/g and 3m²/g. The amount of titanate for finer or nano particulates would be proportionately greater. The results are again significant and show that all manner of pigments may be coupled either in the water or organic phase with minor amounts of titanate coupling agent.

Talc and Wollastonite Fillers: Tables 17 to 20 (talc) and Table 21 (Wollastonite) show how viscosity data is used to help select a titanate and then determine its optimal dosage for a mineral filler. The study was undertaken for a proprietary “acrylic wire and cable application”.

Conclusions for the talc study:

1. 0.75% of neat (undiluted) NZ 12 by weight of Nylal 7700 is the best treatment for acrylic W&C application. NZ 12 zirconate is preferred over the LICA 12 titanate here because titanates often reduce peroxide free radicals [16].
2. 0.70% LICA 38 is the best coupling agent for non-polar thermoplastics. There is a significant shift in the CPVC (Critical Pigment Volume Concentration) point of the talc indicating higher loadings are possible in coatings and plastics.

3. Drying does not benefit coupling and residual atmospheric moisture is not a major issue.
4. Henschel treatment of ambient talc for coupling with 0.75% neat NZ 12 via dropwise addition over 1-minute at 1800 rpm's followed by 1-minute post mix gives slightly better results than in situ coupling.

Conclusions for the Wollastonite study:

1. Dilution of LICA 38 1:3 with mineral oil in pretreatment gives best results. Spray application should eliminate the need for mineral oil dilution.
2. More is not better: 0.5 and 0.7% dosage better than 1.0%. This observation even translates from wollastonite back to the aforementioned γ -ferric oxide based copier toners wherein Toda Chemicals and Xerox observed that 0.5% pyrophosphato titanate gave the best digital copier toner SAD (Specific Area Density – a measure of visual print sharpness) results over all other surfactants and silanes tested. 1% of the same titanate produced the worst results.

Filled and Unfilled Composites Based on Function 1 Coupling and Function 2 Catalysis – Some work by others is offered to demonstrate titanate Function 1 coupling and Function 2 catalysis.

CaCO₃/PP/HDPE : M. N. Ichazo et al. [199] stated: “*This study clearly demonstrated that the incorporation of the coupling agent to CaCO₃ modifies the mechanical properties of PP/HDPE/CaCO₃ composites. The best coupling agent concentration resulting is 0.7 wt% for all coupling agents studied and the best enhancement in mechanical properties was obtained with LICA 12.*”

CaCO₃/HDPE: Z. H. Liu provided [200] a study on the: “*Effects of coupling agent and morphology on the impact strength of high density polyethylene/CaCO₃ composites*”.

CaCO₃/PO's: 2.4.3 Gonzalez et al. provided [201] results on the: “*Analysis of thermogravimetric data of blends of polyolefins with calcium carbonate treated with LICA 12*”.

CaCO₃/PP/HDPE : Gonzalez et al. [202] commented: “*...This study clearly demonstrated that the addition of the coupling agent to CaCO₃ modifies the mech. properties of the PP/HDPE/CaCO₃ composites. Values of the mech. properties indicate that due to its characteristics, each coupling agent gives rise to increases in a particular mech. property. In the case of LICA 01 an increase was verified in Young's modulus at 0.7 weight% and in elongation at break at both concns. (0.3 and 0.7 weight %), whereas NZ 12 brought about an increase in elongation at break. The 1:1 mixture of LICA 12 and LICA 01 caused impact resistance of the blend of PP/HDPE with CaCO₃ to increase considerably.*”

CaCO₃/PP: Doufnoune and Haddaoui corresponded [203] with Monte providing results of their studies of CaCO₃ filled PP – particularly with LICA 12. Their Figure 5 showed that optimum elongation properties of 0.2, 0.3 and 0.4% LICA 12 treated CaCO₃ occurs in the 20 to 40 wt. % loading providing impact strengths 35 to 65% greater than the unfilled control (see also [116] – Fig. 127). Interestingly, although both impact data points above 40% are lower than virgin, the 70% CaCO₃/PP with 0.2% LICA 12 is greater than the 40% CaCO₃/PP control confirming the shift in the CPVC of the system. Their Figure 1 showed the monolayer, as determined by a plot of viscosity vs. % titanate (see [16] – Figure 21 for procedure), occurred at 0.40 to 0.50% by weight of the CaCO₃ used.

<i>Treatment</i>	<i>% CaCO₃</i>	<i>Tensile Stress (Mpa)</i>	<i>Elong. Strain (%)</i>	<i>Mod. (Mpa)</i>
<i>None</i>	<i>10</i>	<i>48.70</i>	<i>6.59</i>	<i>12.50</i>
	<i>20</i>	<i>40.18</i>	<i>3.40</i>	<i>12.90</i>
<i>Stearic Acid</i>	<i>10</i>	<i>44.20</i>	<i>2.98</i>	<i>14.83</i>
	<i>20</i>	<i>40.00</i>	<i>2.99</i>	<i>13.37</i>
<i>0.4% LICA 12</i>	<i>10</i>	<i>63.23</i>	<i>11.50</i>	<i>17.20</i>
	<i>20</i>	<i>52.67</i>	<i>9.14</i>	<i>19.50</i>

Using 0.4% LICA 12 as a treatment level, the table above was generated showing that 0.4% LICA 12 treatment for 10 and 20% CaCO₃ filled PP increases elongation by three to fourfold while tensile strength is increased ~50%. The titanate therefore makes the 20% CaCO₃/PP composite 3.5 times tougher than the untreated or stearic acid treated controls. Titanate chemistry, rather than ammonium quats, has a much

better chance of working in MMT/PO's and other nanofilled thermoplastics. And the ammonium chemistry can cause foaming and degradation. For example, when ammonium quat modified nanofiller was run with pyrophosphato titanate in an EVA compound at conventional temperatures foaming occurred from the nitrogen in the quat. The problem was solved by lowering the process temperature by 13%, which is not only a benefit of titanate use, but a necessity if one is to have an optimal resulting composite. Replacing the ammonium quat with the pyrophosphato titanate quat can only be done in the water slurry at the MMT clay mine.

CaCO₃/PP: Doufnoune and Haddaoui's work confirmed work by Sharma et al., who studied earlier [204] the effects of KR TTS on CaCO₃ filled PP. The abstract reads in part: *"Composites of polypropylene – CaCO₃ coated with isopropoxy triisostearoyl titanate have been prepared on a Buss Ko-Kneader. These composites have been evaluated for mechanical properties, melt index, dispersion, and adhesion of polymer to filler using the scanning electron microscope. ...Uniform dispersion of filler in the composite and long alkyl chains of the coupling agent provide additional advantages such as improved melt index, higher tensile elongation, and better optical properties."*

CaCO₃/ATH/PP: Szijártó et al studied [205] the effects of calcium stearate and KR TTS on 75 and 150 phr CaCO₃ and ATH filled PP. They concluded: *Comparing a surfactant (calcium stearate) with a coupling agent (titanate) we found a great difference between the effectivity of the two treatments on the flow properties. The difference between the effectiveness of the two treatments is smaller in the case of impact properties. In both cases the titanate was more effective"*.

Hydroxyapatite/HDPE: Sousa et al. studied [206] the interfacial interactions and structure development in injection molded HDPE/hydroxyapatite prosthetic composites using a titanate (LICA 12) & zirconate (NZ 12).

Hydroxyapatite/Starch/EVOH-Synthetic Human Cortical Bone: Vaz et al. claim [207]: *"The optimization of these coupling processes associated with the introduction of higher amounts of filler, may be an effective way to produce composites with mech. properties analogous to those of the human cortical bone"*. Specifically, the abstract reads: *"Different zirconate, titanate and silane coupling agents were selected in an effort to improve the mech. properties of starch and ethylene-vinyl alc. copolymer (EVOH)/hydroxylapatite (HA) composites, through the enhancement of the filler particles-polymer matrix interactions and the promotion of the interfacial adhesion between these two phases. The mech. performance was assessed by tensile tests and discussed on the basis of the resp. interfacial morphol. (evaluated by SEM). The main relevant parameters were found to be the surface properties and reactivity of the filler (non-sintered HA) and the chem. nature (pH and type of metallic center) of the added coupling agent. Significant improvements in the stiffness were achieved (about 30% increase in the modulus) when using the acidic zirconate coupling agents. The acidic zirconate combined the capability of crosslinking the polymer matrix with the establishment of donor-acceptor interactions and hydrogen bonding between it and the ceramic particles, leading to very good interfacial adhesion. The optimization of these coupling processes assocd. with the introduction of higher amts. of filler, may be an effective way to produce composites with mech. properties analogous to those of the human cortical bone."*

Wood Fibre/MAH/Polyolefin: Maleic Anhydride was found to work synergistically with LICA 12 and LICA 38 for Andersen Corporation for wood fiber filled polyolefins in work by Godavarti, S. et al. [208] entitled: *"Polyolefin wood fiber composite containing compatibilizers"*. Abstract: *"The patent relates to a weatherable, mech. Stable thin walled complex profile composed of a composite comprising: (a) greater than about 25 weight % of a polyolefin polymer composition having a melt index of less than about 5 gm/10 min a m.p. of about 145° to about 158°; and (b) greater than about 50 up to about 75 weight % of a wood fiber, the fiber having a moisture content of less than about 5000 parts of water per million parts of the profile, a particle size of about 100 to about 2000 μm and an aspect ratio of about 1:2 to about 1:5; wherein the profile comprises an extruded complex hollow member having a defined support direction and a wall thickness of less than about 5 mm, the tensile modulus of the profile is greater than about 5.105 psi, the heat distortion temperature of the profile in the defined support direction is greater than about 75° at about 264 psi. The composite comprises a compatibility polyolefin*

wherein the polyolefin is a maleic anhydride grafted polyolefin, with 1 to 100 mol maleic anhydride per mol of polyolefin, the tensile modulus is at least about 8.105 psi. The profile is used in the manufacture of the fenestration components such as windows and doors”.

Wood Adhesion – Amino Titanate vs. Amino Silane as a Wood Anti-Tannin: When a 1.5 nanometer titanate or zirconate reacts at the atomic monomolecular level, it doesn’t know whether it’s in a thermoplastic or thermoset composite – or a coating or ink for that matter. So, cross-discipline advances in materials science advance the state of the art, and we all can learn from them. Such is the case with painting wood – thinking of it as an analog for painting a molten polyolefin coating on to a wood fibre. A major challenge in putting a coating on to a wood substrate is to maintain adhesion and to protect the wood from permeation by water, oxygen and chemicals. An even greater reverse challenge is to stop the tannin from wood and wood knots from permeating to the coating surface to ruin its color and appearance. Sherwin Williams discloses: “*Tannin stain-inhibiting coating compositions* [209] **DETAILED DESCRIPTION OF THE INVENTION**

This invention relates to a coating composition comprising a titanate coupling agent. This invention also relates to a process for inhibiting tannin staining in a tannin-containing substrates. The combination of the titanate coupling agent with a aqueous polymer creates a coating that effectively prevents tannin stains from migrating into after-applied water-based finishes...Organotitanates found to effective for improved tannin stain blocking in unpigmented and pigmented water-based coatings include aminotitanates and neoalkoxytitanates, such as neoalkoxy-tri(N-ethylaminoethylamino) titanate (available as LICA 44 from Kenrich Petrochemicals, neoalkoxy-tri(dioctylphosphato) titanates (available as LICA 12 and LICA 38 from Kenrich Petrochemicals) and the like...The following non-limiting examples are provided to further illustrate the coatings prepared according to the present invention and useful in tannin stain blocking systems. These examples are intended to be illustrative of the present invention and are no way intended to limit the scope of such except as further delineated in the claims.

Test Method for Tannin Stain Blocking

Staining substrates such as dark-staining cedar and Redwood are used in this test and are planed and sanded. Boards are chosen with a consistent grain pattern across the length of the board to avoid variability in the test. The test panel is divided into equal sections. Test primers are applied by brush to equal spread rate (i.e. approximately 400 square feet per gallon determined by weighing of the test paint) and allowed to dry. A high-hiding topcoat paint, which permits the passage of tannins is then applied to the entire panel, also at 400 square feet per gallon. The panel is then immediately placed in a sealable 12 cubic foot misting chamber for continuous misting with 40° F water. The panel is allowed to remain in the misting chamber for 16 hours. The panel is then removed from the misting chamber, and allowed to dry for at least 16-24 hours. The panel is then rated for tannin stain blocking.

A water-based tannin stain blocking pigmented primer paint. (38.9% pigment volume concentration; 32.7% volume solids) is used as a control in all examples which contain titanate coupling agents.

Tannin stain blocking can be measured qualitatively by visually comparing the test panels to the control, and ranking each panel on a scale of 1 to 8 (1=best; 8=worst) In this method of judging tannin stain blocking, two (±2) units are considered significantly different...

Example 1 of Tannin Stain Blocking of Paints

Pigmented paint samples were modified with 0.5%, 0.75% and 1.0% by weight of LICA 44 and tested

Sample ID	Description	Rating (1-8)					
		(1=best/8=worst)					
		#1	#2	#3	#4	#5	Total
A	Control 0.00% LICA 44	6	8	8	8	8	38
B	0.50% LICA 44	1	4	4	4	3	16
C	0.75% LICA 44	3	4	2	1	1	11
D	1.00% LICA 44	2	1	7	2	2	14

for tannin stain blocking. The emulsion composition is 48% by weight butyl acrylate, 50% by weight methyl methacrylate, 1-2% by weight methacrylic acid and 1-2% by weight acrylic acid. The paint formulation is 19.5% pigment volume concentration and 37.4% volume solids.

The addition of neoalkoxy-tri(N-ethylaminoethylamino) titanate (LICA 44) improves tannin stain blocking of pigmented coatings as evidenced by rating values. The lower the value in a rank sum analysis evidences a more effective stain blocking effect. The coatings containing the titanate coupling agent effectively blocked and prevented tannin from migrating into the coating. The control did not prevent the tannin stains from migrating into the applied coatings.

Example 2-Tannin Stain Blocking of Pigmented Primers on Redwood-LICA 44 compared to Z6020
The polymer is as in Example 1.

Sample ID	Description	Rating (1-8)					
		(1=best/8=worst)					
		#1	#2	#3	#4	#5	Total
A	Control 0.00% LICA 44	6	8	8	8	8	38
B	0.5% LICA 44	1	4	4	4	3	16
	0.5% Z-6020	6	3	5	4	6	23
D	1.0% LICA 44	2	1	7	2	2	14
	1.0% Z-6020	8	6	4	8	4	30

The addition of neoalkoxy-tri(N-ethylaminoethylamino) titanate (LICA 44) improved tannin stain blocking of pigmented coatings as compared to Aminoethyl-aminopropyltrimethoxysilane (Z-6020) as evidenced by rating values. The lower the value in a rank sum analysis evidences a more effective stain blocking effect. The coatings containing the titanate coupling agent effectively blocked and prevented tannin from migrating into the coating. The control did not prevent the tannin stains from migrating into the applied coatings.

Function 2 Ti and Zr Catalysis Functionality Added to the Filler Interface – Ammonium quats, sodium based surfactants, metal stearates, and other exfoliating agents that may be considered for dispersion/deagglomeration of a filler or nano particulate generally cannot surpass the proven performance of Ti or Zr as catalysts in polymer art. For example, the combination of: a three to ten-fold efficiency on a weight basis of a titanate when compared to an ammonium quat in the exfoliation of nano particulates such as MMT clay; and the beneficial catalysis mechanisms that titanates and zirconates bring to the interface of the post-reactor polymer macromolecule – make subject organometallics logical additive candidates for consideration in developing new and novel nanocomposites.

Replace PP-MFI 120 with PP-MFI 30 and Get Lower Torque: Using titanate, higher molecular weight polymers can be used while increasing flow – thereby gaining the advantage of intrinsic mechanical strength from the lower MFI polymer. For example, typically, the Brabender Torque, Nm @ 180°C for PP-MFI 120 is 2.9 and PP-MFI 30 is 6.1. A private communication from Gerhard Strohle to Monte showed Brabender Torque, Nm @ 180°C using 0.16% phosphato zirconate lowered the torque of PP-MFI 30 from 6.1 to 2.3 (lower than MFI 120) and increased tensile strength by 10% and strain strength by 15% over the starting MFI 30. Also, if a low molecular weight plasticizer is used to increase a polymer’s flow – but creates extraction issues, 0.2% titanate will typically allow a 20% reduction in that plasticizer with no loss of flow or flexibility. This effect may also be translated to polymers used in coatings.

Butadiene – Peroxide Cured Golf Ball Core: Increased stress/strain strength with titanate occurs even in cured thermosets. See Figure 17 – The patented Wilson “TITANIUM” peroxide cured polybutadiene ball based on KR TTS titanate induced increase in COR (Coefficient of Restitution) [1-ref. 43]. This is just another example of imparting “toughness” to the non-polar polymer.

Fiberglass/Filler Reinforced Thermoplastics and Thermosets – Strength from Catalysis: The following examples are instructive in showing that titanates can not only couple fiberglass (FG) or a filler, but catalyze the polymer phase:

- Figure 28 – A 40% FG/PC Ford F-Series Truck Fuse Box Cover (F2TB-15045D64; 4426-2056; PC-WSB-M4D627) was made by injection molding a 57g shot of 40% fiberglass/polycarbonate with 1% CAPS L 12/L and showed: a 60 to 45 sec. reduction in mold cycle time; a 52°C reduction in process temperature; a 45% SPC (Statistical Process Control) reduction in out of tolerance measurements (i.e., improved dimensional stability); and an increase in minimum specific property requirements: tensile strength at yield (54.5 MPa), notched izod (44.6KJ/m²) and melt flow (22.9 g/10 min.).
- Figure 29 – Precompounded 40% FG, Fe₂O₃ filled PC whetstone with poor weld lines without titanate (Top) and with 1% CAPS L 12/L titanate (Bottom). Titanate allowed Diamond Machinery Technology, Inc. to: reduce IM process temperatures by 116°C; eliminate weld line problem; improve red color appearance; and increase impact strength.
- Figure 30 – The 40% FG/Nylon automotive part shown had a 7-second reduction in cycle time and lowered process temperatures (°C) by 11% (rear zone: 282-248; zone 1: 304-254; zone 2: 304-227; nozzle: 310-260) using 1% CAPS L 44/E titanate.
- Figure 31 – FG/MEKP Cured Unsaturated Polyester – Silanes made the FG unsaturated polyester industry what it is today. Interestingly, since silanes react with OH groups, and there are on average 14% OH groups on the FG surface there is the potential for incomplete coverage by the silane. This may be evidenced by delamination on aging or the fibres being visible through a clear resin. For example, Figure 31 shows a swatch of FG (silane sized E-glass)/MEKP cured unsaturated polyester showing glass fibres (left) – indicating that the entire surface of the FG is not wetted. (Right) Same composition except a pyrophosphato titanate added in-situ to the resin does not show the glass fibres. Similar effects were reported for FG reinforced epoxy [2].
- Figure 32 – Foamed MEKP - (Left) Control: Norox® MEKP-925 Cured Ashland Polaris® MR 20000 SHV Polyester exhibited a 50-minute cure with a typical 135°C (274°F) continuous exotherm causing bubbles. (Right) 1% CP-03 proprietary hybrid titanate having pyrophosphato, amino and acrylic functionality exhibited a 7-hour cure, no exotherm – first 6-hours, then exotherm to 34°C (94°F) while exhibiting no bubbles in the final hour of cure leaving a pinhole free composite. Typically, a 20% increase in peroxide offsets any titanate induced free-radical reduction effect. Caution, it is not good practice to add the titanate to the MEKP peroxide because an extreme exothermic reaction ensues. We found cobalt naphthanate not to be useful as an accelerant. In this case, we found heating the mold to be very effective in accelerating the cure time. At 38°C, the control cured in 22-minutes, but at the 18-minute point, breakdown was observed. The color changed from amber to purple and 45 minutes later the color was back to normal. At 38°C, the titanate cured completely in 1:04-minutes and the color changed to purple. At 66°C the control could not be cast, while the titanate cured in 16 seconds and the color changed to purple to green. The titanate discs cured at RT were significantly stronger than the control. The control shattered when dropped from a 6' height while the titanate disc bounced unbroken. New and novel FG/polyester composites are therefore made possible.
- Figure 33 – 60% 3-micron CaCO₃ filled peroxide cured unsaturated polyester resin was cast at 25°C. The control (left) exhibited pinholes while the CP-03 titanate disc (right) was virtually pinhole free. Complete details will be made available in a commercial technical bulletin on CP-03 at the ACMA 2006 (American Composites Manufacturers Association) exhibition in St. Louis, MO – October 18-20.
- Figure 34 is a section of glass reinforced epoxy pipe. The in situ addition of 0.2% aromatic amino zirconate (NZ 97) to epoxy resin wets completely the E-glass (silane sized) reinforcing fiber. The epoxy pipe was used to house an anti-submarine device that was delaminating (left) from hydrostatic pressure created by deep ocean drops. The NZ 97 containing composite (right) did not

fail. Figure 35 shows fiberglass reinforced vinyl ester coupons unexposed and exposed to 5% NaOH with and without aromatic amino titanate LICA 97. The titanate increases the chemical resistance as compared to the silane sized conventional E-glass used. Windmill blades will last longer and still be spinning rather than in a landfill.

