



Extrusion 2022

PT A Plastics Technology Event

December 6-8, 2022

Omni Charlotte Hotel | Charlotte, North Carolina

Tuesday, December 6, 2022

4:00 PM - 4:30 PM

The Extruder as a Reactor for Advanced Mechanical Recycling Using 1.5-Nanometer Titanates and Zirconates

Compounding

Sal Monte



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The Extruder as a Reactor for Advanced Mechanical Recycling Using 1.5-Nanometer Titanates and Zirconates

Salvatore J. Monte

President | Kenrich Petrochemicals, Inc.

201-823-9000 | sjmonte@4kenrich.com | www.4kenrich.com

Advanced Solutions in Mechanical Recycling with 1.5-Nanometer Titanate Catalysts/Coupling Agents

Presentation Outline – Key Points

- **Titanium/Aluminum coupling and catalysis applications are demonstrated in Advanced Mechanical Recycling.**
- **Ziegler, Natta & Kaminisky used Titanium and Aluminum catalysts to produce Addition Polymers – PP & HDPE are Addition polymers;**
- **Titanate catalysts produce Condensation Polymers such as PET;**
- **Heteroatom Titanates couple fillers & catalyze Polymers in the melt;**
- **Monte uses Ti/Al in powder/pellet form to recycle complex multiple Polymer/Filler mixtures in the extruder melt or shear mixer.**
- **Multiple polymer & filler compatibilization is desirable in recycle art.**

Biography:



Salvatore J. Monte, President of Kenrich Petrochemicals, Inc.; Bachelor Civil Engineering-Structures, Manhattan College; M.S.-Polymeric Materials, NYU Tandon School of Engineering; Member Plastics Hall of Fame 2021; BOD-The Plastics Academy; Society Plastics Engineers Fellow & Honored Service Member; Licensed P.E.; S&E Innovative Technologies, LLC – Principal Member; Plastics Industry Association Recycle Subcommittee-Compatibilizers; Board of Governors, Plastics Pioneers Association-MTS Newsletter Chair; 32-U.S. Patents – most recent US Patent 2020/0071230 A1 dated Mar. 5, 2020; 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 – Annual Scholarship named: Salvatore J. Monte Thermoplastic Materials & Foams Division Scholarship; 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, ACMA, SPE, ACS, ACS Rubber Division, ASCE, AIChE, SAMPE, the GRAPHENE COUNCIL, the Vinyl Sustainability Council.





July/Aug. 2022 5-page article
CHAMPION FOR CHANGE



<https://4kenrich.com>

NEWS

TRADESHOWS, CONFERENCES, AND PRESS ARTICLES

SPE MAGAZINE JULY-AUGUST 2022

Sal Monte continues to challenge conventional thinking about coupling agents and catalysts



[Read Article](#)

PLASTICS ENGINEERING MAGAZINE JULY-AUGUST 2022

Kenrich featured in 5-page July-August issue of Plastics Engineering Magazine: CHAMPION OF CHANGE.

[Read More](#)

COMPATIBILIZERS AID RECYCLING & UPCYCLING OF MIXED RESINS

Compatibilizers are proving their worth in boosting critical properties such as impact/stiffness balance of PCR and PIR blends of polyolefins and other plastics.

[Read More](#)

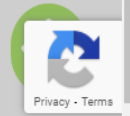


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CHAMPION FOR CHANGE

customerservice@4kenrich.com
technicalsupport@4kenrich.com





July/Aug. 2022 5-page article **CHAMPION FOR CHANGE**

CHAMPION FOR CHANGE

Sal Monte continues to challenge conventional thinking about coupling agents and catalysts by PAT TOENSMEIER

In 1975, shortly before his 40th birthday, a hard-charging chemical executive named Sal Monte attended a communications development seminar in White Plains, a suburb just north of New York City.

During a break, he discussed his business with one of the speakers, James Cusimano. Monte told Cusimano that he helped his company, Kenrich Petrochemicals Inc., of Bayonne, N.J., develop organometallic coupling agents for titanate, zirconate and aluminate technologies. The additives, which also have value as catalysts, improved the properties and processability of numerous materials, such as thermoplastics, composites, color concentrates, coatings, adhesives and rubber.

Monte, who was vice president of the company at the time, believed the coupling agents were suitable for use with all sorts of materials, not just plastics and rubber, and had the potential to upgrade resin properties in diverse applications. Cusimano probably didn't follow all the technical aspects of the conversation, but he did recognize Monte's enthusiasm for and commitment to the products.

"Sal Monte," Cusimano said, "what if I told you your mission in life is to teach people how to use raw materials more efficiently through titanium? Does that mean anything to you?"

For Monte it sounded like affirmation of the work he started in 1973. "The Holy Spirit gave me a message, and



Sal Monte and wife, Erika, strike a familiar pose while promoting Kenrich products at yet another trade show or conference: this time at ANTEC 2013. Photos courtesy of Sal Monte





July/Aug. 2022 5-page article **CHAMPION FOR CHANGE**

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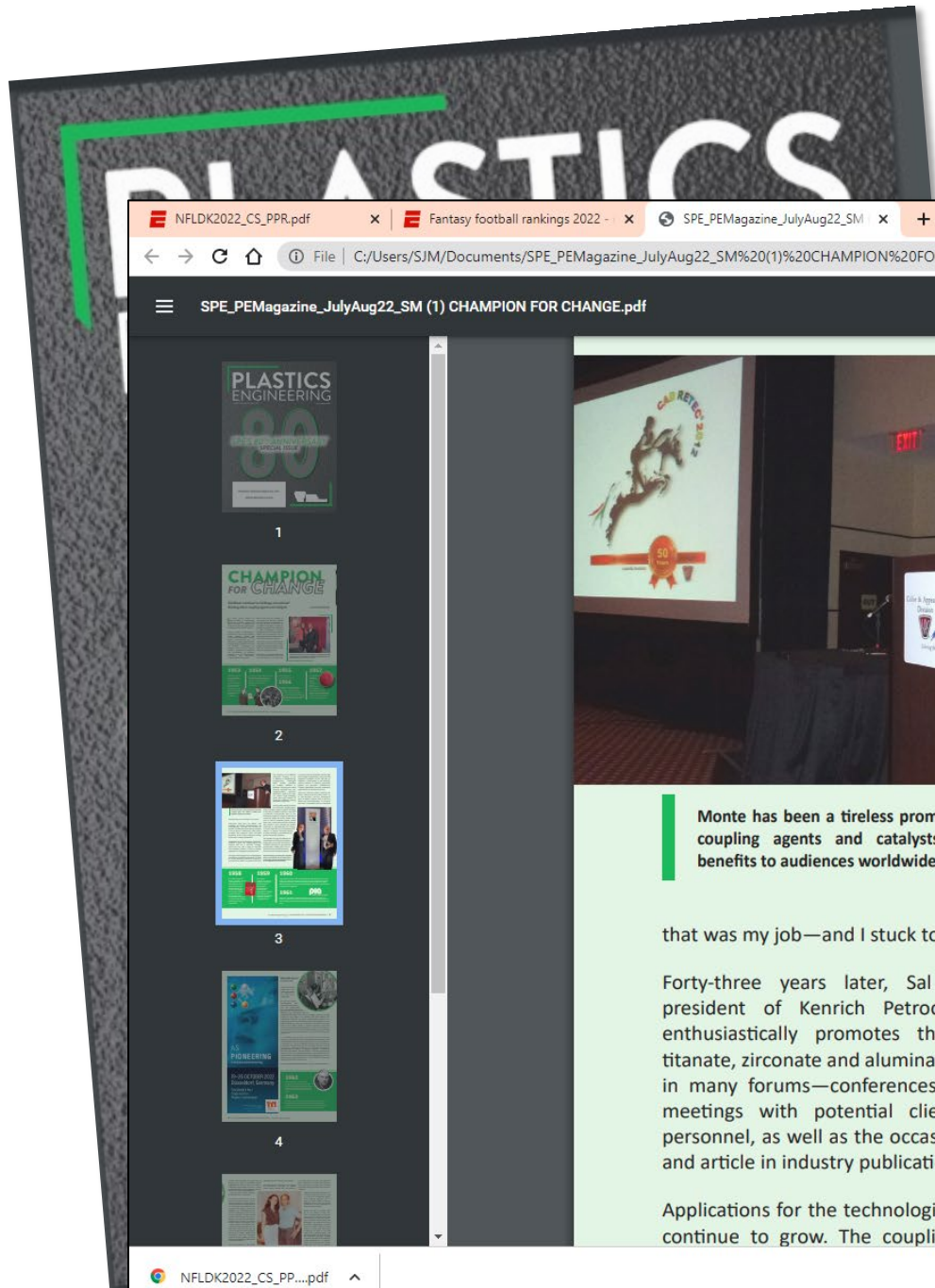


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KENRICH PETROCHEMICALS, INC.
WWW.4KENRICH.COM



July/Aug. 2022 5-page article **CHAMPION FOR CHANGE**



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Page navigation: 3 / 6 | 175% | [Icons]

Thumbnail gallery (left):

- 1. PLASTICS ENGINEERING 80
- 2. CHAMPION FOR CHANGE
- 3. [Image of people]
- 4. [Image of people]

Monte has been a tireless promoter of Ken-React coupling agents and catalysts, detailing their benefits to audiences worldwide.

that was my job—and I stuck to it,” he says.