Function 3–Flame Retardance via 2-Nanometer Atomic Monolayer Ti-Phosphorus Intumescence –

The following discussion discusses how nanotitanium phosphorescence can be imparted to any surface. The author has demonstrated in: Ammunition and Explosives – the ability to control the flame spread of nitramine RDX explosive in spalls of burning 19-perf LOVA ammunition propellant (85% RDX/CAB – cf. Figure 36) with LICA 12 [214] (under DoD Secrecy Orders – 15 yrs.); reduce the burn rate and burn rate exponent of AP/Al/HTPB PU solid rocket fuel with LICA 38 [215] (under DoD Secrecy Orders – 12 yrs.); and render CaCO₃ filled LLDPE flame retardant with LICA 38 [216]. There is the possibility of nanophosphorus titanate chemistry as: a transparent flame retardant with transparent nanofiller; as a synergist for improved mechanical properties at reduced levels of FR filler to equivalent FR performance; or as a synergist at conventional art levels. The FR fountainhead is in the phosphato and pyrophosphato Function 3 the organometallic molecules used in the compositions next discussed.

Phosphato Titanium Coupled CaCO₃ as a Flame Retardant: The author prepared [216] flame retardant 3-micron CaCO₃ by Henschel pretreatment using 3% LICA 38. The CaCO₃ was charged to the Henschel, which was then turned on to low speed (1800 rpm's). LICA 38 was then added dropwise to the center of the CaCO₃ vortex over a 1-minute period followed by a 50-second postmix. As discussed, if the filler were Mg(OH)₂ then 3 to 5 minutes dropwise addition would be required. The thus treated CaCO₃ was then incorporated at 44% by weight into a 20-melt LLDPE on a 2-roll mill. The filled LLDPE was sheeted off and pressed into a slab and then cut into uniform strips as shown in Figure 37. The process was repeated with a control of 44% untreated CaCO₃ filled LLDPE. Alternately, the pyrophosphato titanate could have been incorporated into the polymer followed by addition of untreated CaCO₃ using the reactive compounding techniques as discussed previously. As can be seen from Figure 37, after 2-min.:26-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 over a period of 2-min.:37-secs.

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. Monte believes that when increasing pyrophosphato or phosphato titanate above the atomic monolayer on the FR interface, the excess titanium phosphorus in the polymer interphase acts as a nano intumescent synergist allowing diminishment of the FR particulate in direct proportion to the amount of pyrophosphato titanate added. For example, in the aforementioned solid rocket fuel grains, 0.5% LICA 38 controls the burn rate while 2% extinguishes it, thus allowing rocket motors with stacked start/stop grains [215].

Also, keep in mind that titanate Function 2 allows most unfilled and unfilled polymers to be processed at ~10% lower temperatures thus allowing HOH releasing FR's such as ATH (see Figure 38) and Mg(OH)₂ to be processed more readily. For example, Braga et al [217] of Basell used ATH treated with LICA 12 to obtain "Flame-proof polyolefin compositions". 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.*"

Titanate/Zirconate Quats for Use in the Water Based Phase – In order to be effective at the atomic monomolecular level, the coupling agent must be solubilized or finely emulsified into the water/organic (solvent, plasticizer, polymer) phase. LICA 38 may be rendered water soluble for latex systems via quaternization with N,N-dimethylamino-alkyl propenoamide to form a pyrophosphato titanate quat (LICA 38J). SBR latex film containing 150 phr CaCO₃ and 1.5 phr pyrophosphato titanate quat shows no change in modulus, tensile or elongation when oven aged at 121°C for 24 hours while a control with no coupling agent lost half of its original elongation [cf. ref. 116 - table 264]. Reactivity with CaCO₃ and the importance of solubilizing or finely emulsifying the titanate in the dispersion phase is demonstrated in Table 22. LICA 38 was preblended with varying amounts of ethoxylated nonyl phenol (ENP – Rhodia Igepal CO 660), emulsified into the water followed by addition of the CaCO₃. The viscosity reduction achieved from 3,600,000 to 3,000 cps is significant.

What Table 10 also teaches is that a 1.5-nanometer atomic monolayer is the length your thumbnail grows in a second and the emulsification or solubilization has to be complete to work efficiently. The degree of emulsification of water insoluble LICA 38 is more important than the amount used and 0.39% of an active titanate emulsified atomically is much more efficient than 0.69% of the same titanate emulsified incompletely – see images next:

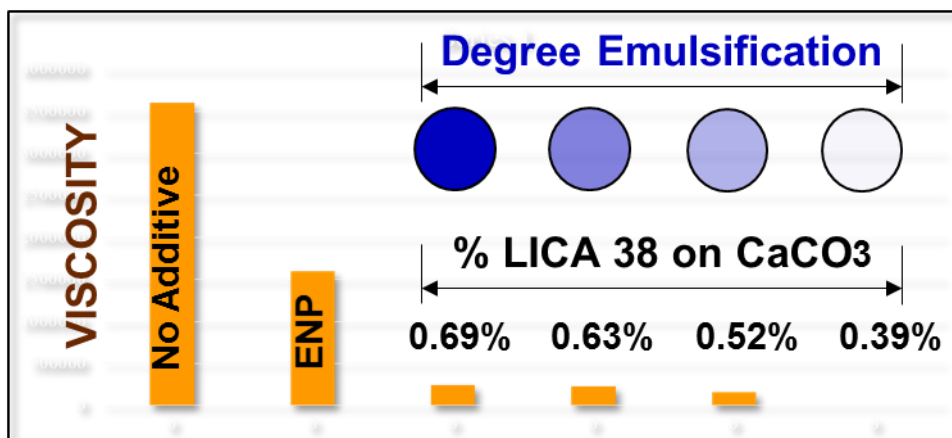
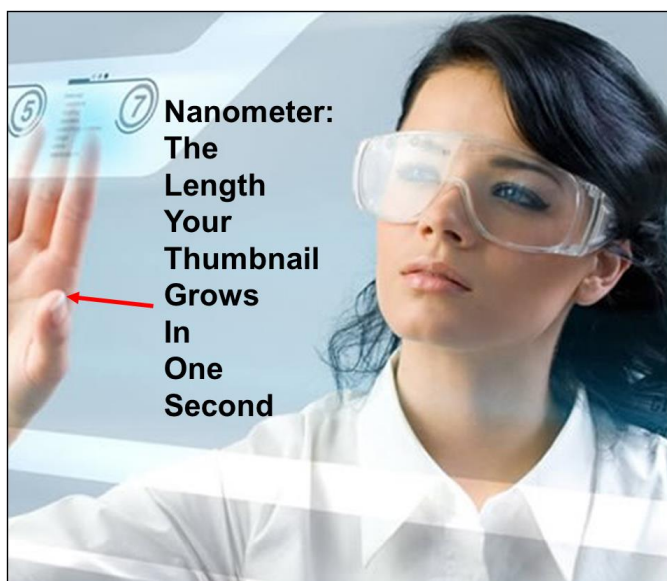


Figure 39 demonstrates that 20% pyrophosphato titanate is hydrolytically stable and water insoluble. Experience shows the titanate does not hydrolyze in the water – even after standing for 1-year. Titanates such as TIPT are known to be hydrolytically unstable. The quaternized titanate – LICA 38J is readily

water soluble. The effect of the emulsified titanate will vary as to particle size and surface treatments used in the “wet cake” before the pigment is dried and ground for commercial use.

A pyrophosphato titanate quat (KR 138D) provides corrosion resistance to mild steel (cf. Figure 40). As is the case with CaCO_3 , the emulsifiable LICA 38ENP makes water a solvent for carbon black (cf. Figure 41). Figures 42, 43, and 44 are a time lapse study of the effect of a directly water emulsifiable dodecylbenzenesulfonyl titanate (LICA 09) on conductive Cabot XC-72R carbon black in water. Normally, carbon black is hydrophobic and “floats” on water. The LICA 09 “dispersed” the carbon black electrochemically without mechanical stirring. Efficacy in the water phase carries over to all manner of pigments such as ultramarine blue (cf. Tables 11-16).

Silicate Systems - This paper represents an extension of the art with respect the usage of organotitanium and zirconium based organopyrophosphates as anti-corrosives in clear coat silicates and in zinc rich silicate systems. Based on data developed in this study (cf. Tables 23-25), it appears that the primary mechanism for benefaction of silicate systems by organotitanium and/or zirconium organopyrophosphates is a consequence of surface passivation. Uniformity of lay down and extreme adhesion of silicate based coatings in formulations containing such additives also undoubtedly play a significant role in improving performance.

Combinations of organotitanates and zirconates were found to be uniformly more efficient than strontium chromate as anti-corrosives in aqueous lithium silicate systems subjected to either salt spray or 315°C, high humidity, air thermal cycling. These same combinations of organometallics were shown to provide significant improvements in corrosion resistance to attack by air saturated 10% aqueous acetic acid containing 5% dissolved salt at 93°C, and 38 - 482°C air thermocycles employing 5% sulfur trioxide and 10% water as the corrosive medium. Similarly combinations of organotitanium pyrophosphates and organozirconium pyrophosphates were shown to provide substantial performance upgrade with respect to the resistance of an ammonium silicate based zinc rich coatings on carbon steel and aircraft aluminum against oxygen saturated, 5% caustic in a -4 - 66°C thermocycle. It should be noted that benefits observed by the usage of indicated combinations of organometallics are measured on a comparative basis against equal or greater proportions by weight of strontium chromate and simultaneously against no additive control systems subjected to comparable environments under identical conditions. Further details regarding the specific tests performed are given in Tables 23-25.

Anticorrosive Water Based Acrylics - Two water based coatings formulated with 46% styrenated acrylic polymer (Joncryl RC 537) having a Tg 44°C and a MFFT 42°C using QB 012 and either ZPA [Zinc Phospho Aluminate (WB-06)] or ZMP [Zinc Molybdate Phosphate (WB-07)] out-performed a solvent based red lead, zinc chromate alkyd coating when exposed to 750 hours ASTM B-117 salt spray. The QB 012 containing acrylic coatings dried faster (less than one hour when compared to six hours for the control), exhibited better adhesion (crosshatch/tape adhesion), and just plain looked better and glossier (cf. Figures 45 and 46).

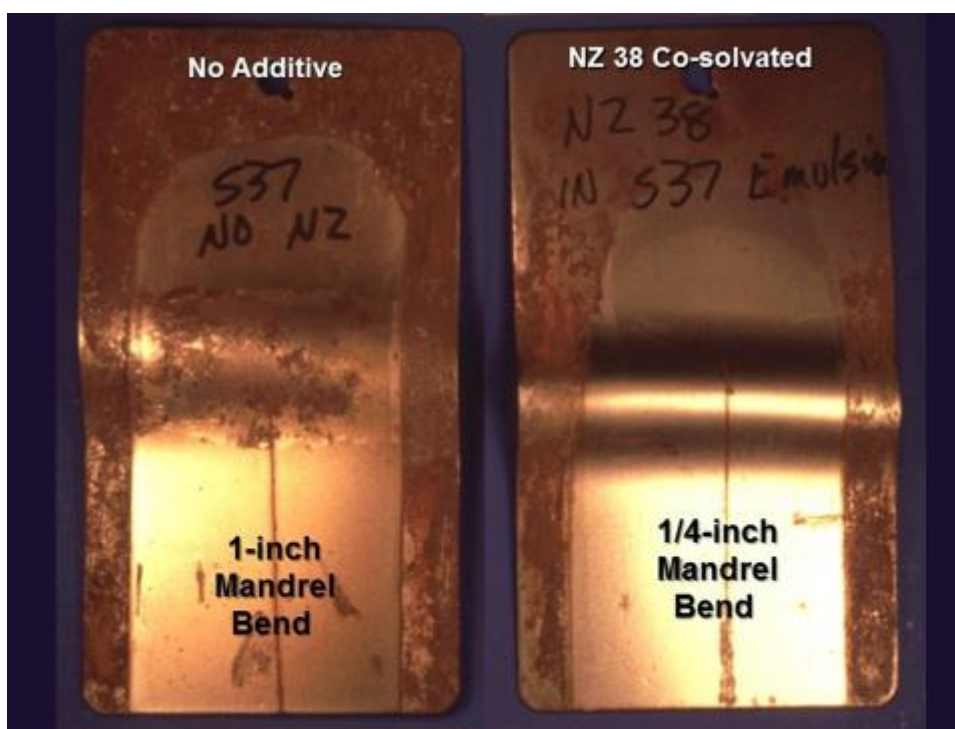
A water based acrylic primer coating using 0.25% QB 012 by weight of total solids out-performed an acrylic control and a C.G.S.B. 1-GP-48M red lead, zinc chromate alkyd primer coating when exposed to 1300 hours ASTM B-117 salt spray (cf. Figures 47 and 48).

A blue pigmented water based acrylic (Joncryl RC 537) coating containing NZ 38J applied directly to unprimed R38Q panel (tin steel auto) and baked 15 minutes at 65°C exhibited excellent gloss after exposure to 300 hour carbon arc (UV weathering) and 500 hours 96% relative humidity at 35°C. NZ 38J is not soluble in hard water, but it solubilizes readily into the acrylic emulsion polymer (cf. Figure 49).

A gray-pigmented water based acrylic (Joncryl RC 537) coating containing QB 012 was applied to Q panels and air-dried for 12 hours. Test panels showed: no loss of gloss when subjected to 300 hour carbon arc; no corrosion after two hour immersion in 10% HCL acid followed by 1300 hours exposure to 96% relative humidity at 35°C; no loss of adhesion or rupture when subjected to ½ inch mandrel blend (cf. Figure 50).

Three clear water based acrylic (Joncryl RC 537) coatings were applied to Q panels containing: a no additive control; 0.5% NZ 38J Quat; and 0.5% NZ 38 let down into the acrylic emulsion polymer as a solution of 10% NZ 38 in a 90% ester alcohol co-solvent (cf. Figure 51). The panels were then baked for 10 minutes at 65°C, conditioned in air for one hour and then immersed eight hours in 5% NaCl solution at 3.27 pH. The control exhibited severe discoloration and complete delamination when subjected to 1” mandrel bend, with significant corrosion exhibited on the exposed bent metal. The NZ 38J containing panel showed no discoloration, no breakage when subjected to ¼” mandrel bend, and very mild corrosion at the scribe. The NZ 38 co-solvent emulsion-containing panel showed no discoloration, no breakage and no corrosion at the scribe. This test demonstrated that the pyrophosphato zirconate functionality controls corrosion and adhesion performance, and the amine used to quaternize it detracts somewhat from its performance.

Why is a WB Acrylic coating as shown in Figure 51 relevant to UV/EB coatings? If Acrylic monomers and oligomers are the building blocks of UV/EB coatings, then the Function (2) catalysis ability of a zirconate or titanate to increase the flexibility of the unfilled Acrylic coating – as well as the adhesion and anti-corrosion performance – offers the formulator latitude in selecting the oligomer to monomer ratio:



Why Ammonium Quats as Nanoparticulate Exfoliating Agents Are Not Always Useful – The nano-interfacial reactions with subject organometallics preclude that the formulator be aware of any surface treatments on “as received” materials. Sometimes nano-material vendors are more concerned with shipping exfoliated material than they are on the effect the nano-exfoliating additive in the polymer next. For example, Table 26 shows the many tests needed just to get to the correct ratio of Cloisite 15A (Southern Clay) to mineral oil so as to be able to begin the necessary in situ ladder study to determine optimum dosage. Since Cloisite 15A (A as in Ammonium – Southern Clay) is a natural montmorillonite modified with 35% or more of a quaternary ammonium salt, the reaction to increasing amounts of LICA 38 was not beneficial, but rather a non-functional viscosity growth log curve indicating interference at the interface by the ammonium quat. The formulator would be better served to receive a less exfoliated nano-material such as Cloisite Na⁺ and do the exfoliation in situ with subject additives.

Nano Clay Reinforced Elastomer – The work below by Wang et al. is typical of the current shotgun approach to the nano/polymer interface. The author’s first titanate produced was an isopropoxytitanium

tristearate made in 1973 – and it is listed with two silanes in Wang’s work. I fail to see how a quaternary ammonium salt such as cetyltrimethylammonium chloride on the interface of a MMT clay will help to make it compatible with a non-polar thermoplastic PP or a thermoset EPR rubber – but, may work in a thermoplastic Nylon or thermoset polyurethane.

TI Method for preparation of modified montmorillonite for rubber-inorganic nanocomposite materials

IN Wang, Xiaoping; Jia, Demin

PA South China University of Technology, Peop. Rep. China

SO Faming Zhuanli Shenqing Gongkai Shuomingshu, 13 pp. CODEN: CNXXEV

PI CN 1624033 A 20050608

AB The method comprises mixing 100 parts powd. montmorillonite (Ca/Na montmorillonite) with 1-50 parts organic modifier (e.g., organic amine, organic quaternary ammonium salt, or their mixture) at room temperature to 150°, stirring at 50-150° for 10-100 min, and cooling to obtain the modified montmorillonite. Organic quaternary ammonium salt is selected from cetyltrimethylammonium chloride, cetyltrimethyl ammonium bromide, octadecyl tri-Me ammonium chloride, octadecyl tri-Me ammonium bromide, etc. Organic amine is chosen among aniline, laurylamine, octadecylamine, caprolactam, 6-aminocaproic acid, etc.

IT 68443-53-8, Isopropoxytitanium tristearate

IT 78-08-0, Vinyltriethoxysilane 107814-75-5, γ -Glycidoxypropyltrimethylsilane

MMT Nanoclay (Cloisite Na⁺) Exfoliation in Water with Various Titanate Quats – Figure 38 showed the typical and desirable effect of 60% non-Nano ATH in Mineral Oil as viscosity is reduced from 800,000 to 9,600 cps using 0.7% LICA 38 water insoluble pyrophosphato titanate in situ (not pretreated) in the mineral oil. We needed to develop similar data that demonstrated water soluble pyrophosphato quats could be used similarly to exfoliate MMT clay such as Cloisite Na⁺ in water or booklets of calcined clay as shown previously in Figure 16. Table 28 shows that with Nano clay in water – even 20% is too high a loading to demonstrate the typical dramatic titanate dispersion or exfoliation of a particulate. So, we reduced the MMT clay loading down to 7% and waited to see what happened to viscosity, which typically climbs on aging in most pigment to binder dispersions. It did. The control went from 65 cps to 14,000 cps in 2 hrs. – and then to 96,000 cps in 72 hrs. Several titanate quats and blends were tried, some of which are shown in Table 28. A particular quat blend (QB 046) displayed novel viscosity reduction effects as 72 hr. viscosity was reduced from 96,000 to 1,400 cps (see Table 27 and Figure 52).

Silica Exfoliation in Water with Pyrophosphato Titanate Quat – Figure 53 illustrates the almost instantaneous exfoliation experienced as 2.4% LICA 38J by weight of silica solids was stirred into the liquid silica sol gel causing it to exfoliate into a powder as the opened up surface area absorbed all the available moisture: Top photo – (left)-34% 20-nanometer silica sol gel (Nyacol) control with no titanate; (right)-2.4% LICA 38J by weight of silica is stirred into the sol gel exfoliating the silica which absorbs all the water to form a powder. Middle photo – (left)-a 34% 20-nanometer silica sol control with no titanate oven dried at 120°C for 3 hours; (right)-2.4% LICA 38J has been added and oven dried at 120°C for 3 hours to yield a higher bulk volume. Bottom photo – (left)-a 34% 20-nanometer silica sol control with no titanate evaporated @ ambient for 2 weeks results in a solid/glassy hard pack silica at the bottom of the beaker; (right)-the same weight of 34% 20-nanometer silica sol to which 2.4% LICA 38J and dried in the same way shows a fluffy/exfoliated character and greater bulk density. See abstracts next:

TI Organic modification of nano-SiO₂ particles in supercritical CO₂

AU Wang, Zhi-Wen; Wang, Ting-Jie; Wang, Zhan-Wen; Jin, Yong

CS Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peop. Rep. China

SO Journal of Supercritical Fluids (2006), 37(1), 125-130 CODEN: JSFLEH; ISSN: 0896-8446

PB Elsevier B.V.

AB 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 thermogravimetric 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 19.81×10^{-7} mol/m², i.e. 1.19 mol titanate coupling reagent/nm², when the apparent concentration of titanate coupling reagent is 0.6% (weight).

IT 67691-13-8, KR 38S

TI Non-directional electrical steel sheets having good insulating coating quality

IN Takeda, Kazutoshi; Ishizuka, Kiyokazu; Arai, Satoshi; Fujii, Hiroyasu

PA Nippon Steel Corp., Japan

SO Jpn. Kokai Tokkyo Koho, 11 pp. CODEN: JKXXAF

PI JP 2005240125 A2 20050908

AB Elec. steel sheets are coated with an aq. soln. contg. colloidal SiO₂ having particle diameter ≤30 nm, acrylic resin emulsion 10-100, and titanate coupling agent 0.01-10 weight parts at 0.5-2.0 g/m² (as dried state) without foundation treatment.

IT 7631-86-9, Silica, uses 25085-34-1, Acrylic acid-styrene copolymer 59989-96-7, Isopropyltricumylphenyl titanate 61417-49-0, Isopropyltriosostearoyl titanate 64060-97-5, Tetraisopropylbis(dioctylphosphite) titanate 64157-14-8, Tetra(2,2-diallyloxymethyl-1-butyl) bis(ditridecyl) phosphite titanate 65460-53-9 65467-75-6 67691-13-8, Isopropyltris(dioctylpyrophosphate) titanate 67729-57-1 90959-84-5, Isopropyl tris(decylbenzenesulfonyl) titanate

Nanofilled Composites – Work by others to further demonstrate titanate and zirconate coupling agent composite efficacy – with an emphasis on nanotechnology – is herein offered. The specific commercial titanate is named since the additive mentioned in the abstract is often only identified by a CAS # or arcane nomenclature, which is often not meaningful to the uninitiated.

Nanoclay filled SBS: Andrea Galanati, et al. found [218] KR TTS useful: *“A series of composites based on a block-polystyrene (SBS) copolymer sample and clays was prepared using iso-Pr tristearoyl titanate (KR TTS), a coupling agent. The composites with the surface-modified clays (Montmorillonitic nanoclays) present lower temperature of mixing and torque than the analogous composites prepared without coupling agent. No side reactions were observed after processing and the thermoplastic and mechanical properties of the unmodified SBS are retained after compounding with the surface-modified inorganic fillers. In addition, elongation at break and heat deflection temperature increase with respect to the starting SBS. Flexible and efficient modeling of the material properties for on-demand tech. requirements is suggested.”*

Functionalizing Metal Oxide Nanoparticles: Furman, Benjamin L.; et al. [219] found NZ 33 useful: *“The title nanoparticles, e.g., zirconium, have a surface comprising hydroxyl groups as a reactive portion (A) and a less reactive portion (B), wherein A can be functionalized with high steric hindered functionalities, i.e., a coupling agent like zirconate...”*

Nano-scale Transparent, Conducting Metal Oxides : Dou, Fan et al. [220] found KR TTS useful: *“The compositions comprise: tin oxide 40-95, antimony oxide 0.5-35, titanium oxide 0.1-15, zirconium oxide 0.1-5, silicon oxide 0.1-15%, and use organic compounds as protective agent (A) and surface covered by a coupling agent (B), wherein all oxides have cryst. diam. of 5-30 nm. and are prepared from corresponding metal chlorides, A is selected from polyvinyl alc., polyvinyl pyrrolidone, potassium sodium tartrate, polyacrylamide, citric acid, EDTA, and fluorocarbon surfactant, and B is selected from silane, titanate, aluminate, zirconate and boroaluminate.”*

Microparticles Coated with Mono-Dispersed Oxides: Takeda, Atsushi, et al. [221] found NZ 44 useful: *“Cosmetics contain microparticles prepd. by (1) jet spraying of target powders with ≥0.1 wt. part film-forming materials comprising hydrolysis-resistant organometallic compds. And ultrapure water and/or hydrolysis-controlling org. solvents in dry mixers, (2) formation of precursor films by drying the materials without damaging the organometallic compds., and (3) removing functional groups of the organometallic compds. by high-energy UV and/or plasma irradiation while completely dispersing the precursors using ultrasonic horn with longitudinal amplitude ≥40 μm. Red No. 202 was coated with silica ultrathin film”.*

Nanocomposite Materials: Lindsay, C. I. [222] found LICA 12 useful: “A nano dispersion of a layered clay and a monomer, crosslinker (e.g. isocyanate), and functional compound intercalated within the gallery regions of the clay, where the compound contains ≥ 1 hydrophilic terminal groups such as ethylene oxide-propylene oxide polyol, is curable to give a polyurethane thermoset elastomer”.

Inorganic/Organic Hybrid Nanocomposites: Wang, Z. [223] found NZ 39 useful: “A method for producing an org./inorg. hybrid nanocomposite comprises (a) subjecting a dispersion of inorg. particles to ultrasonic agitation to produce a dispersion of nanosized inorg. particles having at least one linear dimension of a mean size from 0.1 to 250 nm, and (b) reacting the nanosized inorg. particles with an organic coupling agent to modify the surface of the particles to inhibit agglomeration of the particles. Thus, alumina C nanoparticles having an average size of 121 nm were produced by ultrasonic and mech. Agitation in methanol for 1 h, mech. agitation only produced alumina particles having an average size of 15-20 μm . The alumina nanoparticles were surface modified with 1-5%-methanol solution of NZ 39, and the dispersions were homogeneously mixed with an organic resin producing a UV curable nanocomposite comprising alumina nanoparticles (10.0), NZ 39 surface modifier (0.05), Z 6030 adhesion promoter (0.48), Ebecryl 8402-tripropylene glycol diacrylate 50/50 mixture (91.03), and Irgacure 184 photoinitiator (3.64 parts).”

Nanocomposites with Novel Co-Interclated Clay: Wu, L. et al. [224] used a pyrophosphato titanate quat (KR 238T), similar to the titanate quat (LICA 38J) used by Monte in Figure 32: “Polypropylene copolymer (PP)/montmorillonite clay nanocomposites (PPCN) were prepared by melt-intercalation of co-intercalated organophilic clay which has larger interlayer spacing than ordinary organophilic clay modified only with stearyl ammonium compds. One of the co-intercalation is a titanate coupling agent which can react with hydroxyl radicals at the clay surface at the time of intercalation and improve the interfacial compatibility. The dispersibility of clay in the PP matrix was observed by x-ray diffraction and TEM under melt mixing using twin screw extrusion. Maleic anhydride grafted polypropylene (PP-MA) was added to enhance the dispersion of clay in PP. The crystallization of PPCN was studied by DSC. Both the crystallization temperature and crystallization rate of PP increased by the introduction of PP-MA and clay which functioned as nucleation center during the crystallization process of PP. The incorporation of clay and PP-MA into PP led to increasing of modulus, impact strength, and fracture strength.”

Nano-TiO₂ filled SBS/PS: Sun, F. et al [225] used KR 12 titanate to treat nano-TiO₂: “The surfaces of nano-TiO₂ particles were treated by titanate ester coupling agent before blending with polystyrene (PS). The interaction between nano-TiO₂ and the coupling agent was studied by IR spectrum and TEM. The influences of TiO₂ and rubber elastomer additive content were studied by measuring the mech. and flowing property. The results show that nano-TiO₂ can be uniformly dispersed in PS. And PS can be toughed by nano-TiO₂. The properties of SBS/TiO₂/PS composite are better than that of TiO₂/PS and SBS/PS composites. In addition, nano-TiO₂ can improve the fluidity of PS.”

Nano-Mg Modified with Titanate and Silane: Zhu, L. et al [226] found KR 12 titanate to perform better than silane (silicone) KH 150: “Nano-Mg/PP composites were prepd. by mixing polypropylene and nano-magnesium powder modified with silicone (silane) and titanate coupling agents. The modification effect of titanate coupling agent is better than that of silicone, and results in good mech. Properties. The experiment result shows that 2% of titanate is an optimal content for the composite. The IR spectroscopy anal. confirms that chemical bonds are built up between nano-magnesium particle and titanate.”

Nanocrystalline PVC Effect on PVC/CaCO₃ Composites: Xiong, C. et al. [227] investigated the effect on nanocrystalline PVC and varying amounts of KR TTS titanate in CaCO₃ filled PVC.

Ti-containing Nanocomposite Magnet Powder Particles: Nishiuchi, T. et al. [228] found KR TTS titanate useful in polyamids: “Preferred embodiments of the present invention provide a compd. For a rare-earth bonded magnet, which can minimize the deterioration in magnetic properties due to heat applied to form a bonded magnet by a compaction process, can improve the compactibility including flowability, and can make a rare-earth bonded magnet with excellent magnetic properties and anticorrosiveness. A compound for a rare-earth bonded magnet includes a rare-earth alloy powder and

a binder. The rare-earth alloy powder includes at least .apprx.2% of Ti-containing nanocomposite magnet powder particles with a composition represented by $(Fe1-mTm)100-x-y-zQxRyMz$, where T is Co and/or Ni; Q is B with or without C; R is at least one rare-earth element substantially excluding La and Ce; M is at least one metal element selected from Ti, Zr and Hf and always includes Ti; and $10 < x \leq 20$ atomic%; $6 \leq y < 10$ atomic%; $0.1 \leq z \leq 12$ atomic%; and $0 \leq m \leq 0.5$. The particles include at least two ferromagnetic crystalline phases, in which hard magnetic phases have an average crystal grain size of .apprx.10 nm to .apprx.200 nm, soft magnetic phases have an average crystal grain size of .apprx.1 nm to .apprx.100 nm; and the average crystal grain size of the soft magnetic phases is smaller than that of the hard magnetic phases.”

Inorganic/Organic Hybrid nanocomposite: Wang, Z. [229] used NZ 39 zirconate to deagglomerate and Z 6030 silane as an adhesion promoter: “A method for producing an org./inorg. hybrid nanocomposite comprises: (a) subjecting a dispersion of inorg. particles to ultrasonic agitation to produce a dispersion of nanosized inorg. particles having at least one linear dimension having a mean size between 0.1 and 250 nm; and (b) reacting the nanosized inorg. particles from step (a) with an organic coupling agent to modify the surface of said particles to inhibit agglomeration of said particles. Thus, nanocomposite of 10.0 parts silica modified with 88.9 parts Eb 1290, a hexafunctional IPDI-based polyurethane acrylate, in the presence of 1.00 parts acrylic acid as catalyst and 1.03 parts Z 6030 as an adhesion promoter, when cured, has a abrasion resistance of greater than 20,000 cycles without failure.”

Nanoparticle Titanium-based Catalysts Immobilized on Pyrolytic Inorganic Nanoparticles to Produce PET and PETN Polymers: Thiele, U. et al. [230] used titanates KR 12, KR 38S and Tyzor LA: “A method is disclosed for manif. of high-mol. wt., colorless polyesters of terephthalic and naphthalenedicarboxylic acids in the presence of titanium-based catalysts $Ti(OR)_4$, I, II, III and $ROTi(OR)_2[OTi(OR)_2]_nOR$ [R = H, alkyl, aryl, $PO(OR')_2$, $HPOOR'$ or SO_2R' , X = O or S, Y = CH, disubstituted C or P] immobilized on pyrolytic inorg. nanoparticles such as silica or aluminum oxide having diameter 1-25 nm.”

Maleated Ethylene-Vinyl Acetate Copolymer (EVA)/Alumina Trihydrate (ATH) Nanocomposites: Zhang, X et al. [231] used KR 38S as a synergist with MAH: “Ethylene-vinyl acetate copolymer (EVA)/alumina trihydrate (ATH) nano-composites were prepared by melt-blending. Two kinds of interfacial modifiers were used in this research, a titanate coupling agent and maleated ethylene vinyl acetate copolymer (MEVA), which acted as a compatibilizer. The effects of modifiers on the properties of EVA nanocomposites were studied by thermogravimetric anal., tensile and combustion tests. The dispersion and adhesion patterns of the ATH nano-particles in EVA matrix were characterized through Molau solution test, TEM and SEM. The exptl. results demonstrated that the use of untreated ATH could clearly decrease the tensile properties of EVA composites. It was found that the combined addition of the two kinds of interfacial modifiers led to a dramatic increase in tensile and flame retardant properties of the nanocomposites. Also the thermal stability of this system, in terms of the thermal degradation test, was enhanced. These effects would be diminished if only one modifier was used. The improvement in the properties of interfacial modified EVA/ATH nanocomposites is mostly attributed to a better dispersion of surface modified filler and a strong adhesion between the filler and matrix.

Nano TiO₂, ZrO₂, Cr₂O₃, Fe₂O₃, MgO Filled Polyamide, Polyamide-Polyimide, Polyester Resins: Ma, H. et al. [232] found phosphato titanates and a sorbitan tristearate useful as dispersing agents: “The electromagnetic glazed wire, a common one with a nano inorg. Metal oxide/organic insulating material composite protective layer in its insulating layer, is manufactured by microwave drying nano inorg. Metal oxide for 30 min, mixing with insulating polymer resin (at a ratio of 1:10) in organic solvent, homogenizing and sand milling in the presence of dispersing agent to obtain composite insulating resin lacquer; coating the Cu wire with prime coating, coating with the above composite insulating resin lacquer, and then making the glazed wire. The inorg. oxide is TiO₂, ZrO₂, Cr₂O₃, Fe₂O₃, MgO, etc. The polymer resin is polyamide, polyamide-polyimide, polyester resin, etc. The organic solvent is methylpyrrolidone, BuOAc, etc. The dispersing agent is isoPr tri(di-O-octylphosphoryloxy) titanate, 2-hydroxypropanoyl bis(di-O-alkylpyrophosphoryl) titanate, or sorbitan

tristearate.”

Nano ZnO Slurry: Liu, F et al. [233] used KR TTS, Anti-Terra 202 and other additives: “*The nanometer ZnO slurry compn. Is composed of <100 nm ZnO 10-65, polymer dispersing agent 0.5-11, and solvent to 100%. Thus, petroleum ether 40 g, trichloroethane 10 g, Anti-Terra 202 12.5 g, 200 nm ZnO 116.06 g were dispersed to give a nanometer zinc oxide slurry, showing storage time 396 days and average particle diameter 145 nm.*”

Nano: Calcium Carbonate, Molybdenum disulfide, Alumina, Silica Filled UHMWHDPE: Zhang, W. et al. [234] used KR 9S: “*The compn. Comprises polyethylene ultra-high-mol.-wt. polyethylene 100, inorg. Nanoparticles (e.g., CaCO₃) 0.5-10, a dispersing agent (liquid paraffin and acetone) 1-10, a flow modifying agent (e.g., low-d. polyethylene, high-d. polyethylene, polysiloxane and Perfluoropropylene- vinylidene fluoride copolymer) 0.5-30, a coupling agent (e.g., titanate ester) 0.05-1, a compatibilizer (e.g., ethylene-acrylate copolymer) 0.5-15, and an antioxidant (e.g., Antioxidant 1010) 0.02-1 parts.*”

Nanoclay (Cloisite 15A) Filled Polypropylene: Mani, G. et al. [235] used LICA 12: “*Polypropylene-clay nanocomposites were prepd. by a soln. technique and a subsequent melt-mixing process. A titanate coupling agent was used to improve the compatibility of the nanoclay particles with the polypropylene. The dispersion of the nanoclay particles in polypropylene was studied with X-ray diffraction (XRD) and transmission electron microscopy (TEM). An increased d-spacing value of the clay particles in the nanocomposites was observed, and it was compared with the values of as-mined (pristine) and as-received (organophilic) clay particles. The number of intercalated layers in a single clay crystallite was determined to be 4, and the number was confirmed with XRD data and TEM images. On the basis of the Daumas-Herold model (which is widely used for graphite intercalation compds.), the stage 2 and stage 3 structures of montmorillonite particles in polypropylene were recommended. A study on the stage structure suggested a way of determining the presence of polymer mols. in the clay galleries. The results confirmed the existence of single-layered platelets with improved dispersion in polypropylene.*”

Author’s comment: Although the LICA 12 titanate was effective in increasing the number of intercalated layers of clay, the choice of Cloisite Na⁺ over Cloisite 15A may have shown even better results.

Nano Al₂O₃/SiO₂ Photocatalyst Coatings: Hirata, H et al. [236] used KR 238S: “*The overcoats contain aluminum oxide (A) powders (av. diam. of primary particle ≤50 nm), a binder liquid containing silica sol (B), and organic solvents, wherein the A/B (based on Al₂O₃/SiO₂) ratio is (1/9)-(9/1). The multilayer coatings containing the overcoats show good photocatalyst activity, transparency, and high hardness.*”

Nano SiO₂ Stabilizer Coatings: Guan, Y. et al. [237] used KR 138S and triethylmethylsilane: “*The UV stabilizing agent comprises SiO₂ nanoparticle 20-40, polyethylene glycol nonylphenyl ether 2-8, 2-amino-2-methyl-1-propanol 0.5-2.5, 1,2-propanediol 2-8, 5-Chloro-2-methyl-4-isoxazolin-3-one 0.1-0.2, methyltriethylsilane 0.3-0.7, titanium di(dioctylpyrophosphate) oxyacetate 0.1-0.3, and water 58-66%.*”

Nano-Mg/PP Composites : Peng, H. et al. [238] used KR 38S: “*The powder phases and structures of nano-magnesium powder prepd. by high-energy ball milling and gas condensation methods, i.e. resistance-heating evaporation, are characterized by means of XRD and TEM. Nano-Mg/polypropylene (PP) composites are prepared by melt milling PP, in which process the surface of nano-magnesium powder is modified first and put into the melted PP. That nano-magnesium powder prepared by the milling method improves the tensile strength of the PP matrix and the powder prepared by gas condensation improves the toughness of the PP matrix notably and maintains or improves the strength to some extent at the same time. The SEM observation of the cross-section of the composites shows that magnesium powder disperses in the matrix at a nanometer size. The toughening mechanisms of nano-magnesium powder prepared by the condensation method can be compared to the cool tensile mechanism of rigid toughening.*”

Nano Antistatic Agents: It is often useful to have an ESD effect created without interference from opaque conductive pigments or adhesive effects from blooming antistats that work via moisture attraction

from the relative humidity in the surrounding atmosphere. Minor amounts of thermally and hydrolytically stable combined dissimilar neoalkoxy titanates and/or zirconates can be added directly into the polymer during the thermoplastic or thermoset compounding phase from room temperature to temperatures in excess of 200°C (after gradual increase from room temperature in the first three zones of the extruder to below the initial boiling point of the combined zirconates) to form nano bipolar conductive organometallic layers that provide a transparent, non-blooming Ti or Zr electron transfer circuit resulting in a volume as well as surface antistatic effect [239] – see Figure 54. Figure 55 and Table 28 provide some recent results on incorporation of the zirconate based antistat in five PVC test films. Figures 56 and 57 demonstrate ESD effects in a thermoplastic polyurethane floor coating and a waterbased clear acrylic coating respectively using straight and emulsified blends

Function 5 – UV Reactive Composites – The following are a series of some recent UV related abstracts wherein the Function 5 of subject organometallics is utilized by various investigators to functionalize fillers, pigments, Dyes, LCD's and other articles.

TI Surface functionalization of pigments and/or dyes for radiation-curable printing inks and coatings and their preparation

IN Wang, Zhikai; Wu, Bin

PA UCB, S.A., Belg.

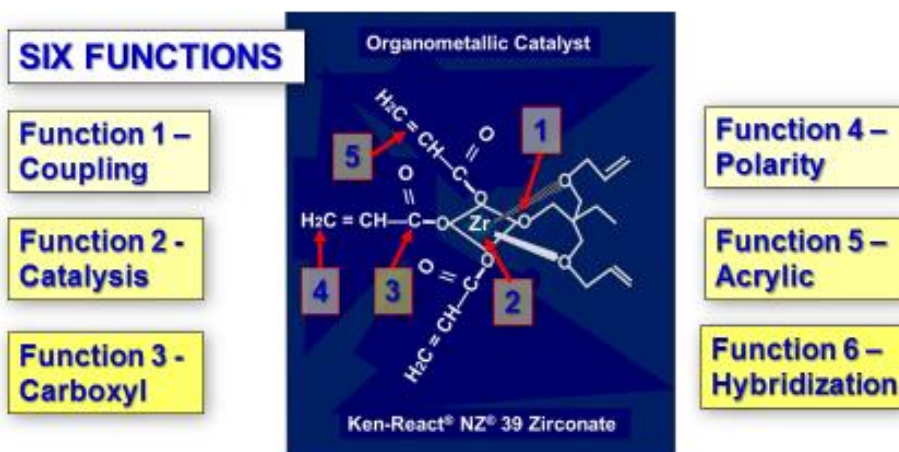
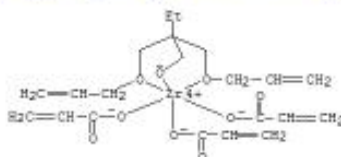
PI WO 2002048272 A1 20020620

AB The functionalized pigment is prepd. by reaction a pigment and/or a dye with a radiation-reactive organometallic coupling agent (RO)mM(OXR'Y)n (M = metal atom from IIa, IIIb, IVb, Vb, VIb, VIIb, VIII, Ib, IIb, and IIIa; R = (un)substituted C1-8 alkyl; X = org. functional group; R' = org. group; Y = radiation curable functional group; m, n = 1-3). Thus, a UV-curable powder coating compn. comprising Uvecoat 2000 (UV-curable powder coating resin) 72.1, Irgacure 819 (photoinitiator) 3.5, TiO2 20.0, RX 05613 [NZ 39 (neopentyl(diallyl)oxytriacyrl zirconate)]-treated TiO2 4.0 and degassing agent 0.4 parts showed gloss (60°) 99.0%, Haze 40.0 and pencil hardness (scratch) 3H.