Forty-three years later, Sal Monte, now president of Kenrich Petrochemicals, still enthusiastically promotes the benefits of titanate, zirconate and aluminate technologies in many forums—conferences, trade shows, meetings with potential clients and R&D personnel, as well as the occasional interview and article in industry publications.

Applications for the technologies, meanwhile, continue to grow. The coupling agents and

the chemistry of the additives mechanical recycling can be as effective at repolymerizing/copolymerizing commingled waste streams generated by curbside collection as advanced recycling (also called chemical recycling) that uses depolymerization processes. Mechanical recycling also does not require huge processing plants and large amounts of energy like advanced recycling does. More on this later.

The Ken-React titanate, zirconate and aluminate coupling agents come as powders, liquids or pellets. According to the Kenrich website, they form a less than 2-nanometer monomolecular layer on the surface of any organic or inorganic material and chemically bridge non-silane reactive fillers such as calcium carbonate (CaCO₃), carbon black, silica, metal oxides and other chemicals with polymers. As an example, the website notes that an organotitanate nano coating on carbon black will act as a metallocene-like catalyst in a polymer and lower Mooney viscosity, resulting in increased flow and greater mechanical properties.

The benefits of using the additives are considerable. According to the website, adding just 0.2 to 0.6 phr of titanate to

or more; mechanical properties improve; high filler loadings of carbon black, CaCO₃, ATH and magnesium hydroxide can be used with no tradeoffs in processability or part flexibility; polymer adhesion to aramids, polyamides, graphite and glass-fiber reinforcements increases significantly; and part smoothness, pigmentation and paintability improve.

These may sound like miracle materials, but there’s nothing miraculous about them; it’s all nano-chemistry, and their development owes to Monte’s original idea in the early 1970s that transesterification of isostearic acid with a tertraalkoxy titanium compound

INDUCTEE

Salvatore J. Monte
President
Kenrich Petrochemicals, Inc.

Salvatore J. Monte, President of Kenrich Petrochemicals, Inc., B.C.E., Manhattan College, M.S. Polymeric Materials, NYU Tandon School of Engineering; Member, Plastics Hall of Fame 2021; the Plastics Academy, Society Plastics Engineers Fellow & Honorary Service Member; Licensed P.E., Plastics Industry Association, Recycle Subcommittee Chair/Co-Chair; Board of Governors, Plastics Pioneers Association; RTTS Newsletter Chair; 32 U.S. Patents – most recent US Patent 2020/0191229 A1 issued Mar. 5, 2020; Lectured Worldwide on Titanate & Zirconate Coating 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 Innovative Multistage Program; Lifetime member of the National Defense Industrial Association; Lifetime Member of the IBCO-SPE Trans-Plastics Materials & Foams Division – Annual Scholarship named Salvatore J. Monte Transplastic Materials & Foams Division Scholarship.

Kenrich Petrochemicals, Inc. logo: Kenrich Petrochemicals

Plastics Hall of Fame logo: PLASTICS Hall of Fame

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July/Aug. 2022 5-page article **CHAMPION FOR CHANGE**



**Finishing a
Marathon is hard**



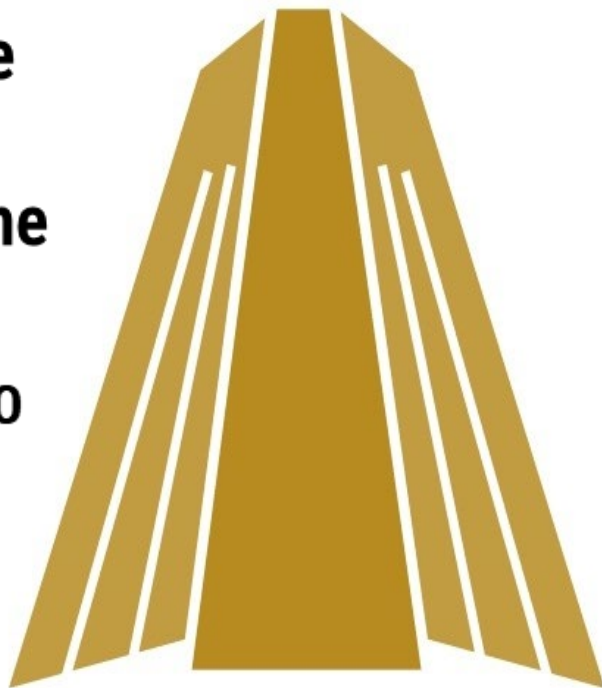
**Being a
Champion of Change
is harder**



Salvatore J. Monte
Inducted Into The
Plastics Hall of Fame

MAY 2, 2022

Aqua Blu Hotel CHICAGO



PLASTICS

Hall of Fame

Three People
Per Annum
Globally



Salvatore J. Monte
President
Kenrich Petrochemicals, Inc.

Salvatore J. Monte, President of Kenrich Petrochemicals, Inc.; B.C.E. Manhattan College; M.S. Polymeric Materials, NYU Tandon School of Engineering; Member Plastics Hall of Fame 2021; the Plastics Academy; Society Plastics Engineers Fellow & Honored Service Member; Licensed P.E.; Plastics Industry Association; Recycle Subcommittee-Comp. Polymers; Board of Governors, Plastics Pioneers Association; MTS Newsletter Chair; 32 U.S. Patents – most recent US Patent 2020/007230 A1 dated Mar. 5, 2020; 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; Fellow of the Inertive Munitions Program; Lifetime member of the National Defense Industrial Association; Lifetime Member of the BOD-SPE Thermoplastics Materials & Foams Division – Annual Scholarship named Salvatore J. Monte Thermoplastics Materials & Foams Division Scholarship; External Advisory Committee-ICE 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 Miller; Member PIA, SPE, ACS, ASCE, AIChE, SAMPE, the GRAPHENE COUNCIL, the Viny Sustainability Council.



PLASTICS
HALL OF
FAME



Voting Member & Recycle Sub-Committee



SPE Fellow & Honored Service Member



PPA Board of Governors – Newsletter Chair



450- ACS CAS Abstracted Works by S.J. Monte



32-US Patents Filed Worldwide



Classified TOP SECRET for U.S. DOD IMEM Program



**Plastics Hall of Fame
MAY 2, 2022**

Report: Prioritize mechanical recycling to meet climate goals

By Steve Toloken
Plastics News Staff

Using pyrolysis-based chemical recycling to meet plastic recycled-content targets could emit up nine times the greenhouse gases compared with traditional mechanical recycling, according to a new study from the environmental group Zero Waste Europe.

“As an industry, we are totally supporting the hierarchy of waste — that is, if it can be mechanically recycled, then it should [be]. We support that as an industry.”



John Sewell
Chemical Recycling Europe

cineration. But he suggested it would compare favorably.

“Of course, there are some benefits of chemical recycling compared to new plastics,” Betz said. “And there’s also a benefit of chemical recycling vs. incineration.

“We should use chemical recycling up to a certain point, but this point has to be very, very, very small as chemical recycling has not as much benefit as mechanical recycling,” Betz said.

Another panelist, Fanny Rateau, a program manager with the Environmental Coalition on Standards, noted that the study found the biggest overall GHG benefit from a reduction in overall single-use packaging, of 20 percent, combined with enhancements to mechanical recycling.

“What is most important for packaging is to eliminate unnecessary packaging and transition from single-use to reusable plastic packaging,” she said. “What’s important is to prioritize mechanical recycling.”

Sewell said the chemical recycling group also favored pri-



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recycling and other steps to

boost mechanical recycling.

“The revision of the PPWD

should serve as a lever to make

the packaging sector more cir-

But Sewell said it could prove difficult to meet any new targets without chemical recycling. He suggested it’s not possible to “wave a magic wand” and have mechanical recycling solve problems processing complex mixtures of plastic waste.

As well, he said that chemical recycling technologies can produce cleaner streams of recycled plastics that could go take food packaging plastic waste and reuse it more easily back into new food-contact plastic.

“Would you not agree with me that you don’t want to wave a magic wand and say that mechanical recycling can solve all

The Sept. 27 study

looked at

of 32

Evco launches Wisconsin expansion

By Bridget Janis

Plastics News Staff

Evco Plastics Inc. is expanding

group

study in a Sept. 27

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“We see that there’s an oppor-

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“... - that is, if it can be mechanically recycled, then it should [be]...”