IT 146987-99-7, Ken-React NZ 39 (coupling agent; surface functionalization of pigments and/or dyes for radiation-curable printing inks and coatings)

The Six Functions of a Neoalkoxy Triacyrl Zirconate

Zirconium, [2,2-bis[[2-propenyloxy-.kappa.O)methyl]-1-butanolato-.kappa.O]tris(2-propenoato-.kappa.O)-



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TI UV-cured transparent electroconductive coating films containing phosphite titanates with good abrasion resistance and adhesion property

IN Nishihara, Akira; Hayashi, Toshiharu

PA Mitsubishi Materials Corp, Japan

PI JP 08067837 A2 19960312 JP 1994-203785 19940829

AB Title coatings, useful for liq. crystal panels, displays, etc., contain solvents, (A) electroconductive fine powders, binders, and 0.4-10% (vs. A) dialkyl phosphite titanates. Thus, powd. Sn oxide 0.41, tetraethoxysilane homopolymer 23.61, Me₂CHOTi[OP(:O)(OC₈H₁₇)₂]₃ 0.0017%, were mixed in EtOH-BuOH solvent, coated on a glass plate, dried at 100°, and UV-irradiated to give a test piece showing light transparency 83.6%, haze 0.3%, and surface resistivity 3.3 x 10⁶ Ω/box..

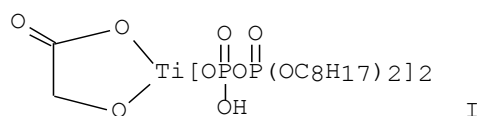
TI UV-curable transparent coatings with excellent electric conductivity, abrasion resistance and adhesion

IN Nishihara, Akira; Hayashi, Toshiharu

PA Mitsubishi Materials Corp, Japan

PI JP 07305003 A2 19951121 JP 1994-99607 19940513GI

(Author's Note: See KR 138S chemical structure next)



AB The coatings comprise solvents, finely powd. elec. conductors, and binders and contain 0.4-10% (on elec. conductor) titanates having dioctyl pyrophosphate groups. A compn. comprising 98:2 EtOH-BuOH mixt. 97.28, Sb-doped SnO₂ powder (av. diam. 0.025 μm) 0.41, binder [prepd. by hydrolysis of Si(OEt)₄] 2.31, titanate I 0.5, and benzyl di-Me ketal 0.0004% was applied to a glass plate, dried at 100°, and irradiated with UV rays to form a coating showing visible light transmittance 88.6%, haze 0.4%, surface resistivity 2.8 + 10⁶ Ω, and good abrasion resistance.

TI Antistatic and scratch-resistant coating compositions containing unsaturated compounds and titanates

IN Hibino, Satoru

PA Three Bond Co Ltd, Japan

PI JP 07292285 A2 19951107 JP 1994-109168 19940426

AB The title compns. useful for protecting optical plastics contain oligomers and/or monomers bearing □1 ethylenic double bonds, polymn. initiators, and specified titanate esters. Thus, a compn. of dipentaerythritol hexaacrylate 40, 1,6-hexanediol diacrylate 30, tetrahydrofurfuryl acrylate 30, 1-hydroxycyclohexyl Ph ketone 5, and iso-Pr tri(dodecylbenzenesulfonyl) titanate 0.5 part was spin-coated on a polycarbonate disk and UV-irradiated to give a test piece showing cross-cut adhesion 100/100, surface resistivity 8 + 10¹² Ω, and no dust attraction after rubbing.

TI Screen printing inks for masking printed circuit boards

IN Shindo, Shigeto

PA Nippon Kayaku Kk, Japan

PI JP 06107993 A2 19940419

AB Radiation-curable strippable inks contain polyester polyol urethane (meth)acrylates, other urethane (meth)acrylates, ethylenically unsatd. compds., and coupling agents. Thus, an ink contained adipic acid-1,4-butanediol-HMDI-2-hydroxyethyl acrylate copolymer 20, neopentyl glycol adipate-PTMG-isophorone diisocyanate-2-hydroxyethyl acrylate copolymer 55, Kayarad R 128 15, Kayarad R 551 10, KR 44 0.5, Irgacure 184 3, SF 8427 1, and Zn stearate 0.5 part.

TI One-component modified-polysulfide sealing material compositions

IN Maeda, Etsuro; Wakabayashi, Ichitami

PA Nogawa Kemikaru Kk, Japan

PI JP 06128559 A2 19940510

AB Title compns. with good extrusion workability without change in sagging property, useful for filling chinks in building or structural materials, contain 100 parts modified polysulfides, 30-100 parts plasticizers, 50-200 parts inorg. fillers, 3-10 parts antisag agents, 0-2 parts UV absorbers, 0-2 parts adhesion accelerators, 2-10 parts curing catalysts, 0-15 parts colorants, and 1-10 parts titanate coupling agents. Permapol P 965 50, Permapol P 795 (modified polysulfide) 50, dioctyl phthalate 100, CaCO₃ 100, clay 100, silicic anhydride 5, 2-hydroxy-4-methoxybenzophenone 0.8, A 187 0.05, A 1100 0.05, PbO₂ 1.0, porous silica 3.5, titanium white 5.0, carbon black 5.0, and KR 38S 5 parts were kneaded under N to give a sealing compn. showing good extrusion workability without change in sagging property.

TI Fire-resistant electrically conductive copper paste compositions for printed circuit boards**IN** Fukase, Toshimitsu**PA** Sumitomo Bakelite Co., Ltd., Japan**PI** JP 04223006 A2 19920812

AB The title compns. with good electromagnetic wave shielding property contain brominated epoxy resins, powd. Cu, carboxylic acids, rosins, and org. titanates. Thus, FCC-SP 88 (powd. Cu) 100, oxalic acid 4, gum rosin 2, Ken-React KR 46B 1.5, Butyl Carbitol 12, Epikote 5049 10 parts, dicyandiamide, and 2-phenyl-4-methylimidazole were kneaded to give a paste, which was screen printed on a paper-phenolic resin laminate having undercoating of a UV-curable solder resist, cured at 160° for 30 min, overcoated with a thermosetting solder resist, and heated at 150° for 30 min to give test pieces showing initial sp. resistivity $2.3 + 10^{-4} \Omega\text{-cm}$, no blister after 1000-h soldering at 260° and 90% relative humidity, and good fire resistance.

TI Electrically conductive copper paste compositions for printed circuit boards**IN** Fukase, Toshimitsu; Matsui, Yasuo**PA** Sumitomo Bakelite Co., Ltd., Japan**PI** JP 03059906 A2 19910314

AB The electromagnetic wave-shielding title pastes contain powd. Cu, thermosetting resins, org. carboxylic acids, rosins, and org. titanates. Thus, PR 51833 (resols) 15, Ken-React KR TTS 1.5, butylcarbitol 12, 30- μm diam. oxalic acid (I) 5, and 30- μm diam. gum rosin 5 parts were mixed to give the title paste, which was screen-printed on a phenolic resin substrate having undercoating of a UV-curable solder resist, cured 30 min at 160°, overcoated with a thermosetting solder resist, and treated at 150° for 30 min to give a test piece showing 8.6% change of sp. resistivity after 1000 h at 60° and 90% relative humidity and no blowing after soldering at 260°, vs. 9.7 and blowing, resp., for the test piece using 700- μm I and 300- μm gum rosin instead.

TI Modified copper powder for electrically conductive paints**IN** Nakamura, Yoshinobu; Sannohe, Kanetaro; Sohama, Yoshio; Iwasaki, Toru; Yamano, Sumiko**PA** Mitsui Mining and Smelting Co., Ltd., Japan**PI** EP 326737 A2 19890809

AB Coating powd. Cu with zirconates or mixts. of Zr acrylate polymers and fatty acids or esters improves the corrosion resistance and storage stability of coatings contg. it. The coatings can be used in electromagnetic wave shielding. Clean Cu powder (sp. surface area 0.4 m²/g, diam. 8.0 μm) coated with 0.05-10.5% isopropoxytriisostearoylato-zirconium showing no tarnish after 2000 h at 85° and 95% relative humidity. Elec. conductive acrylate resin paints contg. this powder, coated on acrylate polymer plates and dried at 50° for 30 min, had vol. resistivity 3-6 m $\Omega\text{-cm}$.

TI Electroconductive resin compositions**PA** Toyobo Co., Ltd., Japan**PI** JP 60088027 A2 19850517

AB A heat- and photo-curable elec. conductive resin compn. with high adhesion, useful as a binder for an ink, comprises an elec. conductive fine powder, a polyfunctional epoxy compd., a carboxy-contg. photopolymerizable compd., a photoinitiator, and an org. titanate. Thus, an ink compn. comprising flaked Ag 70, a binder from Epikote 1001 [25068-38-6] 225, monoacryloyloxyethyl succinate 54, and tetrahydrofurfuryl acrylate 39 parts (viscosity 7.8 P at 25°) 23, 2-hydroxy-2-methylpropiophenone [7473-98-5] 5, an acrylic leveling agent 2, (diethylamino)ethanol 0.5, and titanium bis(dioctyl pyrophosphate) oxyacetate (I) [67729-57-1] 1 part was screen printed on a 125-mm polyester film to a thickness of 20 μm , UV-cured for 40 s, and heat-cured at 120° for 15 min to give a layer exhibiting crosscut adhesion test 100/100 and sp. resistance $2.6 + 10^{-6} \Omega\text{-cm}$, compared with 0/100 and $4.7 + 10^{-4} \mu\text{-cm}$, resp., for an ink not contg. I.

TI Compositions containing crosslinking agents suitable as optical fiber coatings**IN** Fabian, Michelle D.**PA** Corning Incorporated, USA**PI** WO 2002094730 A2 20021128

AB The compn. for optical fiber coatings includes a coupling agent devoid of any Si contg. compd. and has, after curing, a Young's modulus of ≥ 50 MPa. The coupling agent is capable of bonding to an org. compd. and comprises ≥ 1 compd. Selected from titanate-contg. compds., zirconate-contg. compds. and mixts. thereof. It is preferred that the coupling agent is included in an optical fiber layer that is not $< 5 \mu$ away from an outer surface of the glass fiber. The coupling agent-contg. compn. is applied non-directly to the optical fiber surface.

TI Electrically conductive coatings with good humidity resistance

IN Abe, Tomoko; Yasu, Katsuhiko

PA Hitachi Chemical Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 7pp. CODEN: JKXXAF

PI JP 2007106788 A 20070426

AB The coatings contain Ni powders with av. particle diam. $\leq 30 \mu\text{m}$, thermoplastic acrylic polymers with $T_g \geq 20^\circ$, titanate coupling agents, and organic solvents. Thus, a coating comprising Ni powders with average diameter $16 \mu\text{m}$ (Ni 287) 100, Bu methacrylate-2-hydroxyethyl methacrylate-Me methacrylate copolymer with $T_g 65^\circ$ and Mw 85,000 63, toluene 15, Me iso-Bu ketone 15, and di(dioctylpyrophosphato) ethylene titanate (KR 238S) 0.5 part was applied on a 5 mm-thick ABS sheet to show volume resistivity $6.9 \times 10^{-4} \Omega\text{-cm}$ after storing at 60° and humidity 90% for 500 h, change in volume resistivity after the storage +4%, and good adhesion of the coating.

IT 7440-02-0, Nickel, uses

IT 65467-75-6, KR 238S 67691-13-8, KR 38S

TI Electrically conductive coatings with good adhesion and moisture resistance

IN Abe, Tomoko; Yasushi, Katsuhiko

PA Hitachi Chemical Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 8pp. CODEN: JKXXAF

PI JP 2006335976 A 20061214

AB Title coatings contain $\leq 30\text{-}\mu\text{m}$ (Ag-plated) Cu particles, thermoplastic acrylic resins, and 0.001-5.0% (based on 100 parts total solids) titanate couplers. A composition containing FCC CP 10 100, Bu methacrylate-2-hydroxyethyl methacrylate-Me methacrylate graft copolymer 63, and KR 238S 0.6 parts showed resistivity $7.2 \times 10^{-4} \Omega\text{-cm}$ with +3% deviation after 400 h at 60° and 90% relative humidity and good adhesion to ABS plates initially and after cutting.

IT Titanates

IT 61417-49-0, KR TTS 65467-75-6, KR 238S

TI Method for producing thermally conductive single-layer acrylic sheets

IN Yoda, Masaki; Yamazaki, Yoshinao

PA 3M Innovative Properties Company, USA

SO PCT Int. Appl., 18pp. CODEN: PIXXD2

PI WO 2007053475 A1

AB To provide a single-layer thermally conductive sheet having tackiness differing between the front surface and the back surface without requiring an addnl. step of removing surface tackiness, for example, applying a base material, beads or an antiblocking powder. A method for producing a thermally conductive sheet, comprising: (a) shaping a thermally conductive precursor composition into a sheet, the thermally conductive precursor composition comprising a (meth)acrylic monomer or a polymerizable oligomer thereof, a photopolymn. initiator, and a thermally conductive filler present in an amount of 20 vol% or more based on the total volume of the thermally conductive composition obtained, and (b) irradiating the front surface and the back surface of the sheet with UV radiation at different UV irradiation intensities such that the irradiation intensity on the surface irradiated at a higher intensity is 30 times or less the irradiation intensity on the surface irradiated at a lower intensity, thereby curing the sheet and obtaining a thermally conductive sheet consisting of a single-layer thermally conductive composition and having tackiness differing between the front surface and the back surface.

IT 68443-53-8, isopropyl tristearoyl titanate

CONCLUSION

A substantial amount of discussion and data along with references, abstracts, tables and figures have been offered on application of titanates and zirconates in various polymer disciplines with a view towards applications in UV/EB Coatings systems.

Table 29 – THERMOSET RESIN & COATING SELECTION TABLE (10-pages reduced to Acrylics Only for IP Purposes) reflects the teachings in this paper and some of the experience gained in over 47-years of fulfilling my mission statement to provide for more efficient use of raw material through the use of titanate and zirconate coupling agents.

Note: A 211-page Addendum containing over 600-coatings related Abstracts was omitted from the RadTech 2020 technical paper due to size. Pages 103 to 106 were left in to indicate scope of work.

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TABLES

TABLE 1 – ALPHA-NUMERIC CODE & NOMENCLATURE

Alpha-# Code	Chemical Description
KR TTS	Titanium IV 2-propanolato, tris isooctadecanoato-O
KR 9S	Titanium IV 2-propanolato, tris(dodecyl)benzenesulfonato-O
KR 12	Titanium IV 2-propanolato, tris(dioctyl)phosphato-O.
KR 38S	Titanium IV 2-propanolato, tris(dioctyl)pyrophosphato-O.
KR 138S	Titanium IV bis(dioctyl)pyrophosphato-O, oxoethylene-diolato, (adduct) bis(dioctyl)hydrogen phosphite
KR 138D	Titanium IV bis(dioctyl)pyrophosphato-O, oxoethylenediolato, (adduct) 2 moles of N,N-dimethylamino-2-methylpropanol
KR 238S	Titanium IV bis(dioctyl)pyrophosphato-O, ethylenediolato, (adduct), bis (triethyl) amine salt
KR 238M	Titanium IV ethylenediolato bis(dioctyl)pyrophosphato-O, bis(dialkyl) amino alkyl-2-methyl propenoate)
KR 238T	Titanium IV bis(dioctyl)pyrophosphato-O, ethylenediolato, (adduct) bis(dioctyl)hydrogen phosphite
KR 41B	Titanium IV tetrakis 2-propanolato, adduct 2 moles (dioctyl) hydrogen phosphite
KR 46B	Titanium IV tetrakis octanolato adduct 2 moles (di-tridecyl)hydrogen phosphite
KR 55	Titanium IV tetrakis(bis 2-propenolato methyl)-1-butanolato adduct 2 moles (di-tridecyl)hydrogen phosphite
LICA 01	Titanium IV 2, 2(bis 2-propenolatomethyl) butanolato, tris neodecanoato-O
LICA 09	Titanium IV 2, 2(bis 2-propenolatomethyl) butanolato, tris (dodecyl) benzenesulfonato-O
LICA 12	Titanium IV 2,2(bis 2-propenolatomethyl) butanolato, tris (dioctyl) phosphato-O
LICA 38	Titanium IV 2,2(bis 2-propenolatomethyl) butanolato, tris (dioctyl) pyrophosphato-O
LICA 38J	Titanium IV (bis-2-propenolato-methyl)-1-butanolato, bis(dioctyl) pyrophosphato-O, (adduct) 3 moles N,N-dimethylamino-alkyl propenoamide
QB 012	Proprietary Titanate Quat Blend
QB 046	Proprietary Titanate Quat Blend
CP-03B	Proprietary hybrid amino, methacryl, pyrophosphato titanate
LICA 44	Titanium IV 2,2(bis 2-propenolatomethyl), tris 2-ethylenediamino) ethylato
LICA 97	Titanium IV 2,2(bis 2-propenolatomethyl) butanolato, tris (3-amino) phenylato
KZ 55	Zirconium IV tetrakis 2,2(bis-2 propenolatomethyl)butanolato, adduct with 2 moles of di-tridecyl, hydrogen phosphite
KZ TPP	Zirconium IV 2-ethyl, 2-propenolatomethyl 1, 3-propanediolato, cyclo di 2, 2-(bis 2-propenolatomethyl) butanolato pyrophosphato-O, O
NZ 01	Zirconium IV 2,2(bis-2-propenolatomethyl)butanolato, tris neodecanolato-O
NZ 09	Zirconium IV 2.2(bis-2-propenolatomethyl)butanolato, tris(dodecyl)benzenesulfonato-O
NZ 12	Zirconium IV 2,2(bis-2-propenolatomethyl) butanolato, tris (dioctyl)phosphato-O
NZ 33	Zirconium IV 2,2(bis-2-propenolatomethyl)butanolato, tris 2-methyl-2-propenoato-O
NZ 37	Zirconium IV bis 2,2(bis-2-propenolatomethyl)butanolato, bis(para amino benzoato-O)
NZ 38	Zirconium IV 2,2(bis-2-propenolatomethyl) butanolato, tris (dioctyl)pyrophosphato-O
NZ 39	Zirconium IV 2,2(bis-2-propenolato)butanolato, tris 2-propenoato-O

NZ 44	Zirconium IV 2,2(bis-2-propenolatomethyl), tris (2-ethylenediamino) ethylato
NZ 66A	Zirconium IV bis 2,2(bis-2-propenolatomethyl)butanolato, bis(3-mercapto)propionato-O
NZ 97	Zirconium IV (2,2-bis propenolatomethyl), tris (3-amino) phenylato
Tyzor LA	Titanate (2-), dihydroxy bis [2-hydrpropanato (2-)-O ¹ , O ²]-, ammonium salt (DuPont)
SG-Si900	Aminoethylaminopropyltrimethoxy Silane
KH 151	Vinyltriethoxysilane
KH 550	γ-Aminopropyltriethoxysilane
KH 570	γ-Methacryloylpropyltrimethoxysilane
Z-6020	Aminopropyltrimethoxysilane (Dow)
Z-6030	γ-Methacryloylpropyltrimethoxysilane (Dow)
A-187	Gamma-Glycidoxypropyltrimethoxy silane (GE)
A-1100	Gamma-aminopropyl triethoxy silane (GE)
Anti-Terra 202	Solution of an alkyl ammonium salt of a polycarboxylic acid (Byk)

Product Forms – Liquid, Powder and Pellet

Liquid Form (100% Active Coupling Agent)

LICA # = LIquid Coupling Agent, 100% Active Neoalkoxy Titanates.

NZ # = Liquid Coupling Agent, 100% Active Neoalkoxy Zirconates.

KR # = Liquid Monoalkoxy, Coordinate, Chelate Ken-React Titanates.

KZ # = Liquid Monoalkoxy, Coordinate, Chelate Ken-React Zirconates.

Example: **LICA 38** = 100% liquid neoalkoxy pyrophosphato titanate.

Powder Masterbatch Form (65% Active on 35% 20-nm silica)

CAPOW L #/Carrier – Coupling Agent **POW**der of Neoalkoxy Titanate.

Example: **CAPOW L 38/H** = 65% **LICA 38**/35% PPG Hi Sil 233 Silica Carrier

Pellet Masterbatch Form (20% Active in Polymer Binder)

CAPS = Coupling Agent Pellet System

Example: **CAPS L 38/L** = 20% **LICA 38**/10% Silica/70% LLDPE Binder

Note: Ken-React®; KR®; LICA®; NZ®; KZ®; QB®; CAPOW®; CAPS®; Ken-Stat®; KS®; KPR®.