... it sets... content, as... focusing on design for... recycling and other steps to... boost mechanical recycling. “The revision of the PPWD should serve as a lever to make the packaging sector more cir-... cleaner streams of recy-... cled plastics that could go take... food packaging plastic waste... and reuse it more easily back... into new food-contact plastic. “Would you not agree with me that you don’t want to wave a magic wand and say that mech- anical recycling can solve all... what is most important for... packaging is to eliminate unnec-... essary packaging and transi-... tion from single-use to reusable... plastic packaging,” she said. “What’s important is to priori-... tize mechanical recycling.” Sewell said the chemical recy-... cling group also favored pri-



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“... - that is, if it can be mechanically recycled, then it should [be]...” = Extrusion

The words in the presentation title have a specific technical meaning:

The Extruder as a Reactor for Advanced Mechanical Recycling Using 1.5-Nanometer Titanates and Zirconates



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The words in the presentation title have a specific technical meaning:

Extruder as a Reactor ... Reactive Compounding
For Advanced Mechanical Recycling ... because we
use an Extruder & not a Chemical Plant
Using 1.5-Nanometer Titanates and Zirconates ...
Polymers are made with Ti/Al Catalysts



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The words in the presentation title have a specific technical meaning:

**Advanced Recycling ... is
DEPOLYMERIZATION**

**Advanced Mechanical Recycling ... is
REPOLYMERIZATION**

with Titanate Catalysts/Coupling Agents ...
INORGANIC & ORGANIC PIGMENTS,
METAL OXIDES, METAL CARBONATES,
MINERAL FILLERS, CARBON BLACK, etc.

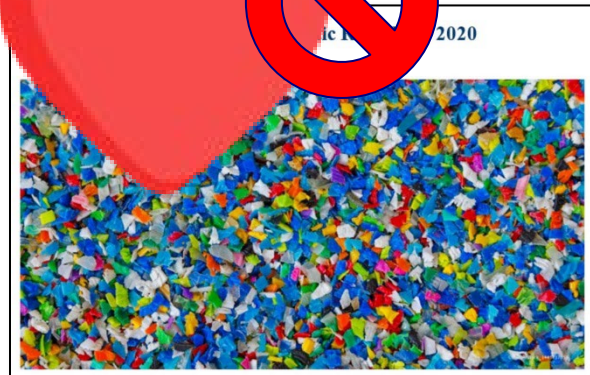
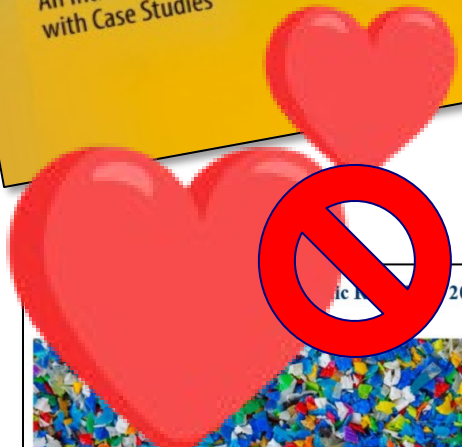
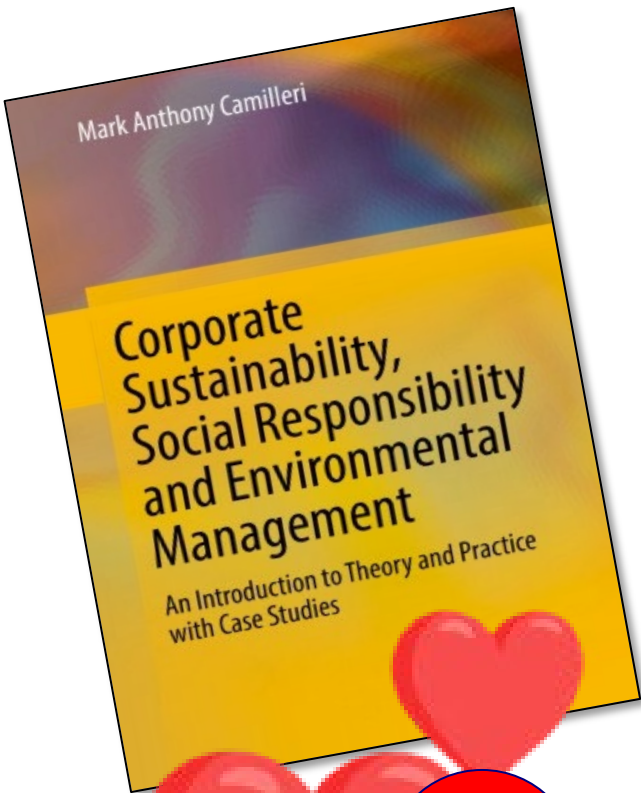


ARE NO LONGER
CONTAMINANTS
IN PLASTIC RECYCLE

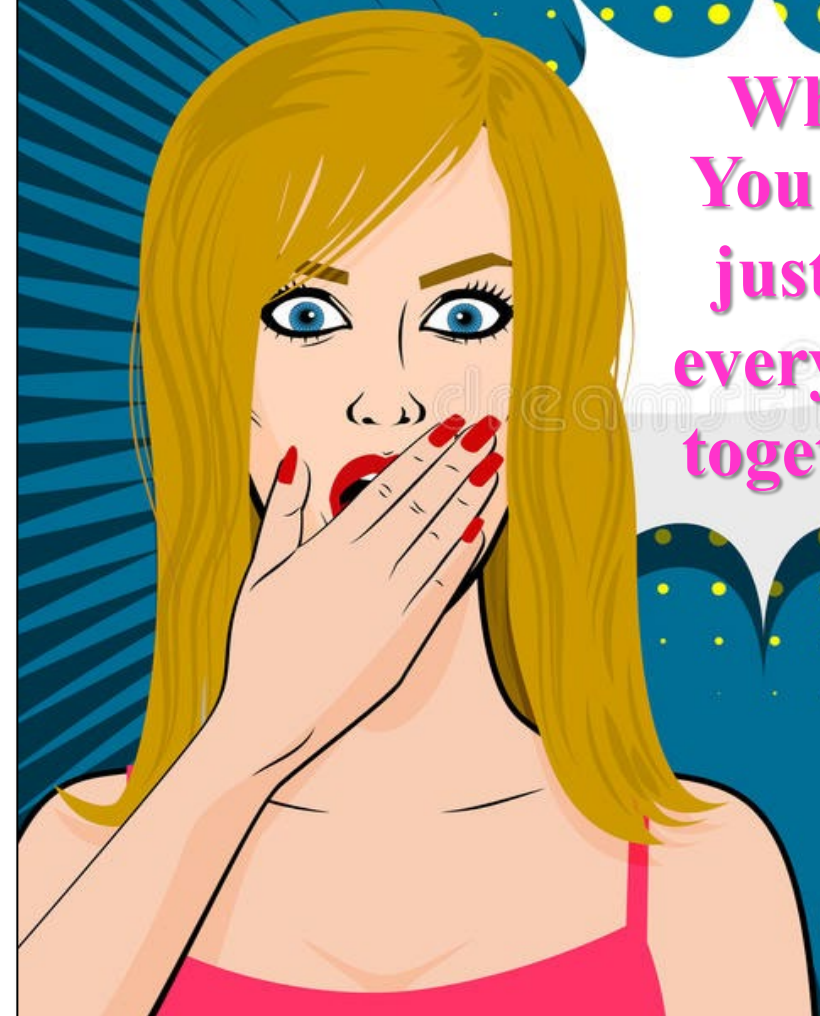
Advanced Solutions Are in Titanium & Aluminum Chemistry

Monte states: Sustainability Goals such as a Circular Economy using Curbside Recycle in new plastic parts is **technically not possible with current industry practices – unless one uses the same chemistry that made the polymers:**

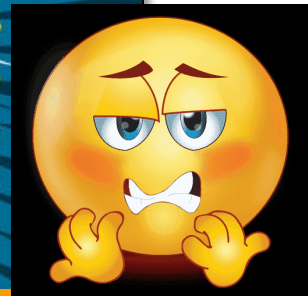
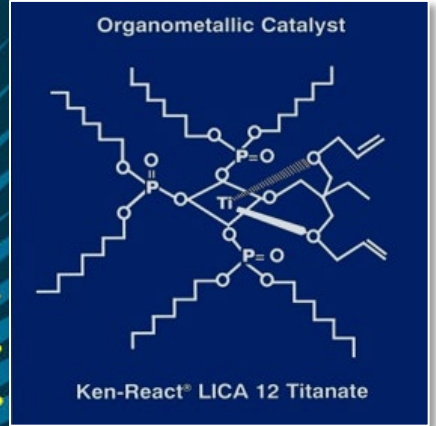