Kenrich Petrochemicals, Inc. is the licensor of record for Plenact KR® equivalents.

TABLE 2 – ACS CAS ABSTRACTS FOR NANOCOMPOSITES USING TITANATE OR ZIRCONATE FOR THE 9-MONTH PERIOD SEPT. 3, 2005 TO MAY 31, 2006

ACS #	KR	Nano Material	Polymer	Country
2	KR 55	Carbon Nanotubes	Polyvinylimidazole	CHINA
3	KR 201	Al(OH) ₃	PO's & PVC	CHINA
19	LICA 44	MMT Clay	Methyl Methacrylate	UK
20	KR 12	CaCO ₃	PVC	CHINA
27	LICA 38	MMT Clay	Polyhydroxybutyrate (PHB)	USA
32	KR 38S	CaCO ₃	PS	CHINA
47	KR TTS	ZrC/Clay	Fibers-Acrylic, PP, PET, PA	CHINA
48	NZ 44	Clay	PEN-PET/PA/PET	USA
56	KR 38S	TiO ₂	Polyolefins	CHINA
67	KR 38S	CaCO ₃	PET/MAH	CHINA
68	KR TTS	MMT	Rubber-NR, SBR, NBR	CHINA
69	LICA 12	Clay	PU	UK
107	KR 38S	CaCO ₃	PVC	CHINA
109	KR 38S	ZnO	PP	CHINA
112	KR 38S	TiO ₂	PS	CHINA
113	KR 12	Talc	PP	CHINA
114	KR 12	CaCO ₃	PVC	CHINA
125	KR TTS	SiO ₂	EPR	CHINA
152	KR's	SiO ₂	WB Acrylic	JAPAN
153	KR 44	Clay	PC	JAPAN
160	KR 44	Alumina	PA	HOLLAND
168	KR TTS	Alumina	PU	CHINA

TABLE 3 – EVALUATION OF VARIOUS COUPLING AGENTS IN FIBER REINFORCED EPOXY COMPOSITES (ORIGINAL/AGED PROPERTIES)

Formulation

Parts by Weight

Resin, DEN 438 (Novalak – Dow)	100
Hardener, Methyl Nadic Anhydride	87.5
Fiber (Short – 5 mm)	40
Additive(s)	as shown

Brookfield Viscosity measured @ 80°C; Cure 30 min. @ 150°C.

Postcure: 4 hr. @ 180°C. Aging 240 hr. in boiling 10% aqueous salt solution.

Carbon Fiber Reinforcement (IM-6, Hercules)

Additive: (PBW)	Long Fiber	Short Fiber Vehicle Only			
	Tensile Pullout Energy J	Viscosity 0.2 rpm/2 rpm: Mega poise	Flexural Strength gPa	Compressive Strength gPa	Falling Ball Impact Str. kJ/m
Control	62/21	0.95:0.62	0.94/0.41	1.72/1.07	1.5/0.5
NZ 97:0.3	113/109	0.38:0.29	1.09/0.89	2.08/1.83	1.9/1.4
NZ 97:0.4	119/113	0.37:0.27	1.24/1.13	2.71/2.49	2.3/1.8
NZ 97:0.5	107/107	0.36:0.24	1.27/1.11	2.38/2.23	2.0/1.7
NZ 37:0.2	108/104	0.94:0.54	1.31/1.20	2.10/2.02	2.7/2.3
NZ 37:0.3	122/119	0.79:0.46	1.42/1.34	2.96/2.70	2.6/2.4
NZ 37:0.4	114/110	0.84:0.53	1.17/1.10	2.71/2.59	2.4/2.3
KR 55:0.2	78/62	0.28:0.21	1.31/1.20	2.07/2.01	3.1/2.7
KR 55:0.3	97/81	0.24:0.17	1.39/1.31	2.28/2.15	3.4/2.7
KR 55:0.4	101/96	0.22:0.15	1.36/1.32	2.46/2.28	3.3/2.8
KR 55:0.5	86/83	0.21:0.15	1.36/1.30	2.26/2.20	3.3/2.8
KR 55:0.3 + NZ 37:0.3	151/148	0.21:0.17	1.72/1.67	2.82/2.69	2.9/2.8
KR 55:0.4 + NZ 37:0.4	132/130	0.23:0.17	1.59/1.46	2.61/2.48	2.6/2.5

(Table 3 continued next page)

Table 3 (continued)

B) Fiberglass Reinforcement (E-Glass, Certainteed)

Additive: (PBW)	Long Fiber	Short Fiber Vehicle Only			
	Tensile Pullout Energy J	Viscosity 0.2 rpm/2 rpm: Mega poise	Flexural Strength gPa	Compressive Strength gPa	Falling Ball Impact Str. kJ/m
Control	54/14	0.67:0.43	0.82/0.40	1.54/1.21	1.7/1.0
A1100:0.4	63/41	0.63:0.48	0.96/0.69	1.69/1.43	1.9/1.5
A-187:0.4	65/37	0.58:0.45	0.92/0.74	1.58/1.51	1.9/1.6
NZ 97:0.4	92/86	0.39:0.34	1.31/1.23	1.92/1.80	1.9/1.7
NZ 37:0.4	113/81	0.61:0.51	1.27/1/28	2/17/2.09	1.8/1.8
KZ 55:0.4	86/80	0.26:0.17	1.14/1.09	1.73/1.67	2.7/2.5
KR 134S:0.4	79/76	0.225:0.18	0.96/0/92	1.81/1.77	2.5/2.4
NZ 37:0.2 + KZ 55:0.2	117/113	0.28:0.19	1.42/1.36	2.16/2.09	2.8/2.4
NZ 37:0.2 + KR 134S:0.2	126/123	0.24:0.17	1.37/1.31	2.23/2.11	2.9/2.7
NZ 37:0.2 + A-187:0.2	129/121	0.59:0.47	1.61/1.50	2.32/2.23	2.1/2.0

C) Aramid Reinforcement (Kevlar, Dupont)

Additive: 0.4 (PBW)	Long Fiber	Short Fiber Vehicle Only			
	Tensile Pullout Energy J	Viscosity 0.2 rpm/2 rpm: Mega poise	Flexural Strength gPa	Compressive Strength gPa	Falling Ball Impact Str. kJ/m
Control	59/38	1.57:1.42	1.16/0.69	2.32/2.03	1.9/1.1
A-1100	62/49	1.52:1.40	1.29/1.14	2.42/2.23	2.1/1.3
NZ 97	76/67	0.63:0.57	1.41/1.27	2.84/2.58	3.5/2.8
NZ 37	84/72	1.24:1.09	1.42/1.38	2.79/2.67	3.2/2.7
KR 134S	73/67	0.51:0.42	1.31/1.27	2.27/2.14	2.9/2.9
KZ 55	68/64	0.82:0.67	1.24/1.11	2.42/2.21	3.0/2.8

TABLE 4 – EFFECT OF NEOALKOXY TITANATE AND NEOALKOXY ZIRCONATE ON THE PROPERTIES OF INJECTION MOLDED UNFILLED ACRYLIC

Resin: Acrylic Type – Lucite 239K (DuPont)							
Molding Temperature: 480°F (Nominal) – Resin Predried							
CAPOW® Coupling Agent Additive	Weight % of Resin	Tensile Yield K psi	% Elong- ation @ Break	Flexural Strength K psi	Flexural Modulus Psi x 10⁴	Notched Izod @ R.T. ft.lb/in.	% Water Absorption @ R.T. 24 Hr. Imm.
None	-	1.2	5	15	26	0.3	0.27
L 01/H	0.1	1.4	17	17	29	0.5	0.22
L 01/H	0.3	1.5	23	20	30	0.9	0.21
L 01/H	0.5	1.2	28	18	25	1.1	0.18
L 09/H	0.1	1.3	19	16	31	0.4	0.22
L 09/H	0.3	1.5	24	24	30	0.7	0.22
L 09/H	0.5	1.4	27	23	26	0.8	0.20
L 12/H	0.1	1.5	16	20	22	0.5	0.17
L 12/H	0.3	1.7	31	23	29	0.7	0.15
L 12/H	0.5	1.6	26	24	28	0.8	0.12
L 12/H	0.75	1.5	28	21	20	0.7	0.09
L 38/H	0.1	1.4	13	21	38	0.4	0.22
L 38/H	0.3	1.7	28	24	43	0.6	0.21
L 38/H	0.5	1.3	34	20	27	0.4	0.22
L 44/H	0.1	1.7	24	19	40	0.5	0.30
L 44/H	0.3	2.2	16	31	52	0.7	0.31
L 44/H	0.5	2.5	12	24	57	0.5	0.28
L 44/H	0.75	2.0	9	20	48	0.3	0.24
L 97/H	0.1	1.9	12	19	38	0.4	0.16
L 97/H	0.3	2.1	20	24	44	0.5	0.14
L 97/H	0.5	2.3	16	25	47	0.5	0.11
L 97/H	0.75	2.0	11	19	28	0.2	0.08
NZ 01/H	0.1	1.3	9	15	31	0.4	0.26
NZ 01/H	0.3	1.4	14	18	34	0.5	0.24
NZ 01/H	0.5	1.1	17	13	29	0.7	0.25
NZ 09/H	0.1	1.2	23	16	30	0.3	0.24
NZ 09/H	0.3	1.0	31	19	28	0.5	0.21
NZ 09/H	0.5	1.0	36	18	27	0.5	0.22
NZ 12/H	0.1	1.4	16	19	39	0.5	0.19
NZ 12/H	0.3	1.7	23	24	35	0.7	0.17
NZ 12/H	0.5	1.5	27	17	32	0.6	0.12
NZ 38/H	0.1	1.4	21	14	38	0.5	0.19
NZ 38/H	0.3	1.5	34	17	42	0.7	0.18
NZ 38/H	0.5	1.3	29	16	31	0.7	0.18
NZ 44/H	0.1	1.9	17	17	42	0.6	0.31
NZ 44/H	0.3	2.0	15	26	47	0.7	0.34
NZ 44/H	0.5	2.0	9	21	44	0.2	0.38
NZ 97/H	0.1	1.7	11	21	38	0.3	0.16
NZ 97/H	0.3	2.2	10	24	47	0.4	0.12
NZ 97/H	0.5	2.5	10	23	52	0.4	0.09
NZ 97/H	0.75	2.1	6	19	55	0.3	0.09

TABLE 5- EVALUATION OF THE CORROSION RESISTANT PROPERTIES OF BASIC LEAD SILICO CHROMATE (BLSC M-50), UNTREATED SILICA, AND SILICA TREATED IN SITU WITH 0.5% KR 38S IN AN EPOXY POLYAMIDE PRIMER ON STEEL

FORMULATIONS Part A	Units	BLSC M-50 Control		Untreated Silica Control		Silica + 0.5% KR 38S^a	
Araldite 571 CX-80		210.0		210.0		210.0	
BLSC M-50		480.0		--		--	
KR 38S		--		--		3.3	
Ti Pure R-900		30.0		30.0		30.0	
R-2200 Red Oxide		15.0		15.0		15.0	
DeGussa R-974 Silica		6.4		6.4		6.4	
Asbestine 3x		235.0		235.0		235.0	
Imsil A-108				260.0		400.0	
Xylol		192.7		192.7		192.7	
Diacetone Alcohol		96.2		96.2		96.2	
Beetle 216-8		10.5		10.5		10.5	
Part B							
Araldite 820		105.0		--		--	
Xylol		24.0		--		--	
Butanol		12.0		--		--	
Total Weight	lbs.						
Part A		1275.8		1055.8		1199.1	
Part B		<u>141.0</u>		<u>141.0</u>		<u>141.0</u>	
		1416.8		1196.8		1340.1	
Total Yield	gals.						
Part A		91.8		89.2		95.5	
Part B		<u>18.8</u>		<u>18.8</u>		<u>18.8</u>	
		110.6		108.0		114.3	
RMC	\$/gal.	5.67		3.55		3.45	
Note ^a: Add KR 38S to the mill base and solvate before adding pigments							
Test Results							
Viscosity	KU						
Initial		100		99		102	
Two Weeks @ 25°C		96		99		93	
Two Weeks @ 49°C		100		97		100	
Four Months @ 25°C		121		109		108	
Maximum Change		21		10		9	
Salt Fog Exposure - 500 and 1000 Hours	ASTM D-714	500 Hours	1000 Hours	500 Hours	1000 Hours	500 Hours	1000 Hours
Blistering	Score ^b	10	10	10	10	10	10
Rusting Overall	Score	10	10	9+	6	9+	10
Rusting at "X"	Score	7	5	6	2	6	4
Peeling at "X"	Score	10	10	10	6	10	10
Table 5 Results (continued next page)							

Humidity Resistance – 500 Hrs. @ 49-100% R.H.	ASTM D-714				
Blistering	Score	10	6D	10	
Rusting	Score	10	10	10	
Appearance - Stripped	Score	10	2	9+	
Note b: Subjective observations above quantified according to the following scoring scheme:					
Score	Performance	Effect	Score	Performance	Effect
10	Excellent	No Change	4	Fair	Moderate
9	Exc. – V.G.	Trace	2	Poor	Considerable
8	Very Good	Very Slight	0	Very Poor	Severe
6	Good	Slight	-	-	-

TABLE 6 – IN SITU EFFECT OF VARYING AMOUNTS OF LICA 38 AND LICA 97 ON VISCOSITY OF 50% NANOCOR® CWC CLAY DISPERSED 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
LICA 97, 0.5%*	50	50	416,000

*LICA 97 incompletely soluble, thus non-functional.

TABLE 7 – VISCOSITY EFFECT OF VARYING DOSAGES OF LICA 38 ADDED IN SITU TO: 55% MINERAL OIL/45% CLOISITE Na⁺ NANOCCLAY (MONTMORILLONITE; HYDRATED ALUMINUM SILICATE-SOUTHERN CLAY)

Cloisite Na⁺ Nanoclay	Mineral Oil	LICA 38*	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

*Dosage = % Wgt. of Clay

**TABLE 8 – Mg(OH)₂ (Magnifin H 5 – Martin Marietta)
TREATED WITH 0.7% PYROPHOSPHATO TITANATES**

Test #	Item	Parts by weight			Viscosity, cps@ 25C
		Mg(OH) ₂	Mineral Oil	Titanate	
1	Control	50	50	-	1,152,000
2	LICA 38 in situ ¹	50	50	0.35	6,400
3	LICA 38 neat pretreated ²	50	50	0.35	192,000
4	LICA 38 dilute pretreated ³	50	50	0.35/1.05	6,400
5	KR 38S in situ ¹	50	50	0.35	6,400
6	KR 38S neat pretreated ²	50	50	0.35	192,000
7	KR 38S dilute pretreated ³	50	50	0.35/1.05	6,400
8	LICA 38 neat pretreated ⁴	50	50	0.35	6,400

Notes:

- 1 – Tests 2 & 5 – In-situ technique. Titanate added to mineral oil, dispersed and then Mg(OH)₂ added under high shear with a propeller type mixer.
- 2 – Tests 3 & 6 – Neat (no dilution) titanate added dropwise over 1-minute to a fluidized bed of the Mg(OH)₂ created by a Henschel (no cooling or heating on jacket) operating at low speed (1800 rpm) followed by a 1-minute post mix.
- 3 – Tests 4 & 7 – Diluted titanate blended 1:3 with KP 140 [Tri-Butoxyethyl Phosphate plasticizer (CAS 78-51-3)] and pretreated at 2.8% (0.7:2.1) of the blend by weight of Mg(OH)₂ in the same manner as Tests 3 & 6.
- 4 – Test 8 – Neat (no dilution) titanate added dropwise over 5-minutes to a fluidized bed of the Mg(OH)₂ created by a Henschel (no cooling or heating on jacket) operating at low speed (1800 rpm) followed by a 1-minute post mix.

**TABLE 9 - Al(OH)₃ (Martinal OL-104/LE – Martin Marietta)
TREATED WITH 0.7% PYROPHOSPHATO TITANATE**

Test #	Item	Parts by weight			Viscosity, cps@ 25C
		Al(OH) ₃	Mineral Oil	Titanate	
1	Control	50	50	-	500,000
2	KR 38S in situ ¹	50	50	0.35	4,800
3	KR 38S neat pretreated ²	50	50	0.35	6,400
4	KR 38S dilute pretreated ³	50	50	0.35/1.05	6,400

Notes:

- 1, 2 & 3 – See Table 6 for techniques.

TABLE 10 – THE EFFECT OF LICA 12 AND LICA 38 ON VARIOUS PIGMENTS DISPERSED IN MINERAL OIL AND DOP

% Pigment in Mineral Oil				% Pigment in DOP			
% LICA 12 by weight of pigment		% LICA 38 by weight of pigment		% LICA 12 by weight of pigment		% LICA 38 by weight of pigment	
LICA 12	Viscosity Cps	LICA 38	Viscosity Cps	LICA 12	Viscosity cps	LICA 38	Viscosity cps
60 % TiO₂ in Mineral Oil				60 % TiO₂ in DOP			
0.00	512,000	0.00	512,000	0.00	560,000	0.00	560,000
0.25	240,000	0.25	128,000	0.25	128,000	0.25	112,000
0.50	32,000	0.50	32,000	0.50	28,800	0.50	32,000
1.00	16,000	1.00	12,800	1.00	25,600	1.00	12,800
55% Red Iron Oxide in Mineral Oil				55% Red Iron Oxide in DOP			
0.00	800,000	0.00	800,000	0.00	800,000	0.00	800,000
0.25	28,800	0.25	9,600	0.25	32,000	0.25	12,800
0.50	25,600	0.50	6,400	0.50	35,200	0.50	9,600
1.00	22,400	1.00	8,000	1.00	35,200	1.00	9,600
55% Yellow 763ED in Mineral Oil				55% Yellow 763ED in DOP			
0.00	1,920,000	0.00	1,920,000	0.00	1,920,000	0.00	1,920,000
0.25	1,440,000	0.25	960,000	0.25	960,000	0.25	640,000
0.50	1,200,000	0.50	640,000	0.50	640,000	0.50	640,000
1.00	160,000	1.00	32,000	1.00	128,000	1.00	80,000
55% Blue 51-51 in Mineral Oil				55% Blue 51-51 in DOP			
0.00	2,112,000	0.00	2,112,000	0.00	2,080,000	0.00	2,080,000
0.25	800,000	0.25	640,000	0.25	240,000	0.25	320,000
0.50	160,000	0.50	128,000	0.50	96,000	0.50	19,200
1.00	32,000	1.00	9,600	1.00	22,400	1.00	12,800
60% Green F-5687 in Mineral Oil				60% Green F-5687 in DOP			
0.00	880,000	0.00	880,000	0.00	720,000	0.00	720,000
0.25	160,000	0.25	8,000	0.25	240,000	0.25	12,800
0.50	51,200	0.50	6,400	0.50	80,000	0.50	6,400
1.00	32,000	1.00	6,400	1.00	40,000	1.00	6,400
35% Thermax Black in Mineral Oil				35% Thermax Black in DOP			
0.00	880,000	0.00	880,000	0.00	1,120,000	0.00	1,120,000
0.25	368,000	0.25	560,000	0.25	880,000	0.25	720,000
0.50	368,000	0.50	320,000	0.50	880,000	0.50	560,000
1.00	368,000	1.00	320,000	1.00	880,000	1.00	320,000
60% DayGlo Z-15-3 Blaze Orange/M.O.				60% DayGlo Z-15-3 Blaze Orange/DOP			
0.00	2,240,000	0.00	2,240,000	0.00	2,240,000	0.00	2,240,000
0.50	1,920,000	0.50	480,000	0.50	2,240,000	0.50	2,240,000

TABLE 11 – THE EVALUATION OF 0.35% LICA 38ENP BY WEIGHT OF HOLLIDAY ULTRAMARINE BLUE PIGMENT (Grade 5008) IN WATER, TOLUENE AND MINERAL OIL – IN SITU

Item	Ultramarine Blue 5008					
	Water		Toluene		Mineral Oil	
	Control	LICA 38ENP	Control	LICA38 ENP	Control	LICA 38ENP
UB Pigment	67.5000	67.5000	50.0000	50.0000	50.0000	50.0000
Vehicle	32.5000	32.5000	50.0000	50.0000	50.0000	50.0000
LICA 38ENP	-	0.2362	-	0.1750	-	0.1750
Total Weight	100.0000	100.2362	100.0000	100.1750	100.0000	100.1750
Brookfield Viscosity, cps	22,400	35	80,000	25	150,400	16,000

TABLE 12 – THE EVALUATION OF 0.35% LICA 38ENP BY WEIGHT OF HOLLIDAY ULTRAMARINE BLUE PIGMENT (Grade 05) IN WATER, TOLUENE AND MINERAL OIL – IN SITU

Item	Ultramarine Blue 05					
	Water		Toluene		Mineral Oil	
	Control	LICA 38ENP	Contr ol	LICA 38ENP	Control	LICA 38ENP
UB Pigment	60	60.00	50	50	50	50
Vehicle	40	40.00	50	50	50	50
LICA 38ENP	-	0.21	-	0.175	-	0.175
Total Weight	100	100.21	100	100.175	100	100.175
Viscosity, cps – 25C	2.96 x 10 ⁵	1.28 x 10 ⁵		1.04 x 10 ⁶	5.6 x 10 ⁶	2.8 x 10 ⁶

Notes:

1. Mineral Oil used as room temperature model for non-polar olefins. If it works in mineral oil, it will work in almost all thermoplastic and thermoset polymers. Catalytic effects on pot life in thermosets such as polyurethane should be checked.
2. Pretreatment of UB to be accomplished by adding 0.2362 pts. (0.35% by weight of UB) to 32.5 pts water – disperse – followed by addition of 67.5 pts UB into water – disperse with propeller or Cowles type mixer and dry in forced air oven at 115C for 24 hours.
3. Dried pretreated UB to be re-dispersed into water, toluene and mineral oil to confirm in situ viscosity response results.