You Need Nano-TITANATE Atomic Compatibilization

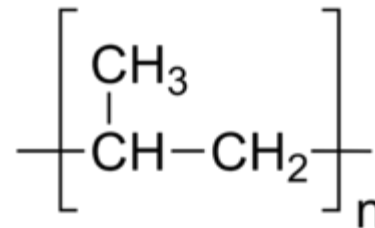
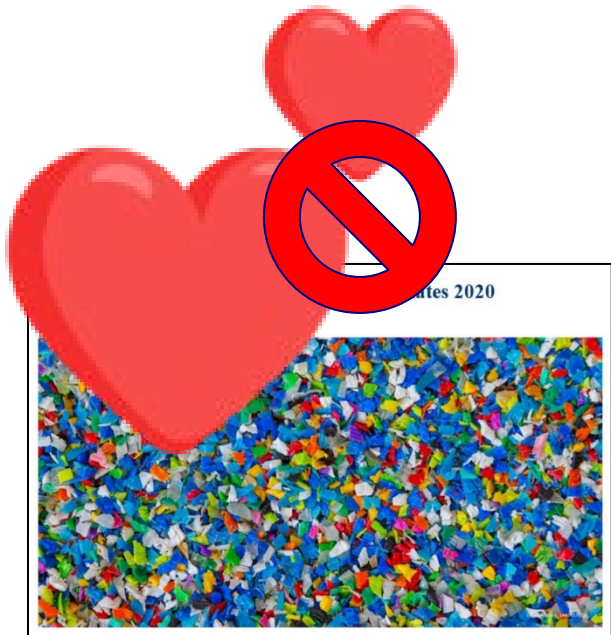
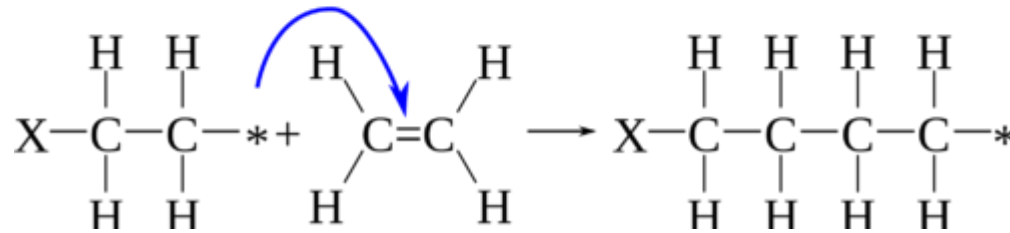
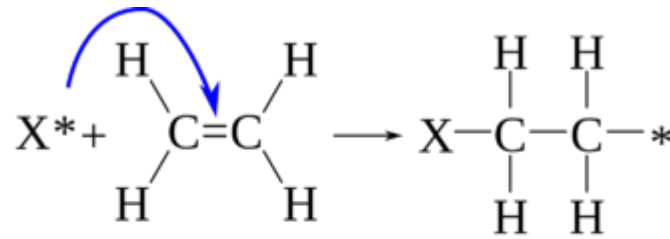
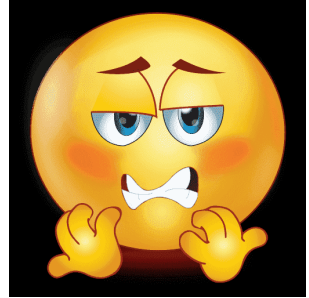


What!
You can't
just mix
everything
together?



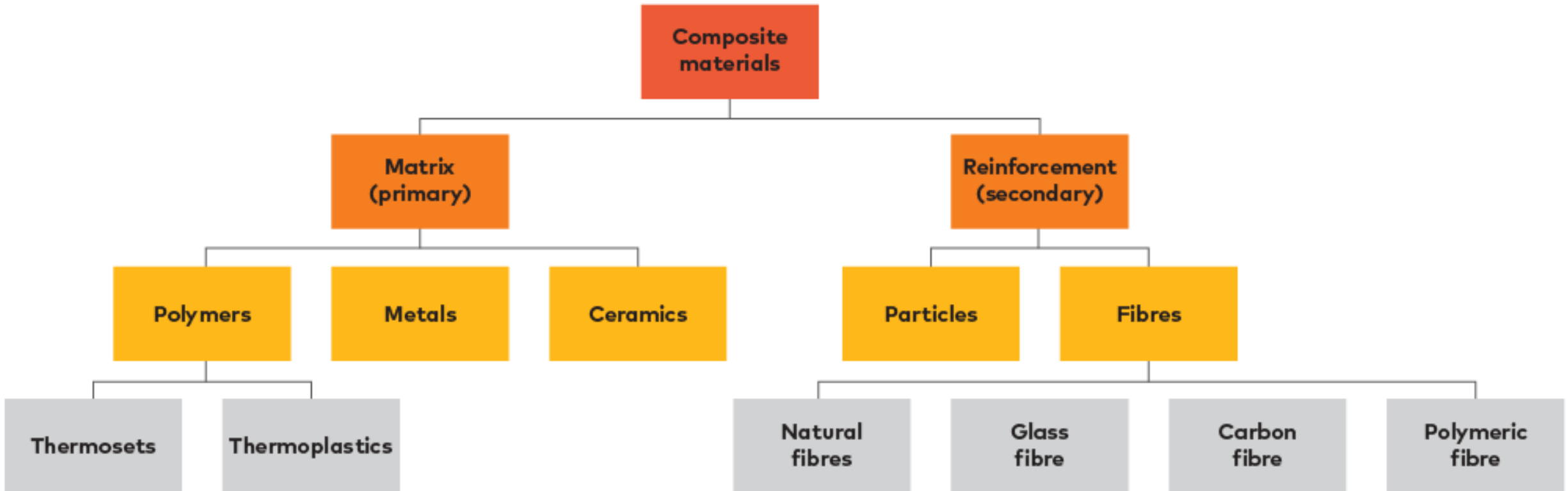
Plastics #1 to #7
are incompatible
with each other

HDPE & PP Are Incompatible



Many Materials in Recycled Polymer Composites Are Incompatible

Types of Composites Classified by Matrices and Reinforcements



RECYCLING is Complicated



In simple terms,

- **There's Advanced Recycling using depolymerization and chemical techniques such as pyrolysis to remake virgin-like recycled polymers with known properties.**

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- **There's Mechanical Recycling that relies on collecting, sorting, separating, cleaning, and size reduction of Post-Consumer**

Recycle to make a feedstock that is either baled, or granulated for making large parts such as furniture, or worked off at low percentages with virgin polymers.



RECYCLING is Complicated

In simple terms,

- There's Advanced Recycling using depolymerization and chemical techniques such as pyrolysis to remake virgin-like recycled polymers with known properties.
- There's Mechanical Recycling that relies on collecting, sorting, separating, cleaning, and size reduction of Post Consumer Recycle to make a feedstock that is

- There's Post-Industrial Mechanical Recycling that relies on large supplies of known materials employing maleated polymers or thermoplastic copolymers for compatibilization.

TPO Car Bumpers

RECYCLING is Complicated

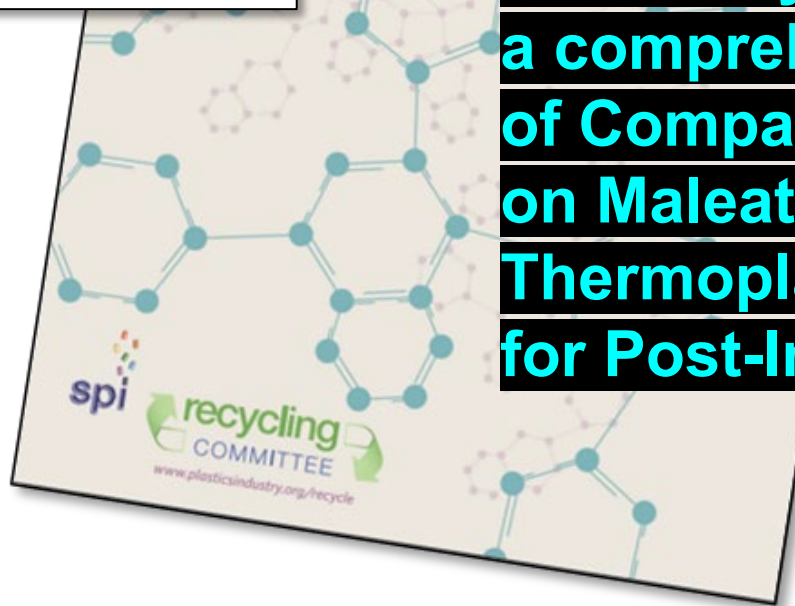
https://www.plasticsindustry.org/sites/default/files/Compatibilizers%20Whitepaper%20%28Version%201.0%29_0.pdf



TPO Car Bumpers



A PLASTICS Industry report dated May 2015 has a comprehensive listing of Compatibilizers based on Maleated Polymers & Thermoplastic Copolymers for Post-Industrial Recycle



RECYCLING is Complicated

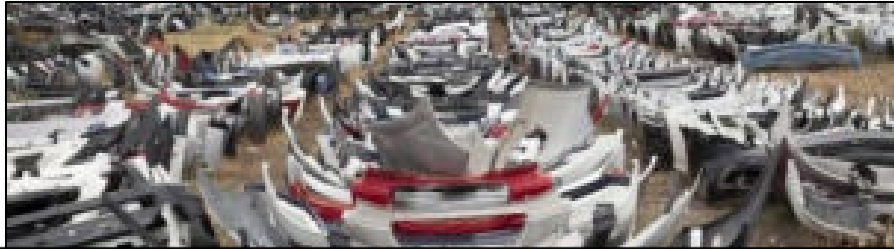
- There are many technical issues such as: intrinsic polymer incompatibility of addition polymers (olefins) and condensation (nylon, PC, PET) polymers; lower mechanical properties due to chain scissoring; negative impact property effects of uncoupled fillers; etc.