TABLE 13 – THE EVALUATION OF 0.35% LICA 38ENP BY WEIGHT OF HOLLIDAY ULTRAMARINE BLUE PIGMENT (Grade 5008) IN WATER, TOLUENE AND MINERAL OIL – PRETREATED

Ultramarine Blue 5008 Pretreated with 0.35% LICA 38ENP

Item	Water	Toluene	Mineral Oil
UB L38ENP	67.5	50	50
Vehicle	32.5	50	50
Total Weight	100.0	100.0	100.0
Brookfield Viscosity, cps	22,400	45	1,700

Note: 455g of the UB 5008/Water/LICA 38ENP – 67.5000/32.5000/0.2362 mixture was placed at ambient into a 4"x8" aluminum pan to a height of about 1+cm, then forced air oven dried at 120°C for 48-hours. After cooling, the UB 5008 sheet was broken up into small pieces with a spatula and then dispersed into the water, toluene and mineral oil as shown. The UB5008LICA38ENP0.35 Pigment showed no response in water (indicating that the ENP portion had been driven off rendering the surface incompatible with water), while the response in toluene was 45 cps vs. 80,000cps for UB5008 Untreated and the response in mineral oil was 1,700 cps vs. 150,400 cps for UB5008 Untreated. In fact, the mineral oil test using the dried, pretreated UB5008 (UB5008LICA38ENP0.35) exhibited a viscosity response of 1,700 vs. 16,000 cps for in situ treated and 150,400 cps for untreated. The results are summarized in Table 12 next.

TABLE 14 – SUMMARY OF THE EVALUATION OF 0.35% LICA 38ENP BY WEIGHT OF HOLLIDAY ULTRAMARINE BLUE PIGMENT (Grade 5008 - 1.3m²/g) IN WATER, TOLUENE AND MINERAL OIL – IN SITU AND PRETREATED

Control	67.5% UB 5008 In Water		50% UB 5008 In Toluene			50% UB 5008 In Mineral Oil		
	0.35% LICA 38ENP		0.35% LICA 38ENP			0.35% LICA 38ENP		
	In Situ	Pre-treat	Control	In Situ	Pre-treat	Control	In Situ	Pre-treat
22,400	35	22,400*	80,000	25	45	150,400	16,000	1,700

Note: * If an emulsifier other than ENP was used that could withstand 48 hrs. @ 120°C, then a water soluble pretreated grade could be accomplished.

TABLE 15 – THE EVALUATION OF 0.35% AND 0.7% LICA 38ENP BY WEIGHT OF HOLLIDAY ULTRAMARINE BLUE PIGMENT (Grade 05 - 3m²/g) IN WATER, TOLUENE AND MINERAL OIL – IN SITU

60% UB 05 In Water In Situ			50% UB 05 In Toluene In Situ			50% UB 05 In Mineral Oil In Situ		
Control	0.5% LICA 38ENP	0.7% LICA 38ENP	Control	0.5% LICA 38ENP	0.7% LICA 38ENP	Control	0.5% LICA 38ENP	0.7% LICA 38ENP
2.96x10 ⁵	4.8x 10 ⁴	4.16x 10 ⁴	2.96x 10 ⁶	6.4x 10 ⁵	2.6x 10 ⁴	5.6x 10 ⁶	Ran out of UB 05	1.3x10 ⁴

TABLE 16 – THE EVALUATION OF 0.35% LICA 38ENP BY WEIGHT OF UB 5008 AND 3.3% LICA 38ENP BY WEIGHT OF UB 05 IN WATER, TOLUENE AND MINERAL OIL – PRETREATED

	Water		Toluene		Mineral Oil	
Ultramarine Blue Grade 5008 (1.2 m²/g)	Control	0.35% LICA 38ENP	Control	0.35% LICA 38ENP	Control	0.35% LICA 38ENP
% UB Pigment	67.5	67.5	50.0	50.0	50.0	50.0
Viscosity, cps	22,400	35	80,000	25	150,400	16,000
Ultramarine Blue Grade O5 (3.0 m²/g)	Control	3.3% LICA 38ENP	Control	2.0% LICA 38ENP	Control	2.0% LICA 38ENP
% UB Pigment	60.0	60.0	50.0	50.0	50.0	50.0
Viscosity, cps	296,000	440	2,960,000	320	5,600,000	16,000

TABLE 17– THE IN-SITU¹ VISCOSITY EFFECTS OF VARIOUS TITANATES/ZIRCONATES ON 55% TALC IN 45% MINERAL OIL

Titanate or Zirconate	Wgt. % of Talc	Brookfield Viscosity, cps @ 25°C
None	0.00	1,184,000
NZ 33	0.25	1,184,000
NZ 33	0.50	1,120,000
NZ 33	0.70	1,120,000
KR 33DS	0.50	1,120,000
LICA 38	0.50	320,000
LICA 38	0.70	96,000
NZ 12	0.50	704,000
LICA 01	0.50	704,000
LICA 12	0.50	480,000
KR TTS	0.50	800,000
Note: 1 – Titanate or Zirconate Added to M.O. Followed By Drill Mixing in the Talc		

TABLE 18 – THE IN-SITU¹ & PRETREATED² VISCOSITY EFFECT OF NZ 12 ZIRCONATE ON 55% TALC IN 45% MINERAL OIL

% NZ 12 by wgt. of Talc	Brookfield Viscosity, cps @ 25°C	
	In Situ	Pretreated
0.00	1,184,000	1,184,000
0.10	1,024,000	1,024,000
0.25	800,000	512,000
0.50	704,000	192,000
0.75	176,000	128,000

Note: 1 – Zirconate added to M.O. followed by drill mixing in the talc.
 2 – Henschel pretreated by dropwise addition over 1-minute at 1800 rpm to talc fluidized bed followed by 1-minute post mix.

TABLE 19 – COMPARISON OF IN SITU AND PRETREATED TALC WITH 0.75% NZ 12 AND 0.7% LICA 38 ON 55% TALC IN 45% MINERAL OIL

Viscosity Data, cps @ 25°C	Talc (Ambient)			Talc (Oven Dried)	
	No Additive	0.75% NZ 12	0.70% LICA 38	0.75% NZ 12	0.70% LICA 38
In Situ	1,184,000	176,000	96,000	320,000	128,000
Pretreated	-	128,000	48,000	320,000	128,000

TABLE 20 – THE VISCOSITY EFFECTS OF 0.75% LICA 38 TITANATE AND NZ 12 ZIRCONATE PRETREATED TALC AT VARIOUS RATIOS OF TALC IN MINERAL OIL

Talc:Mineral Oil Ratio	Brookfield Viscosity, cps @ 25°C		
	Untreated	0.75% NZ 12	0.70% LICA 38
0:100	45	45	45
25:75	7,000	1,000	320
45:55	256,000	80,000	16,000
55:45	1,184,000	128,000	48,000
65:35	16,000,000	5,600,000	2,800,000
70:30	Dry Powder	16,800,000	8,400,000

TABLE 21 – THE VISCOSITY EFFECT OF VARYING AMOUNTS OF LICA 38 TITANATE ON WOLLASTONITE (CALCIUM METASILICATE) IN MINERAL OIL

Method	Wollastonite	Mineral Oil	LICA 38, %	Brookfield Viscosity, cps @ 25°C
In Situ	65	35	0	1,040,000
In Situ	65	35	0.25	16,000
In Situ	65	35	0.5	6,400
In Situ	65	35	0.7	6,400
In Situ	65	35	1.0	9,600
Pretreated	65	35	0.5	6,400
Oven dried-In situ	65	35	0.5	6,400
Oven dried-Pretreated	65	35	0.5	6,400
Pretreated, 0.7pts LICA 38:2.1 pts M.O.	65	33.9	0.7/2.1	3,200

TABLE 22 - EFFECT OF DEGREE OF EMULSION OF LICA 38 WITH ETHOXYLATED NONYL PHENOL (IGEPAL CO-660) ON THE VISCOSITY RESPONSE OF 80% CaCO₃ IN WATER

Formulation:

CaCO₃ (2.5 micron) - 80.0; Water - 20.0; Additive (Ratio as Shown) - 0.5

Additive Ratio LICA 38 : IGEPAL CO-660		Observed Degree Of LICA 38 Emulsion*	Viscosity, cps @ 25°C
0.0	: 0.0	-	3,600,000
0.0	: 1.0	-	1,600,000
1.0	: 0.125	Poor	240,000
1.0	: 0.25	Very Cloudy	232,000
1.0	: 0.5	Less Cloudy	160,000
1.0	: 1.0	Clear	3,000

*Ratio blends of LICA 38 and Igepal CO-660 added to water at 5% concentration and degree of emulsion observed.

TABLE 23 - Organometallic coupling agents as corrosion inhibitors in a lithium silicate conversion coating on metal

EXPERIMENTAL

Sample Preparation:

Five per cent aqueous lithium silicate¹ solutions containing the indicated proportions of stated anticorrosive(s) (PPT as shown) were spray applied to metallic panels. The coatings were tunnel dried at air temperatures of 177°C for 5 minutes.

Salt Spray Corrosion Tests:

Panels were next subjected to attack by oxygen saturated 10 wt. percent aqueous salt spray at cycle temperatures of -4 to 66°C (thermocycle 2.78°C/Min). Sample panels were stripped of coating and accumulated oxide by repeated (5 cycle) dipping in liquid nitrogen and 200°C Dowtherm A, followed by extraction (to constant weight) with 5% potassium tartrate in boiling triglyme containing 0.5% wt. crown 12 phase transfer agent. Panel weight loss was calculated in μ /Year (8766 Hr.) by extrapolation.

RESULTS

CARBON STEEL

<u>Additive(s)</u>	<u>PPT</u>	<u>Corrosion Rates (μ/Year)</u>		
		<u>500 Hr.</u>	<u>1000 Hr.</u>	<u>2000 Hr.</u>
None	--	78	150	1030
Strontium Chromate	9	10	50	150
QB 310	8	<3	<3	18
QB 012	8	5	10	23
QB 521	8	<3	<3	5

AIRCRAFT ALUMINUM

None	--	169	360	2703
Strontium Chromate	9	23	118	530
QB 310	8	5	8	10
QB 012	8	5	8	10
QB 521	8	<3	5	8

ZINC

None	--	122	255	67.3
Strontium Chromate	9	25	122	197
QB 310	8	3	5	10
QB 012	8	<3	<3	10
QB 521	8	<3	<3	5

1 - DuPont Polysilicate 48

TABLE 24 - OXIDATIVE STABILIZATION OF CARBON STEEL, ZINC AND AIRCRAFT ALUMINUM BY COUPLING AGENT MODIFIED LITHIUM SILICATE CONVERSION COATINGS

EXPERIMENTAL

Sample Preparation:

Five per cent aqueous lithium silicate solutions containing the indicated proportions of stated anticorrosive(s) were spray applied to metallic panels. The coatings were tunnel dried at air temperatures of 350°F for 5 minutes.

Oxidation Stability Corrosion Rate Evaluation Test:

Air Thermocycle 0 to 315°C at 11°C/min. (oven temp.) of 5% water (w/w) in air stream at 45° angle to panels. Sample panels were stripped of coating and accumulated oxide by repeated (5 cycle) dipping in liquid nitrogen and 200°C Dowtherm A, followed by extraction (to constant weight) with 5% potassium tartrate in boiling triglyme containing 0.5% wt. crown 12 phase transfer agent. Panel weight loss was calculated in μ /Year (8766 Hr.) by extrapolation.

RESULTS

CARBON STEEL

Additive(s)	PPT	Corrosion Rates (μ/Year)		
		500 Hr.	1000 Hr.	2000 Hr.
None	--	80	75	85
Strontium Chromate	9	48	67	70
QB 310	8	58	60	63
QB 012	8	35	35	48
QB 521	8	50	50	65

AIRCRAFT ALUMINUM

None	--	25	23	20
Strontium Chromate	9	10	18	23
QB 310	8	15	18	20
QB 012	8	5	8	15
QB 521	8	10	15	18

ZINC

None	--	118	157	190
Strontium Chromate	9	15	20	105
QB 310	8	13	20	188
QB 012	8	15	18	53
QB 521	8	15	20	65

1. Lithium Corp - Lithium Silicate 6

TABLE 25 - EFFICACY OF ORGANOMETALLICS AS ANTICORROSIVES IN A ZINC RICH SILICATE COATING

EXPERIMENTAL

Sample Preparation:

Dispersions containing 20 weight percent of zinc dust (-400 mesh) in 10% aqueous tris (hydroxyethyl) ammonium silicate containing the indicated additive(s) concentrations, were spray applied (2 mils. wet) to metal panels. The coatings were air dried at 121°C for one hour prior to evaluation.

Corrosion Test

Panels were subjected to attack by oxygen saturated 5% aqueous caustic at cycle temperatures of 25 to 150°F (thermocycle 2.78°C/Min.). Sample panels were stripped of coating and accumulated oxide by repeated (5 cycle) dipping in liquid nitrogen and 200°C Dowtherm A, followed by extraction (to constant weight) with 5% potassium tartrate in boiling triglyme containing 0.5% wt. crown 12 phase transfer agent. Panel weight loss was calculated in μ/Year (8766 Hr.) by extrapolation.

RESULTS

CARBON STEEL

<u>Additives</u>	<u>PPT</u>	<u>Corrosion Rates (μ/Year)</u>		
		<u>500 Hr.</u>	<u>1000 Hr.</u>	<u>2000 Hr.</u>
None	--	23	35	308
Strontium Chromate	20	23	32	185
QB 310	8	23	25	43
QB 012	8	35	43	55
QB 521	8	10	13	13
AIRCRAFT ALUMINUM				
None	--	72	143	793
Strontium Chromate	20	45	73	408
QB 310	8	60	65	205
QB 012	8	48	53	185
QB 521	8	35	43	48

TABLE 26 – VISCOSITY EFFECT OF VARYING DOSAGES OF LICA 38 ADDED IN-SITU TO 61% MINERAL OIL/39% CLOISITE 15A (MMT; HYDRATED ALUMINUM SILICATE TREATED WITH 35% AMMONIUM QUAT-SOUTHERN CLAY)

Cloisite 15A Nanoclay	Mineral Oil	% LICA 38	Brookfield (HBT) Visc., cps @ 25°C
50	50	0	>3,000,000
45	55	0	>3,000,000
40	60	0	1,280,000
35	65	0	80,000
38	62	0	112,000
39	61	0	400,000
39	61	0.25	160,000
39	61	0.5	112,000
39	61	0.75	112,000
39	61	1.00	128,000
39	61	1.5	160,000
39	61	3.0	320,000
39	61	6.0	400,000

TABLE 27 – THE EFFECT OF VARIOUS PYROPHOSPHATO TITANATE QUATS ON THE VISCOSITY OF CLOISITE NA+ (SOUTHERN CLAY) IN WATER

CA #	Na+	H ₂ O	% CA	Viscosity, x 10 ³ cps @ 25C		
				Initial	2 hrs.	72 hrs.
-	20	80	0	1,280	-	-
1	20	80	3.0	1,120	-	-
1	20	80	6.0	1,040	-	-
2	20	80	6.0	800	-	-
3	20	80	6.0	560	-	-
4	20	80	6.0	465	-	-
-	7	93	0	0.065	14.000	96.000
1	7	93	5.0	0.045	1.820	3.120
2	7	93	5.0	0.030	1.400	2.400
3	7	93	5.0	0.040	0.400	1.680
4*	7	93	5.0	0.025	0.520	1.400

* CA # 4 = Titanate Quat QB 046

Table 28 – THE TRANSPARENT SURFACE AND VOLUME RESISTIVITY EFFECT OF A ZIRCONATE BASED ANTISTAT ON THE SURFACE AND VOLUME RESISTIVITY OF FLEXIBLE PVC SHEETS THAT IS INDEPENDENT OF ATMOSPHERIC MOISTURE DUE TO NANO BI-POLAR CONDUCTIVE NETWORK FORMATION IN THE PVC OF DISSIMILAR TRINEOALKOXY ZIRCONATES IN THE ANTISTAT

PVC Sheet #	Surface Resistivity, Ω/square	Volts Ω	Dr. Theidig Ohm Meter Range	Volume Resistivity, $\Omega \cdot \text{cm}$	Voltage Ω	Dr. Theidig Ohm Meter Range
559A Side 1	7.9×10^{12}	10	200 G/20K	7.4×10^{10}	10	20 G/2K
559A Side 2	4.8×10^{12}	10	200 G/20K	8.9×10^{10}	10	20 G/2K
559B Side 1	3.5×10^{12}	10	200 G/20K	1.9×10^{10}	10	20 G/2K
559B Side 2	4.3×10^{12}	10	200 G/20K	2.1×10^{10}	10	20 G/2K
559C Side 1	8.2×10^{12}	10	200 G/20K	2.6×10^{10}	10	20 G/2K
559C Side 2	7.3×10^{12}	10	200 G/20K	2.1×10^{10}	10	20 G/2K
559D Side 1	7.8×10^{12}	10	200 G/20K	5.5×10^{10}	10	20 G/2K
559D Side 2	4.2×10^{12}	10	200 G/20K	4.5×10^{10}	10	20 G/2K
559E Side 1	3.2×10^{12}	10	200 G/20K	2.9×10^{10}	10	20 G/2K
559E Side 2	2.4×10^{12}	10	200 G/20K	6.5×10^{10}	10	20 G/2K

next pg.) Acrylic	Melamine/ Amide/ Urea	Ketone/ Ester	Pigments	Bake Speed/Overcoat	KR 9S, LICA 09	0.4% of polymer
				Adhesion/Corrosion Cont.	KR 238S, KR 44 , LICA 38, NZ37	0.4% of polymer
	Melamine/ Amide/ Urea	Aqueous	Pigments	Adhesion/Gloss/Dispersion	KR 238S (J Quat), KR 138S TER50 , LICA 38J	0.4% of polymer
				Air Dry	Aqueous	Pigments Steel
		Corrosion Control	KR 238S TER50, LICA38J, KR 238S (J Quat)	0.4% of polymer		
		Metal Adhesion	KR 238S TER50, QB 046, LICA 09	0.4% of polymer		
	Air Dry	Aqueous	Polyester	Adhesion	KR 238S (J Quat), LICA 38J, NZ 12, KR 44	0.4% of polymer
			Plastic	Adhesion	KR 238J	0.4% of polymer
			Rubber/PU	Adhesion	LICA 09, KR 9S Emulsified	0.4% of polymer
			Wood	Anti-Tannin Resistance	LICA 44	0.4% of polymer
			Transparent, Perm.	Antistatic	Ken-Stat KS MZ60WE	4.0% of polymer
	Melamine/ Amide/ Urea	Aqueous	Pigments	Adhesion to Polyester, Glass	<ul style="list-style-type: none"> KR 238S (J Quat), LICA 38J & LICA 09 combo 	<ul style="list-style-type: none"> 0.4% of polymer
			TiO ₂	Puff, Bake Speed	KR 238S TER50, KR 238T	0.4% of polymer
	Acrylic Monomer	-	-	TiO ₂	NZ 38, NZ 39	0.5% of TiO ₂

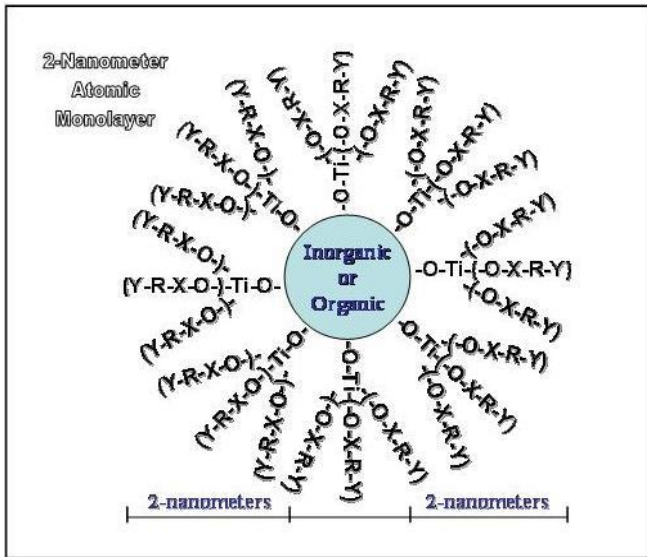


Figure 1—Theoretical 2-nanometer atomic monolayer of organofunctional titanate on an inorganic or organic particulate or substrate.

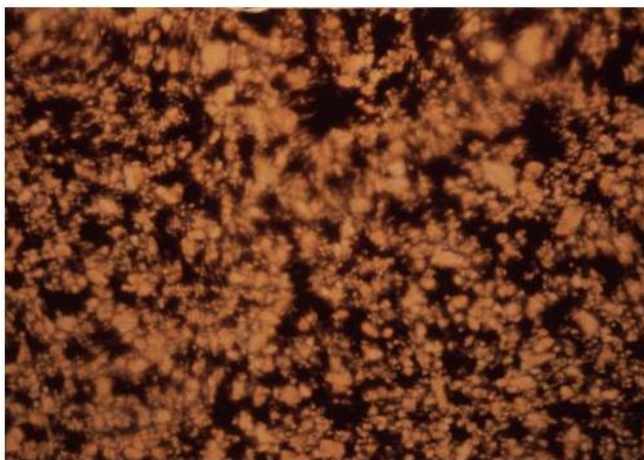
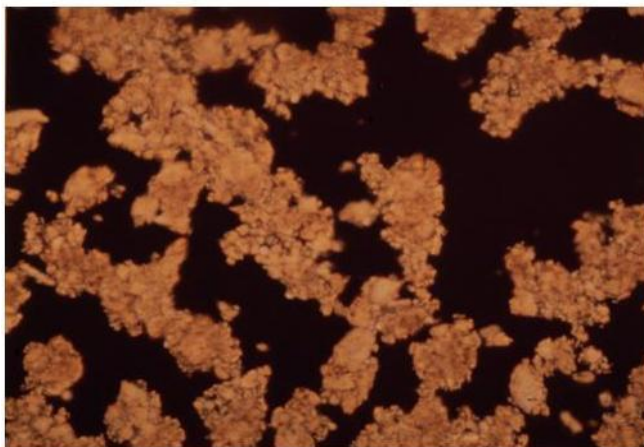


Figure 2—SEM's CaCO₃ dispersed in non-polar liquid paraffin – no titanate (top) & 0.5% KR TTS titanate (bottom).



Figure 3—(Left) 70% 3- μ CaCO₃ in mineral oil has 2,080,000 cps viscosity. (Right) 0.7 wt. % LICA 38 of CaCO₃ added in-situ to mineral oil followed by 70% 3-mircon CaCO₃ has 12,800 cps viscosity.



Figure 4—180° bend of 70% 3-micron CaCO₃, 0.5% KR TTS titanate treated filled PP homopolymer showing rubber-like flexibility and no white stress cracking.



Figure 5—Nervy unfilled EPR (left). EPR derived with 0.2 phr phosphato titanate (right) indicating Function 2 polymer flexibilization.

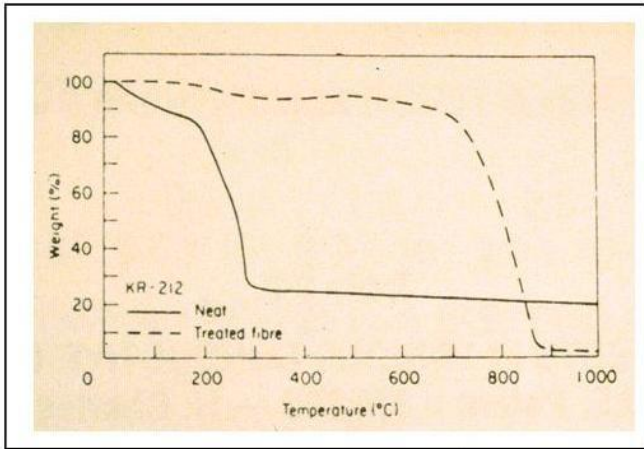


Figure 6—Dynamic TGA of carbon fiber reinforced epoxy showing intumescent protection by use of chelated phosphato titanate (KR 212).

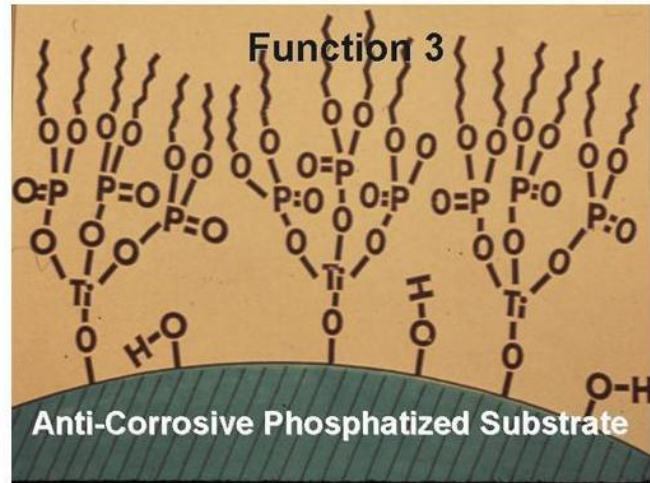


Figure 9—Theoretical 1.5 nanometer atomic monolayer of phosphato titanate to create an anti-corrosive phosphatized substrate.



Figure 7—Epoxy/Polyamide Primer—Painted Panels. A test to demonstrate that a pyrophosphato titanate coupled silica can replace BLSC.

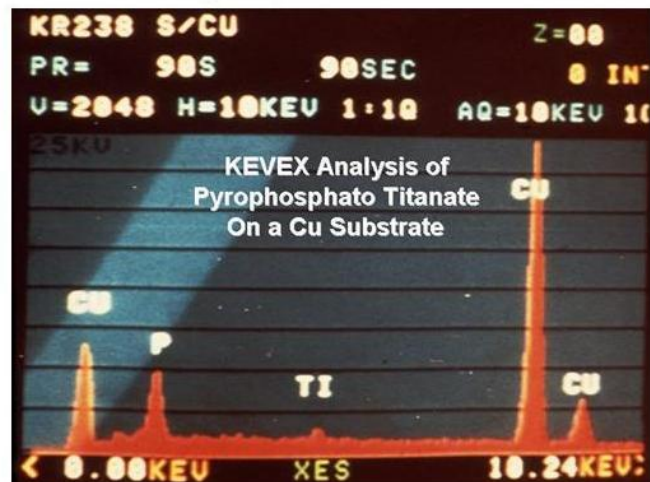


Figure 10—Actual monolayer of pyrophosphato titanate (KR 238S) on Cu substrate.



Figure 8—Epoxy/Polyamide Primer—Stripped Panels. Titanate coupled silica can replace BLSC.



Figure 11—Atomic monolayer of pyrophosphato titanate (KR 38S) provides oxidative protection to heat aged brass metal powder as indicated.

Hydrophobicity

Atomic Monolayer of Titanate on Pure CaCO_3
Compressed Slabs (150 kg/cm^2 for 10 minutes)

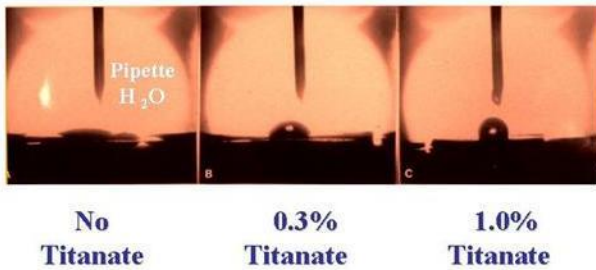


Figure 12—Contact angle of water dropped on to surface of CaCO_3 (left), 0.3% KR TTS titanate (center), and 1.0% KR TTS titanate (right).



Figure 13—(Left) Ceramic powder into solvated PTFE is not wetted out and phase separates. (Center) The center jar had a neoalkoxy phosphato titanate (NZ 12) dispersed into water/PTFE followed by addition of ceramic. Since the NZ 12 is insoluble in water the ceramic is unwetted and the zirconate gave no benefit. (Right) Organosoluble NZ 12 added to a solvent/PTFE @ RT followed by ceramic creates a stable an homogenous mixture.



Figure 14—Creafill TC 4005 (Recycled Flax) in water untreated does not wet. (Right) Creafill TC 4005 treated with 2.0% KR TTSWE25 is wetted by water and sinks to the bottom.

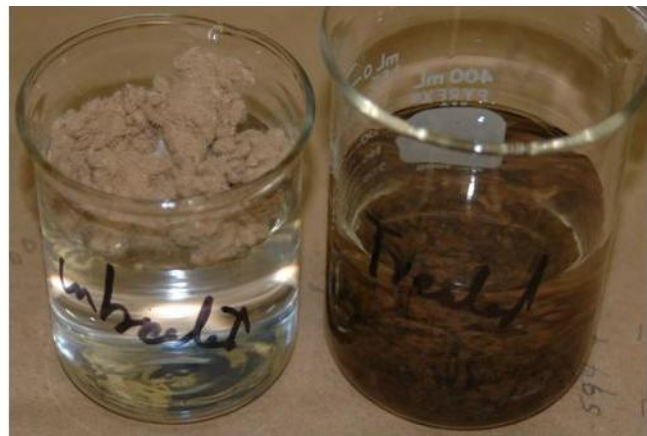


Figure 15—(Left) Creafill TC 2502 (Recycled Kraft Paper) in water untreated does not wet. (Right) Creafill TC 2502 treated with 2.0% KR TTSWE25 is wetted by water and sinks to bottom.



Figure 16—(Left) 40% Calcined Clay in mineral Oil has viscosity of $>2,000,000$ cps. (Right) 0.7 wt. % LICA 38 of calcined clay added in-situ to mineral oil followed by clay has 9,200 cps viscosity.



Figure 17—(Left) 50% $\text{Mg}(\text{OH})_2$ in mineral oil has viscosity of 640,000 cps. (Right) 0.7 wt. % LICA 38 of $\text{Mg}(\text{OH})_2$ added in-situ to mineral oil followed by $\text{Mg}(\text{OH})_2$ has 12,800 cps viscosity.



Figure 18—The dispersion effect of 0.5% LICA 38 on 55% ultramarine blue (Holliday 51-51)/DOP—see Table 10..



Figure 21—The dispersion effect of 0.5% LICA 38 on 60% $\text{Co}(\text{AlCr})_2\text{O}_4$ Green (F-5687)/Mineral Oil—see Table 10.



Figure 19—The dispersion effect of 0.5% LICA 38 on 55% PbChromate Yellow/DOP—see Table 10.



Figure 22—(left) 55% 0.3μ ZnO in mineral oil has a viscosity of 1,600,000 cps. (Right) 0.5 wt. % LICA 38 of ZnO has 12,800 cps viscosity.



Figure 20—The dispersion effect of 0.5% LICA 38 on 55% red iron oxide (R 2200)/DOP—see Table 10.



Figure 23— 60% TiO_2 /min. oil (left to right): no titanate = 512,000 cps; with LICA 38: 0.25% = 128,000 cps; 0.5% = 32,000 cps; 1.0% = 12,800 cps.



Figure 24—Some commercial TiO_2 cosmetic products using CFTA (Cosmetics, Fragrances and Toiletries Association) approved KR TTS.



Figure 27—The patented Wilson “TITANIUM” peroxide cured polybutadiene golf ball based on KR TTS titanate (the Titanium) induced increase in COR (Coefficient of Restitution).



Figure 25—Some commercial ferrite magnetic recording media products using titanate.



Figure 26—The sheet containing 11% untreated carbon black in 20 MI LLDPE (left) off a two roll mill is rough w. poor appearance while the sheet (right) using the same concentration of 0.75% LICA 38 pretreated carbon black is smoother.



Figure 28—40% FG/PC Ford F-Series Truck Fuse Box Cover-57g shot I.M. with 1% CAPS L 12/L showed: a 60 to 45 sec. cycle reduction; a 52°C temp. reduction; a 45% SPC reduction in out of tolerance measurements; increase in properties: Tensile Strength (54.5 MPa), notched izod (44.6KJ/m²) and MFI (22.9 g/10 min.).



Figure 29—(Top) 40% FG, Fe₂O₃ filled PC part with poor weld lines (Bottom) 1% CAPS L 12/L titanate allowed: reduction of IM process temps. by 116°C; eliminated weld line problem; improved appearance; and increased impact strength.



Figure 30—40% FG/Nylon automotive part had a 7-second reduction in cycle time and lowered process temperatures (°C) by 11% (rear zone: 282-248; zone 1: 304-254; zone 2: 304-227; nozzle: 310-260) using 1% CAPS L 44/E titanate added to the IM machine hopper.



Figure 31—(Left) FG (silane sized E-glass)/MEKP cured unsaturated polyester shows glass fibers. (Right) titanate composition does not show fibers.



Figure 32—(Left) Control: MEKP cured unsaturated polyester has a 50-minute cure with a 135°C continuous exotherm causing bubbles. (Right) 1% CP-03 hybrid titanate exhibited a 7-hour cure, no exotherm – first 6-hours, then exotherm to 34°C (94°F) exhibiting no bubbles – pinhole free.



Figure 33—(Left) 3-μ CaCO₃ filled MEKP cured unsaturated polyester casting shows exotherm pinholes. (Right) Hybrid titanate eliminates pinholes.



Figure 34—(Left) E-glass fiber wound epoxy pipe with no coupling agents shows glass fibers. (Right) 0.2% of an aromatic amino zirconate (NZ 97) is added directly to the epoxy resin and shows no glass fibers due to coupling in-situ to glass and complete wetting by epoxy.



Figure 35—Fiberglass reinforced vinyl ester (Left) No exposure control. (Center) 0.4% of an aromatic amino titanate (LICA 97) shows resistance to 2-month exposure in caustic retaining 100% of Flexural Modulus and 75% of Flexural Strength. (Right) Conventional E-glass without titanate added shows significant aged-deterioration.



Figure 37—(TOP) Start ignition: (left) 44% CaCO_3 /LLDPE. (right) 44% CaCO_3 /3% LICA 38/LLDPE. (BOTTOM) 2 min:26 sec into burn: (left) Burns away completely. (right) 3% LICA 38 titanate/ CaCO_3 extinguishes the burn.



Figure 36—19-Perf. LOVA (LOW Vulnerability Ammunition) 120mm Abrams A1A propellant (85% RDX/CAB) containing 0.5% LICA 12 titanate to: control burn rate & burn rate exponent; couple the RDX to the CAB for better aging; and increase flow of the CAB composite to eliminate “pin drift” during extrusion and maintain concentricity of the perforations.



Figure 38—(Left) 60% fine particle ATH in mineral oil has 800,000 cps viscosity and shows no flow. (Right) 60% ATH in mineral oil with 0.7 wt. % LICA 38 added in-situ has 9,600 cps viscosity and flows readily.

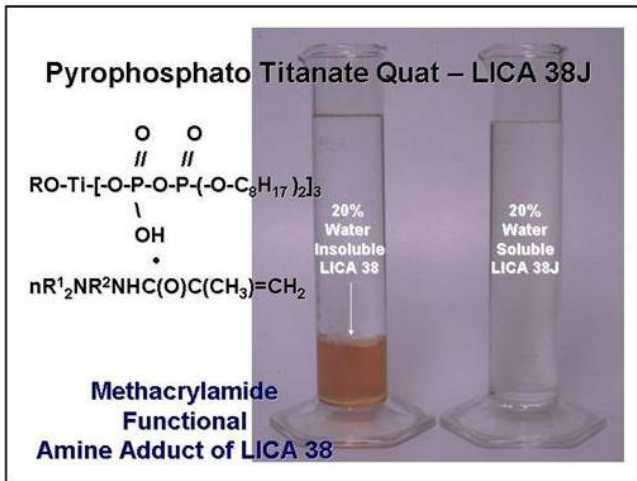


Figure 39—(Left) 20% LICA 38 in water is insoluble. (Right) 20% LICA 38J quat is soluble.

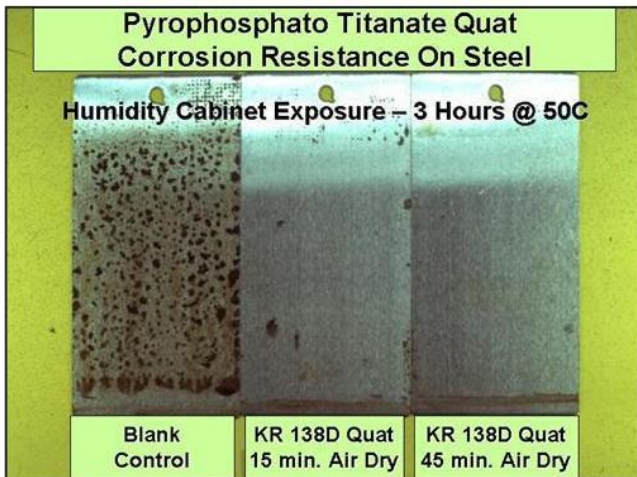


Figure 40—Humidity cabinet exposure—3 hrs. @ 50°C—Mild Cold Rolled Steel. (Left) Control. KR 138D pyrophosphato titanate quat was diluted to 10% in H₂O wiped on panels and allowed to dry (Center) for 15-min. and (Right) 16-hrs.



Figure 41—Carbon Black rendered water compatible and wettable with 1.2 wt. % LICA 38ENP .



Figure 42

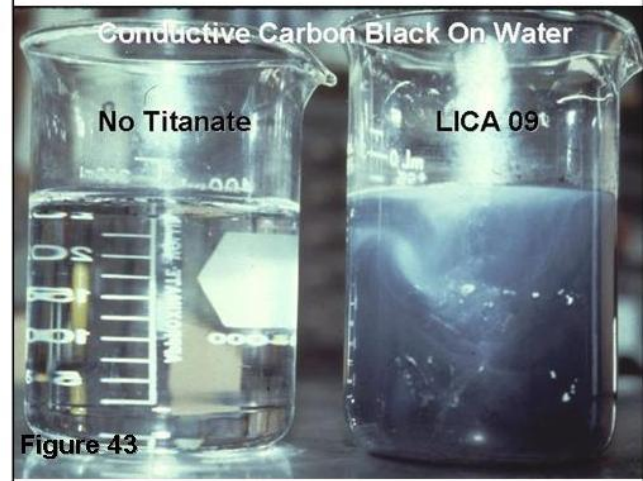


Figure 43



Figure 44

Figures 42, 43 & 44—Carbon Black is rendered water compatible and wettable using water emulsifiable LICA 09. (Top—Middle—Bottom) (Left) Cabot XC-72R carbon black is placed on water and floats. (Right) Time lapse: LICA 09 is emulsified directly into water and begins and instant reaction with the carbon black that causes it to be completely dispersed without any stirring.



Figure 45—Painted: WB Acrylic systems with QB 012 titanate quat replace heavy metal alkyd.



Figure 48—Scored: WB acrylic with QB 012 outperforms acrylic heavy metal alkyd controls.



Figure 46—Stripped: WB Acrylic systems with QB 012 titanate quat replace heavy metal alkyd.

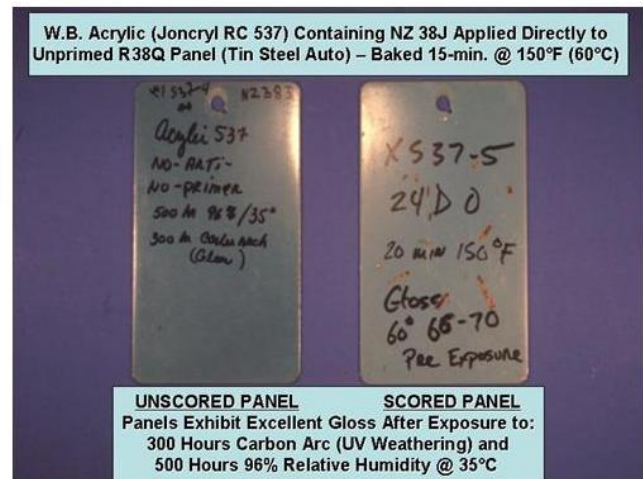


Figure 49—NZ 38J zirconate quat used as primer for WB Acrylic on tin steel auto panels.



Figure 47—Painted: WB acrylic with QB 012 outperforms acrylic heavy metal alkyd controls.