CHAIN SCISSORING DURING MELT PROCESSING
IS WHAT MAKES RECYCLE & REGRIND
WEAKER THAN VIRGIN



RECYCLING is made LESS Complicated

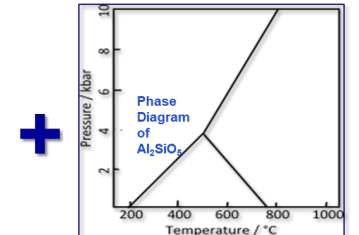
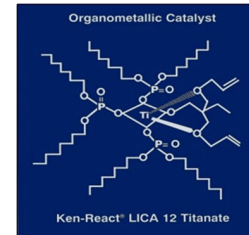


CHAIN SCISSORING DURING MELT PROCESSING IS WHAT MAKES RECYCLE & REGRIND WEAKER THAN VIRGIN



Monte offers Advanced Mechanical Recycling using titanium/aluminum chemistry of filler **COUPLING** and in situ polymer **CATALYSIS** in the polymer melt just as titanate catalysts are used to make Condensation polymers and the *Kaminski-Titanocene* and *Ziegler-Natta Ti-Al* catalysts used in the polymerization of Addition polymers.

Ti-Al pellet additive

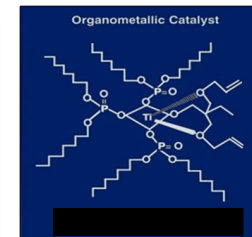


RECYCLING is made LESS Complicated

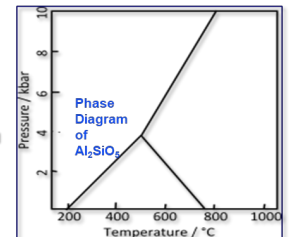


The rocket science reduces to adding the **Ti-Al pellet additive** at 1.50% to 1.75% by weight of all recycle materials and adjust mixing conditions such as 10% lowering of temps. to maintain reactive compounding shear.

Ti-Al pellet additive – Ken-React® CAPS® KPR® 12/LV



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RECYCLING is made LESS Complicated

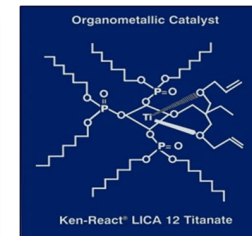
T-Al Catalyst

Synergistic with:

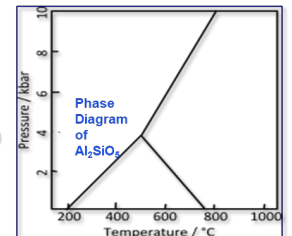
- Copolymer Compatibilizers
- Maleic anhydride-PP

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Ti-Al pellet additive – Ken-React® CAPS® KPR® 12/LV



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RECYCLING is made LESS Complicated

T-Al Catalyst Advantages

Synergistic with:

- Copolymer Compatibilizers

Use much less additive.

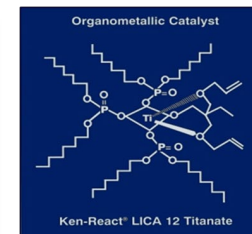
Less sorting.

- Maleic anhydride-PP

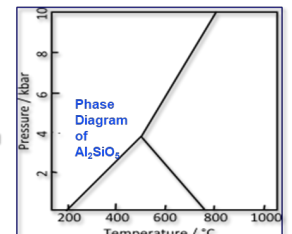
Does not Depolymerize PET

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Ti-Al pellet additive – Ken-React® CAPS® KPR® 12/LV



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RECYCLING is Complicated – GOOGLE tried to wrap its arms around it:

Google Report: “Closing the Plastics Circularity Gap”



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Google explores how to capture 4.5 billion tons of plastic

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RECYCLING is Complicated – GOOGLE tried to wrap its arms around it:

Google explores how to capture 4.5 billion tons of plastic

Published: August 18, 2021
Updated: August 18, 2021
by [Colin Staub](#)

Plastics Recycling

[in](#) [f](#) [t](#)

Google Report: “Closing the Plastics Circularity Gap” lays out a plan to increase plastics recovery to 58% over the next two decades:

- Mechanical (19%)
- Chemical (20%)
- A Virgin Plastic Production Tax (13%)
- Design & Inventory Management (5%)
- Consumer Education (1%)

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- Mechanical (19%) **Monte:** (19%) ***This Number Can Be Much Bigger!***
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Advanced Solutions Are in Titanium & Aluminum Chemistry

The Nobel Prize in
Chemistry 1963



Karl Ziegler
Prize share: 1/2

Giulio Natta
Prize share: 1/2



- If Ziegler, Natta & Kaminisky used **Titanium & Aluminum** catalysts to produce **Addition Polymers**;
- If **Titanate** catalysts are used to produce **Condensation Polymers**;
- If heteroatom **Titanate** coupling agents compatibilize **Fillers with Polymers**;
- Why not use **Titanate and Aluminum** as a catalyst and coupling agent for compatibilizing the **Fillers and Polymers** (both **Addition** and **Condensation**) used in the **Plastic** to be **Recycled**.



What if we used Ti & Al
as Catalysts to Recycle
more efficiently?

Advanced Solutions Are in Titanium & Aluminum Chemistry

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Prize share: 1/2

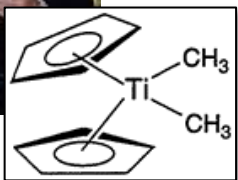
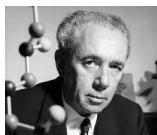


Giulio Natta
Prize share: 1/2

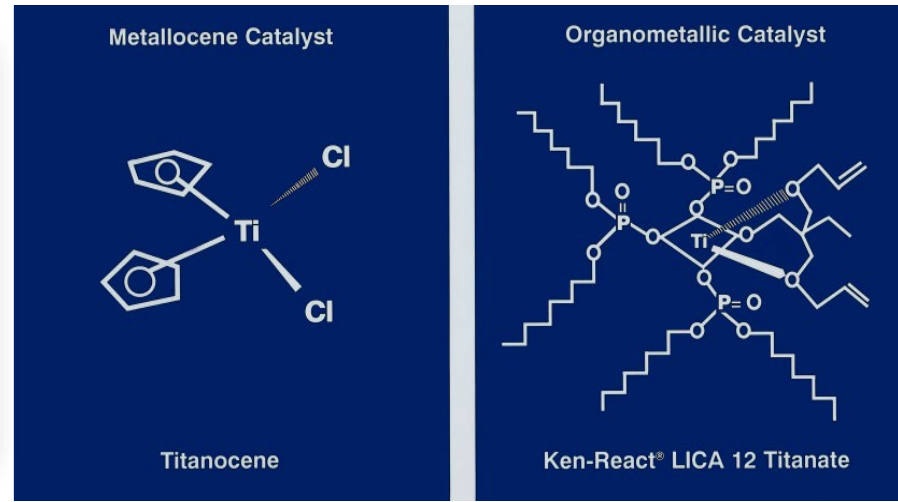
German Karl Ziegler, for his discovery of first titanium-based catalysts, and Italian Giulio Natta, for using them to prepare stereo regular polymers from propylene, were awarded the Nobel Prize in Chemistry in 1963.

Ziegler–Natta catalysts have been used in the commercial manufacture of various polyolefins since 1956.

- Ziegler showed a combination of TiCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ useful for the production of polyethylene.
- Natta used crystalline $\alpha\text{-TiCl}_3$ in combination with $\text{Al}(\text{C}_2\text{H}_5)_3$ to produce the first isotactic polypropylene.
- Kaminsky discovered that titanocene and related complexes emulated some aspects of these Ziegler-Natta catalysts but with low activity. He subsequently found that high activity could be achieved upon activation of these metallocenes with methylaluminoxane (MAO) $-\text{[O-Al(CH}_3\text{)]}_n$.

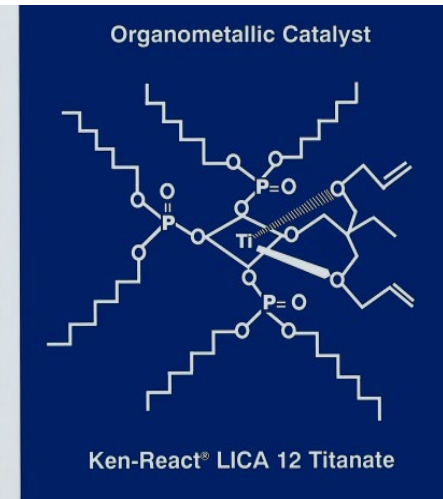
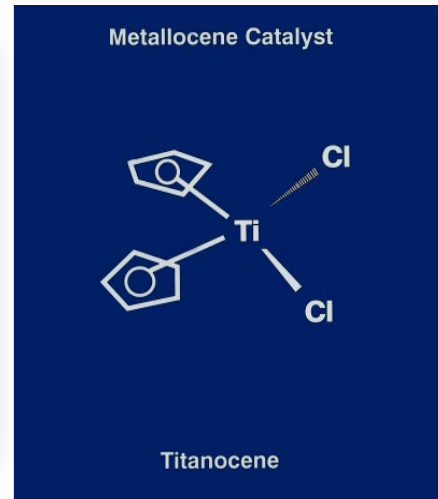


Titanium and Aluminum Additive Chemistry

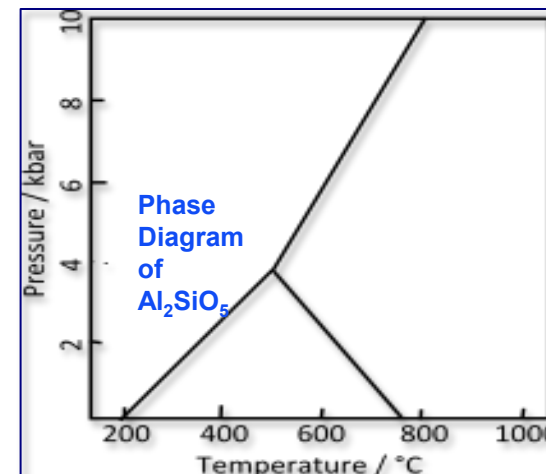
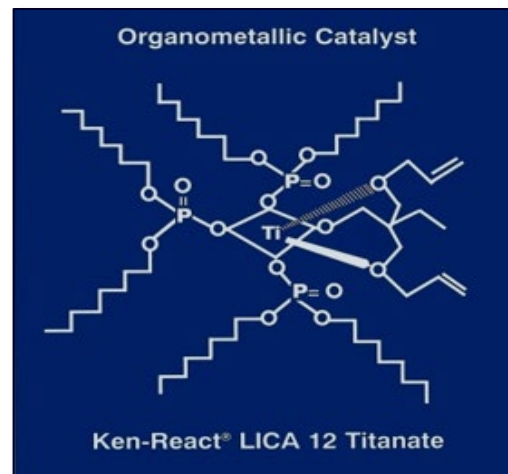


- Monte uses **Neoalkoxy Titanate** in combination with **Al₂SiO₅** mixed metal catalyst in Powder & Pellet forms for **In Situ Macromolecular Repolymerization and Copolymerization** in the melt – i.e. Polymer Compatibilization... AND ... The **Neoalkoxy Titanate** proton coordinates with inorganic fillers and organic particulates to couple/compatibilize the dissimilar interfaces at the nano-atomic level reducing the need for expensive sorting of materials in **Recycled Plastics**.

Kamininsky Titanocene – Monte Titanate



New Titanium and Aluminum Additive Chemistry

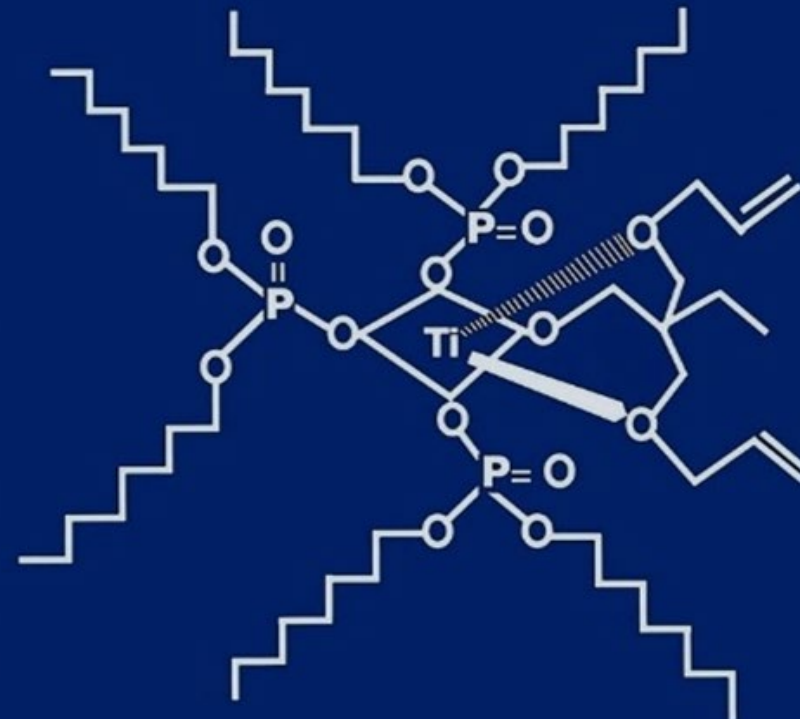


Introducing Titanium & Aluminum Additive Chemistry

This
is
The
Titanium
Catalyst
Portion



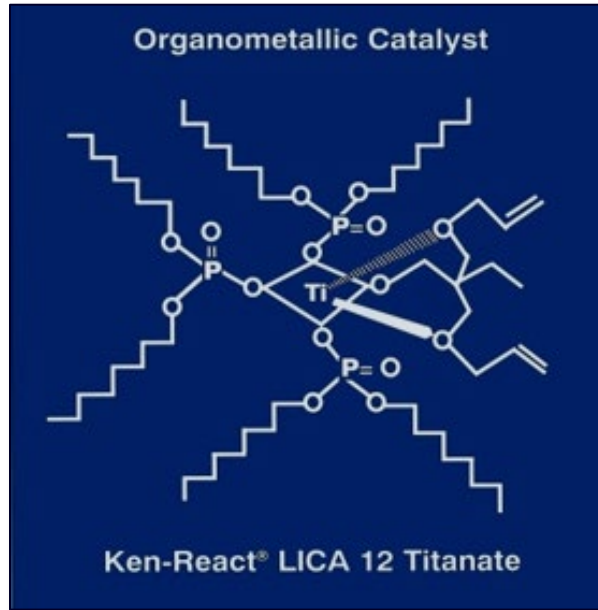
Organometallic Catalyst



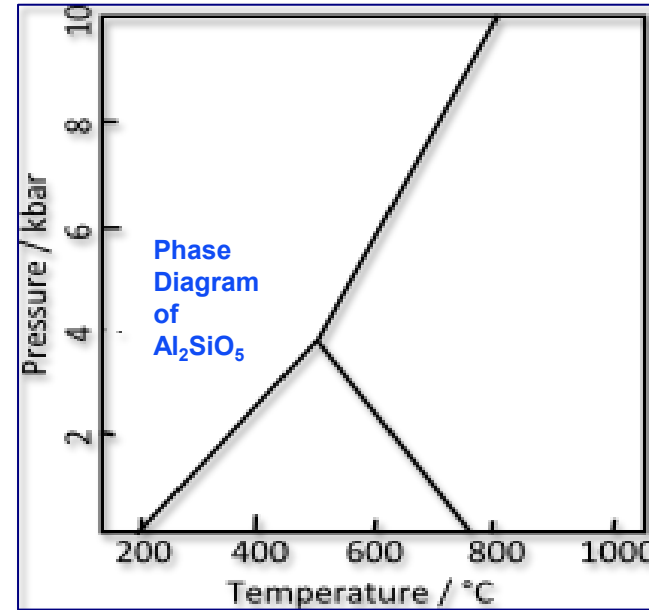
Titanate

Introducing Titanium & Aluminum Additive Chemistry

**This
is
The
Titanium
Catalyst
Portion**



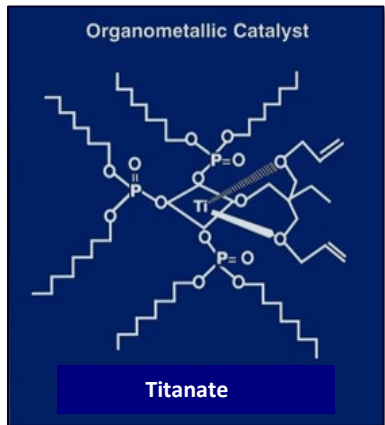
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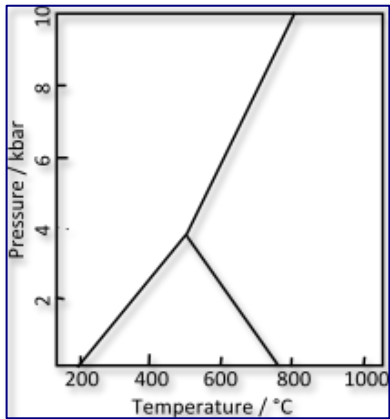
**This
is
The
Mixed
Metal
Catalyst
Portion**