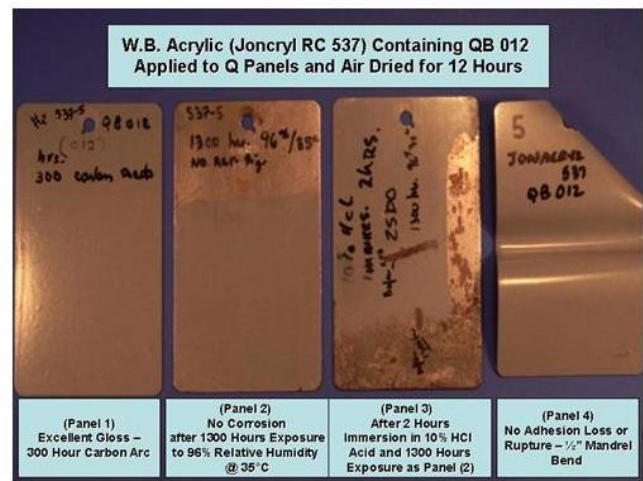


Figure 50—WB Acrylic containing QB 012 exhibits good performance in a series of tests.

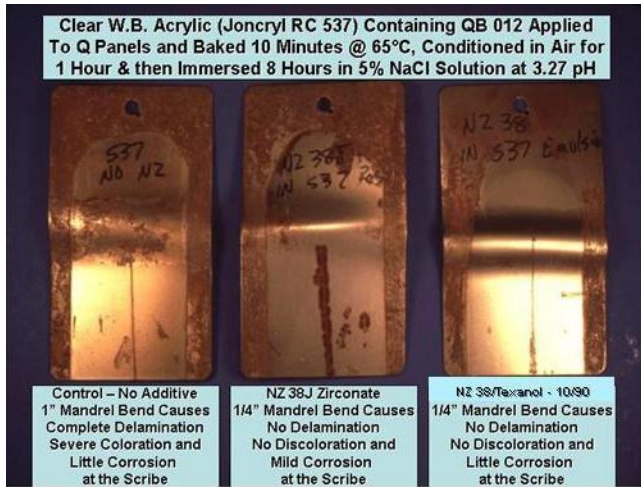


Figure 51—Q Panels immersed in 5% NaCl at 3.27 pH. (Left) WB Acrylic control: 1" mandrel bend; (Center) NZ 38J pyrophosphato zirconate quat: 1/4" mandrel bend-mild corrosion; (Right) NZ 38 emulsified with Texanol—10/90: 1/4" mandrel bend-little corrosion .



Figure 52—(Left) 7% Cloisite Na+ MMT Nano Clay in Water has 96,000 cps viscosity and shows no flow—had to hit jar several times to make the gel move. (Right) 7% Cloisite Na+ MMT Nano Clay in Water having 5.0 wt. % QB 046 titanate quat added in-situ has 1,400 cps viscosity and flows readily.



Figure 53—Right hand column. Top photo - (Left)-34% 20-nm silica sol gel (Nyacol) control - no titanate. (Right)-2.4% LICA 38J by silica wgt. causing exfoliation & water absorption to form powder. Middle photo - (Left)- Control - no titanate oven dried at 120°C - 3 hrs. (Right) - 2.4% LICA 38J w. higher bulk vol. Bottom photo - (Left)-Control - no titanate evaporated @ ambient-2 wks. - a solid/glassy hard pack silica. (Right)- 2.4% LICA 38J - fluffy/exfoliated.

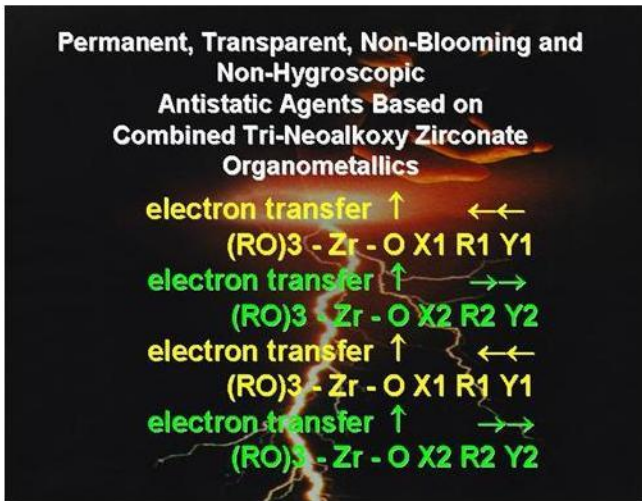


Figure 54—Suggested mechanism for using dissimilar trineoalkoxy zirconates to form a transparent, permanent, non-blooming and non-hygroscopic ESD circuit in polymers—U.S. Patent 5,659,058 filed in 72-countries.

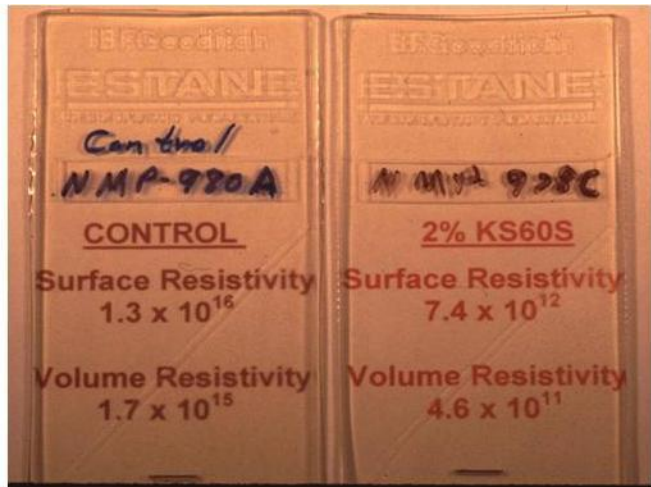


Figure 56—(Left) Thermoplastic polyurethane control shows Surface Resistivity = 1.3×10^{16} Ω/sq. and Volume Resistivity = 1.7×10^{15} Ω·cm. (Right) 2% Ken-Stat KS MZ60S (60% active trineoalkoxy zirconate on silica powder) creates an ESD effect of Surface Resistivity = 7.4×10^{12} Ω/sq. and Volume Resistivity = 4.6×10^{11} Ω·cm.



Figure 55—Five transparent sheets of flexible PVC contain a 60% powder masterbatch of a combined dissimilar trineoalkoxy zirconate antistat that forms a nano Zr electron conducting network exhibiting 10^{12} surface resistivity, Ω/sq. and 10^{10} volume resistivity, Ω·cm.—independent of atmospheric moisture.

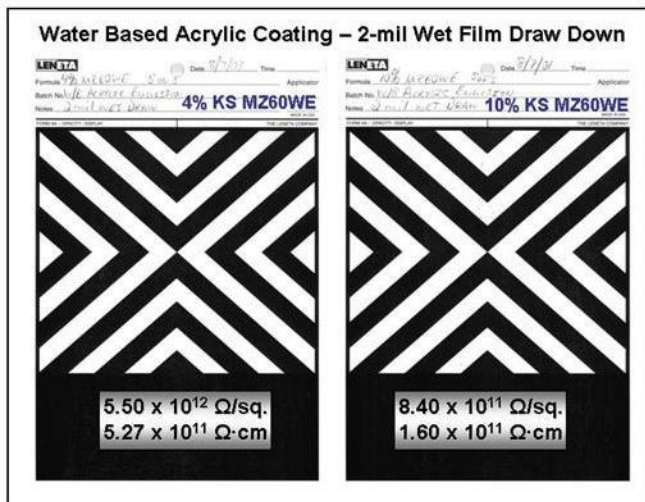


Figure 57—ESD transparent WB Acrylic Coatings. (Left) 4% Ken-Stat KS MZ 60WE (Water Emulsifiable) and (Right) 10% Ken-Stat KS MZ 60WE.

ADDENDUM

The abstracts provided in this Addendum point directly to the theme of the interests of polymer formulators. The claims made are quite interesting – and are often based on early work by the author – and point to many titanate/zirconate effects that are discussed in the main body of this technical paper. It is recommended strongly that the reader examine the abstracts in the addendum to gain an appreciation of the enabling and innovative applications scope of subject titanates and zirconates in coatings and related polymer art gathered from around the world. The abstracts point directly to the theme of the interests of polymer formulators.

For example, the following abstract from Algeria is instructive as it points to the difference between a zirconate and a silane as it relates to what we will discuss as Function 1 coupling claiming that the zirconate forms atomic 1.5 nanometer monomolecular layers while silanes oligomerize:

TI The interactions of silane and zirconate coupling agents with calcium carbonate

AU Doufnoune, R.; Haddaoui, N.; Riahi, F.

CS Laboratoire de Physico-Chimie des Hauts Polymeres (LPCHP), Departement de genie des procedes, Faculte des sciences de l'ingenieur, Universite Ferhat-ABBAS, Setif, Algeria

SO International Journal of Polymeric Materials (2007), 56(3), 227-246 CODEN: IJPMCS; ISSN: 0091-4037

PB Taylor & Francis, Inc.

AB The structure and form of the deposit on calcium carbonate were studied for two types of silane coupling agents and a zirconate one. The structure of the deposited layers as well as their interactions with the filler were investigated by means of Fourier Transform Infra-Red Spectroscopy. The extent of the recovery was determined using the dissoln. method, which allowed measurement of the adsorbed quantity and to estimate the mol. area occupied by each coupling agent as well as the orientation of the mols. on the surface of CaCO₃. The structure of the aminosilane layers deposited on calcium carbonate appeared to be greatly influenced by the initial conditions of treatments. These include the pH, the concentration of the aqueous bath of impregnation, duration, and method of application. The results showed the formation of polymerized structures of the silanes on the surface of CaCO₃ and the deposit was composed of monomers and oligomers that were both physisorbed and chemisorbed. The study of the chemical structure of the zirconate agent that was deposited on the surface of CaCO₃ showed that a monomol. layer was chemical adsorbed. The physisorbed part of the zirconate was mainly constituted of monomers that were soluble in the solvent used for the extraction

IT Coupling agents

(interactions of silane and zirconate coupling agents with calcium carbonate and structures of deposited coupling agents)

IT 471-34-1, Alcal UF-5, processes 919-30-2, A-1100 1760-24-3, Z-6020 103373-95-1, NZ 44

RL: PEP (Physical, engineering or chemical process); PROC (Process)

(interactions of silane and zirconate coupling agents with calcium carbonate and structures of deposited coupling agents)

The following abstract from South Korea is instructive concerning current efforts towards sustainability since a neoalkoxy pyrophosphato titanate demonstrates the ability to react with various organic and bio based pigments, fillers and polymers. For example, using titanate treated domestic rice bran as a filler to prevent environmental pollution:

TI Manufacturing method of wood substitute by using rice bran for preventing environmental pollution

IN Moon, Won Gi; Choi, In Taek

PA S. Korea

SO Repub. Korean Kongkae Taeho Kongbo, No pp. given CODEN: KRXXA7

PI KR 2006018133 A 20060228

AB A manufg. method of a wood substitute by using rice bran is provided to promote health, to prevent environmental pollution and to cut down manufacturing cost by recycling rice bran and to making the environment-friendly wood substitute containing rice bran of more than 70%. Crushed rice bran is put into a driver and dried with moisture content of 0.02%. A compound is mixed at temperature of 90 to 100°C by mixing dried rice bran of 70 to 85 wt%, synthetic resin of 15 to 30 wt%, a plasticizer of 5 wt%, a dispersing agent of 5 wt%, a flowing agent of 5 to 10 wt% and a coupling agent of 0.5 wt%. The compound is agitated and cooled at normal temperature by a cooling apparatus The cooled material is supplied qual. and extruded in a twin extruder with a screw rotating at the rate of length to diameter of 34 to 1. The extruded material is injected into a mold and formed. The coupling agent includes neopentyl(diallyl)oxytri(dioctyl) pyrophosphate titanate, and the synthetic resin includes polypropylene.

IT Bran

(rice; manufacturing method of wood substitute by using rice bran for preventing environmental pollution)

IT 103432-54-8 LICA 38

RL: MOA (Modifier or additive use); USES (Uses)

(manufacturing method of wood substitute by using rice bran for preventing environmental pollution)

The following abstract from the United States is instructive in that it is well known in silane art that thermally conductive pigments such as boron nitride are non-reactive while in contradistinction, a coordinate phosphito titanate and a cycloheteroatom pyrophosphato zirconate are efficacious:

TI Surface-treated boron nitride and polymer composites filled with surface-treated boron nitride

IN Paisner, Sara N.; Hans, Paul Joseph; Meneghetti, Paulo

PA General Electric Company, USA

SO U.S. Pat. Appl. Publ., 17pp., Cont.-in-part of U.S. Ser. No. 327,709. CODEN: USXXCO

PI US 2007054122 A1 20070308

AB A boron nitride compn. comprises boron nitride powder having its surface treated with a coating layer comprising at least one of silane, siloxane, carboxylic derivative, and their mixts., the coating layer adhering to at least 10% of the boron nitride surface. The boron nitride powder surface is first treated by calcination, or coating with at least one inorg. compound to form a plurality of reactive sites on the surface containing at least one functional group that is reactive with at least one functional group in the above coating layer. A polymer composite comprises a polymer matrix selected from melt-processable polymers, polyesters, phenolic resins, silicones, acrylic resins, waxes, thermoplastic polymers, and epoxy molding compds., and a filler comprising particles of boron nitride surface-treated as described above. The polymer composites containing surface-treated boron nitride have improved processability at high filler loadings, and can be used in applications demanding high thermal conductivity

IT 928773-60-8, Ken-React KR 41B 928773-67-5, Ken-React KZTPP

RL: MOA (Modifier or additive use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)

(surface-treated boron nitride used as filler in polymer composites)

The following abstract from South Korea is instructive in that nano-sized metal oxides such as colloidal indium tin oxide nanoparticles can be dispersed using an amino titanate as the preferred coupling agent for transparent and conductive films used as a static charge dissipater for LCD panels:

TI Colloidal indium tin oxide nanoparticles for transparent and conductive films

AU Cho, Young-Sang; Yi, Gi-Ra; Hong, Jeong-Jin; Jang, Sung Hoon; Yang, Seung-Man

CS Center for Intergrated Optofluidic System and Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, 305-701, S. Korea

SO Thin Solid Films (2006), 515(4), 1864-1871 CODEN: THSFAP; ISSN: 0040-6090

PB Elsevier B.V.

AB Nanosized colloidal indium tin oxide (ITO) dispersion was prepared for electrical conductive and transparent coating materials. A titanate coupling agent, iso-Pr tri(N-ethylenediamino)ethyl titanate, was chosen as a dispersant for the stabilization of ITO nanoparticles in organic solvent. ITO sol was deposited on a cathode ray tube panel for antistatic or electromagnetic shielding purposes, and alkyl silicate was used for the formation of an antireflective over-coat layer. The resulting double-layered coating showed low sheet resistance, which satisfied semi-TCO regulation and low reflectance of visible light. To control the electrical and optical properties of the coating layer, the effects of secondary particle size of ITO aggregates and the dispersant concentration of ITO sol were studied. The stability of ITO sol was estimated by measuring the particle size as a function of the storage days and the aggregation of colloidal ITO dispersion with storage day was explained by depletion flocculation.

IT Nanoparticles

(ITO, suspensions; preparation of stable ITO nanoparticle suspensions with titanate coupling agent for processing of transparent conductive films on CRT panels for antistatic or electromagnetic shielding effects)

The following abstract from the United States is instructive in that it embodies many of the teachings of the author that are consistent with the powerpoint presentation at the Turcoat 2009 conference in that a neoloxoxy pyrophosphato titanate may be used in conjunction with a non-ammonium quat exfoliated nanoclay and synergistically with maleated moieties to produce tough biobased composites based on polyhydroxyalkanoates (PHAs – linear polyesters produced in nature by bacterial fermentation of sugar or lipids):

TI Methods of making nanocomposites and compositions of rubber toughened polyhydroxyalkanoates

IN Mohanty, Amar K.; Parulekar, Yashodhan

PA Board of Trustees of Michigan State University, USA

SO U.S. Pat. Appl. Publ., 17pp. CODEN: USXXCO

PI US 2007015858 A1 20070118

AB Polyhydroxyalkanoates (I) are toughened by maleated polybutadiene and an epoxidized natural or synthetic rubber and mixed with clay nanoparticles to prepare composites for automotive uses. Thus, a blend contained I 60, epoxidized rubber 30, and maleated rubber 10 parts.

IT Clays, uses Titanates

RL: MOA (Modifier or additive use); USES (Uses)

(nanocomposites containing rubber-toughened polyhydroxyalkanoates and clays)

IT 103432-54-8, LICA 38

RL: MOA (Modifier or additive use); USES (Uses)

(LICA 38; nanocomposites containing rubber-toughened polyhydroxyalkanoates and clays)

IT 1318-93-0, Cloisite Na⁺, uses 1318-93-0D, Montmorillonite, ammonium-modified 309295-00-9, Cloisite 30B

RL: MOA (Modifier or additive use); USES (Uses)

(nanocomposites containing rubber-toughened polyhydroxyalkanoates and clays)

The following abstract from China is instructive in that it discusses basic research being done with determining the nature of titanate bonds formed on nano TiO₂:

TI Determination of modified effect of nanometer-sized TiO₂ by acid-base titration in nonaqueous phase

AU Zhang, Lei; Zhang, Dan-feng; Jiang, Yu-chun; Chang, Huai-chun

CS School of Chemical Science and Engineering, Liaoning University, Shenyang, 110036, Peop. Rep. China

SO Fenxi Kexue Xuebao (2006), 22(3), 324-326 CODEN: FKKUFZ; ISSN: 1006-6144

PB Fenxi Kexue Xuebao Bianjibu

AB The nanometer-sized TiO₂ was modified by titanate coupling agent, and the new bonds on the surface of nanometer-sized TiO₂ were suggested by FTIR spectroscopy. A method was developed for the determination of the acidity of solid surface by using neutral red as the indicator. The acidity of the solid suspended in benzene was titrated with Bu amine. Basic indicator formed a red color on acidic solid, and

the end-point of the titration was the disappearance of the red color. The mechanism of color development was studied.

IT 62180-92-1, KR 12

RL: NUU (Other use, unclassified); USES (Uses)

(determination of modified effect of nanometer-sized TiO₂ by acid-base titration in nonaq. phase)

The following abstract from China is instructive in that it reflects the teachings of the author as to dosage requirements wherein conventional TiO₂ particles require ~0.35 to 0.7 wt. % titanate while nano TiO₂ requires ~ 2.0 wt. % for an atomic monolayer. The abstract also underscores that most nanoparticulate filled coatings and composites are optimized at 3 to 5 wt. % nanoparticulate in non-polar polymer phases. Non-polar polymers are the least efficient at wetting pigments. This small amount by weight of titanate treated nanoparticulate brings into consideration Function 2 titanate catalysis effects, wherein the author recommends 6 wt. % titanate on nanoparticulates because optimal catalytic effects of titanates and zirconates on unfilled polymers is generally in the range of from 2-6 parts titanate per 1,000 parts of unfilled polymer – and 6% titanate by weight of 3-5% nano pigment introduces 1.8 to 3.0 parts titanate to 1,000 parts of the polymer interface:

TI Investigation on the mechanical properties of nano-TiO₂/PP composites

AU Ji, Guangming; Tao, Jie; Wang, Tao; Yang, Bingpeng

CS College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, Peop. Rep. China

SO Fuhe Cailiao Xuebao (2005), 22(5), 100-106 CODEN: FCXUEC; ISSN: 1000-3851

PB Fuhe Cailiao Xuebao Bianjibu

AB In order to further improve the mech. properties of com. plastics polypropylene (PP), PP composite material incorporated with the surface-modified nano-TiO₂ particles by titanium-acid ester coupling agent KR 38S was prepared through the blending method. The effect of the mass fraction of TiO₂ and the dosage of KR 38S on the toughening and strengthening of PP matrix was investigated based on the results of the differential scanning calorimeter (DSC) and the observation of the impact fractog. of the material. It was shown that the flexural strength, the modulus and the impact strength of the nanocomposite were obviously improved with the increasing of nano-TiO₂ percentage (less than 5%); and the augment of the properties dropped and turned to a decreasing tendency with the further supplement of the nano-TiO₂ content. It was also found that the addition of nano-TiO₂ promoted the crystallization of PP, leading to a much more quantity of finer β grains. Moreover, the homogeneous dispersion of nano-TiO₂ particles enhanced the obstruction to the cracks' propagating in PP. It was indicated that the dosage of titanium-acid ester coupling agent had a parabola-like relation with the mech. properties of nano-TiO₂/PP composite at a fixed nano-TiO₂ content, while the optimal toughening and strengthening effect could be achieved at 2% of KR 38S.

IT Bending strength

Crack (fracture)

Crack propagation

Crystallization

Flexural modulus

Impact strength

Nanoparticles

(mech. properties of nano-TiO₂/polypropylene composites)

IT Fracture surface morphology

(polymeric; mech. properties of nano-TiO₂/polypropylene composites)

IT 13463-67-7, Titania, uses

RL: MOA (Modifier or additive use); USES (Uses)

(titanate coupling agent-modified; mech. properties of nano-TiO₂/polypropylene composites)

IT 67691-13-8, KR 38S

RL: MOA (Modifier or additive use); USES (Uses)

(titania modified with; mech. properties of nano-TiO₂/polypropylene composites)

moldings)