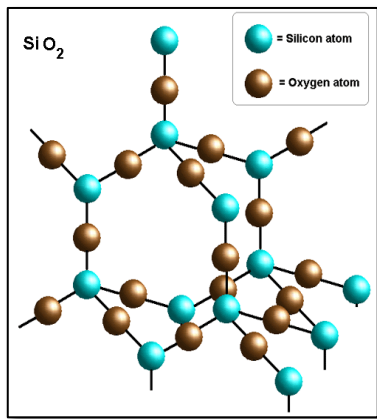
Ti/Al Additive



+



+



+



=



Ti/Al Additive



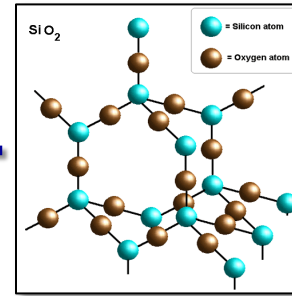
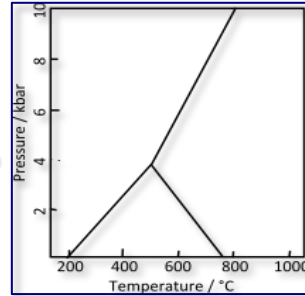
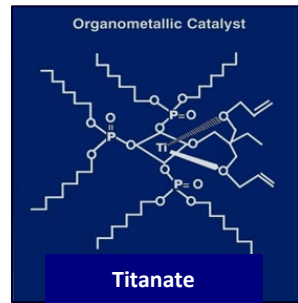
Ti/Al Additive

79% Active Catalyst Powder

Ti/Al Additive

39% Active Catalyst Pellet

**Advanced
Solution
Chemistry**

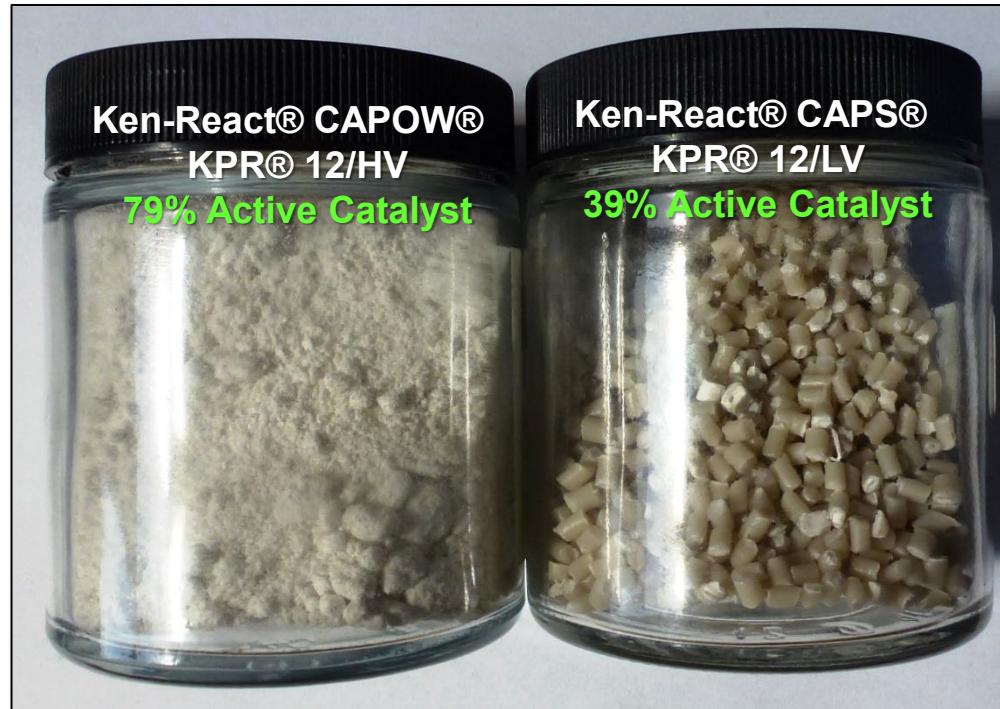


**Ti/Al
Additive**

Monte uses Ti/Al in powder/pellet form to recycle PVC/Polymer compounds in the extruder melt.

Titanium/Aluminum Filler Coupling & Polymer Catalysis Additive for Mechanical Recycling of Polymers #1 to #7

PDS		KENRICH PETROCHEMICALS, INC.	
P.O. Box 22, Bayonne, NJ 07002-0022 USA Tel: 201-423-9000 Fax: 201-423-0891 Email: kreact@kenrich.com Web Site: www.kenrich.com			
PRODUCT DATA SHEET			
Ken-React® CAPS® KPR® 12/LV - Coupling Agent Pellets			
COMPOSITION OF BLEND:	Ken-React® LICA® 12 (CAS # 110438-25-0)		
	Ken-React® N2® 01 (CAS # 110392-54-6)		
	Silicon Dioxide (CAS # 112926-00-8)		
	Pumice (CAS # 1332-09-8)		
	LLDPE (CAS # 25087-94-7)		
CHEMICAL DESCRIPTION: of Ken-React® LICA® 12:	neopentyl(dialkyl)oxy, tri(dioctylphosphato) titanate (Titanium IV 2,2 (bis (2-propenoate)oxy)butanolato phosphato-O)		
of Ken-React® N2® 01:	neopentyl(dialkyl)oxy, tri(neodecanoatyl)zirconate (Zirconium IV 2,2 (bis (2-propenoate)oxy)butanolato, tris neodecanoato-O)		
CHEMICAL STRUCTURE OF TITANATE and ZIRCONATE:			
TYPICAL PROPERTIES OF LIQUID PORTION:	Liquid		
Physical Form	Solid (in IPA Solvent), %		
Color - Descriptive	Red-Orange		
Gardner	4-8		
Viscosity, cps @ 25°C (77°F)	4000 - 8000		
Specific Gravity @ 25°C (69°F)	1.03 ± 0.01		
Flash Point, # (FCC)	>141		
Initial Boiling Point, #, ASTM	200		
pH (aqueous solution)	5.3		
Solubility	5% in xylene, toluene, mineral oil, DOP, DIDP, aromatic plasticizer, and MEK. 1% in Isopropyl alcohol. Insoluble in H ₂ O.		
KEN-REACT® CAPS® KPR® 12/LV PROPERTIES:	Physical Form Solid Pellet or Chip		
Activity	20% Ken-React® LICA® 12 Titanate		
Color, descriptive	Off white/beige Pellets		
PDS CAPS® KPR® 12/LV February 28, 2016			



SDS		KENRICH PETROCHEMICALS, INC.	
SAFETY DATA SHEET			
1. IDENTIFICATION			
Product identifier	Kenrich Petrochemicals, Inc. Safety Data Sheet according to OSHA Hazard Communication Standard, 2012 (29 CFR 1910.1200)		
Product code	PDS001/LLDPE		
Version	1.0		
Issue date	February 28, 2016		
Classification	Oxidizing, Irritant, Acute toxicity, Skin irritation		
Recommended use	Polymer additive, Functional Use Only		
Recommended use	Not for commercial use		
Manufacturer information	Kenrich Petrochemicals, Inc. One Center, LLC - 104 Center Lane Denville, NJ 07832 USA www.kenrich.com		
Emergency Telephone Number	Kenrich Petrochemicals, Inc. Tel: 201-423-9000 Chemical emergency number: Tel: 703-597-2888		
SDS number			
2. HAZARD IDENTIFICATION			
Physical hazards	This chemical is not considered hazardous according to the OSHA Hazard Communication Standard, 2012 (29 CFR 1910.1200).		
Health hazards	Not classified		
Environmental hazards	Not classified		
Label information	This product contains no substances which at their given concentration are considered to be hazardous to health.		
Disposal	Dispose of waste and residues in accordance with local authority requirements.		
3. COMPOSITION INFORMATION ON INGREDIENTS			
Chemical Name	CAS #	Weight %	Classification
Titanium IV 2,2 (bis (propenoate)oxy)butanolato, tris (dioctyl phosphato-O)	110438-25-0	>15	Acute oral toxicity category 3 Skin and eye irritation category 2
neopentyl(dialkyl)oxy, tri(neodecanoatyl)zirconate (Zirconium IV 2,2 (bis (2-propenoate)oxy)butanolato, tris neodecanoato-O)	110392-54-6	<5	Not Classified
neodecanoic acid	7617-26-9	>0	Not classified
Diethyl ether	109-87-3	>0	Not classified
Pumice	1132-09-8	>0	Not classified
4. FIRST AID MEASURES			
Measures	Safety implementation		
First aid procedures	Inhalation: Move to fresh air, until a physician of symptoms abatement or expires. Ingestion: Rinse mouth with water for at least 15 minutes. Get medical attention if irritation develops and persists. Skin: Wash with soap and water. Get medical attention if irritation develops and persists. Eye: Flush eyes thoroughly with water for at least 15 minutes. Get medical attention if irritation develops and persists. In case of oral exposure rinse mouth for at least 15 minutes. For chemical ingestion seek medical attention. Notes to physicians: Treat symptomatically. General advice: Get medical attention if any discomfort develops.		
KEN-REACT® CAPS® KPR® 12/LV February 28, 2016			



1961 to 2015
Products
made in
Bayonne, NJ



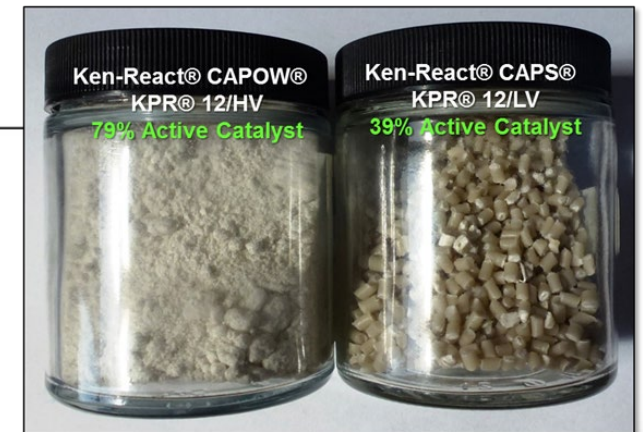
2015 to Now
Products
made in
Decatur &
Dayton, TN



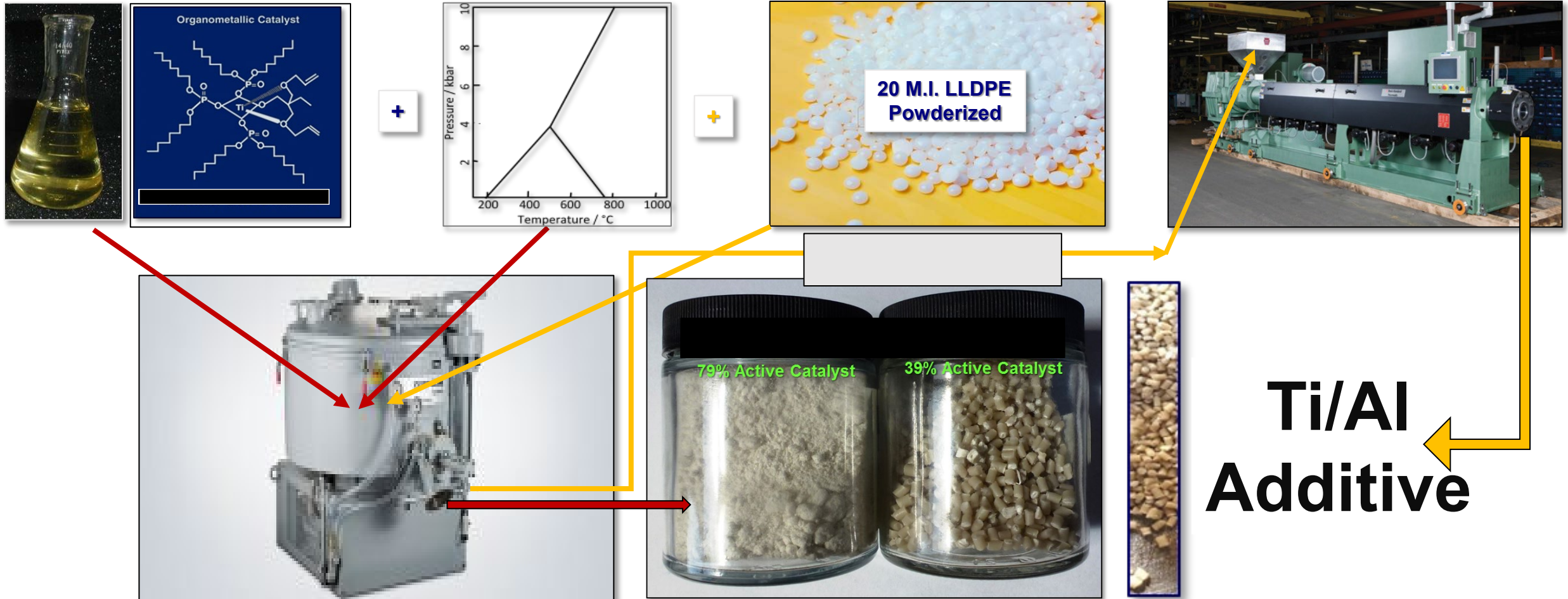
Cymer-Dayton Facility - 411 Manufactures Road, Dayton, TN



Cymer,LLC Decatur Facility – 124 Cymer Lane,Decatur, TN

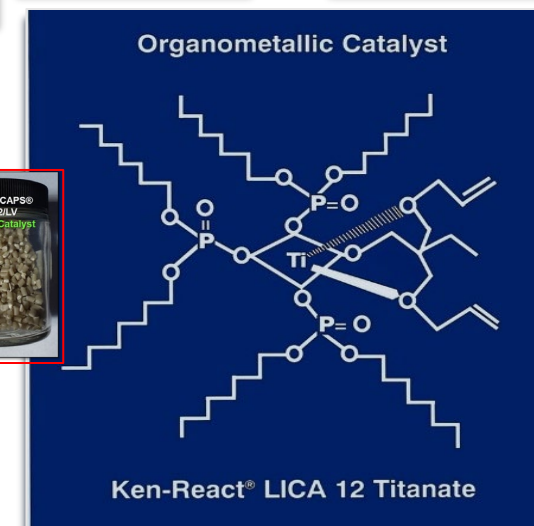
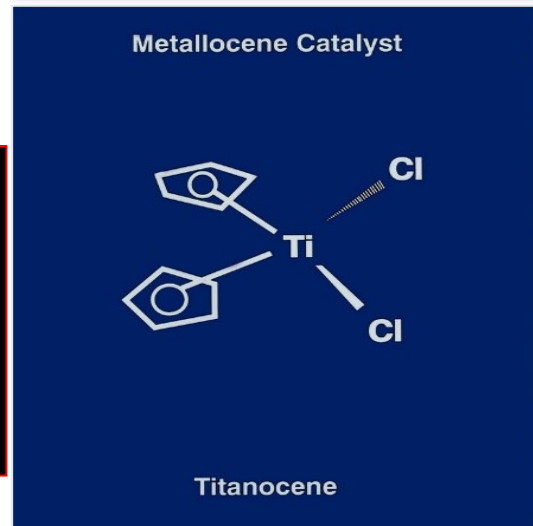
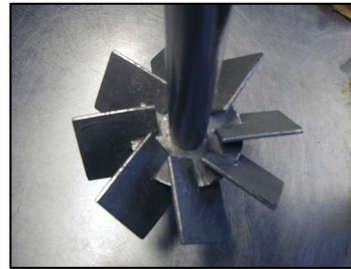
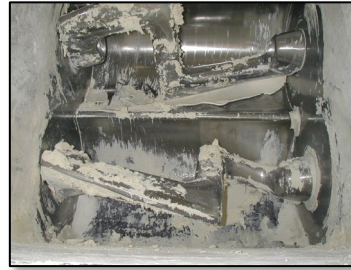
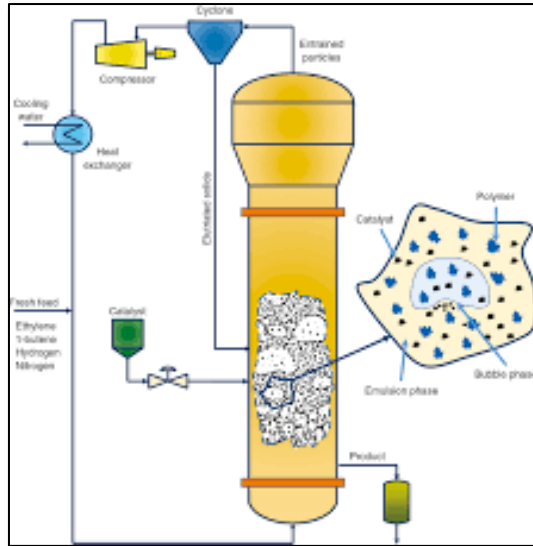


Pellet masterbatches of neoalkoxy titanate/mixed metal catalyst are added at the extruder hopper like a color concentrate – or Compounders use a powder masterbatch



Reactor Titanocene Polymerization – Ethylene Monomer

Extruder – 2-Arm – Planetary – Cowles Titanate Repolymerization – Polymers #1 to #7



**Titanocene:
Monomer
to
Polymer**

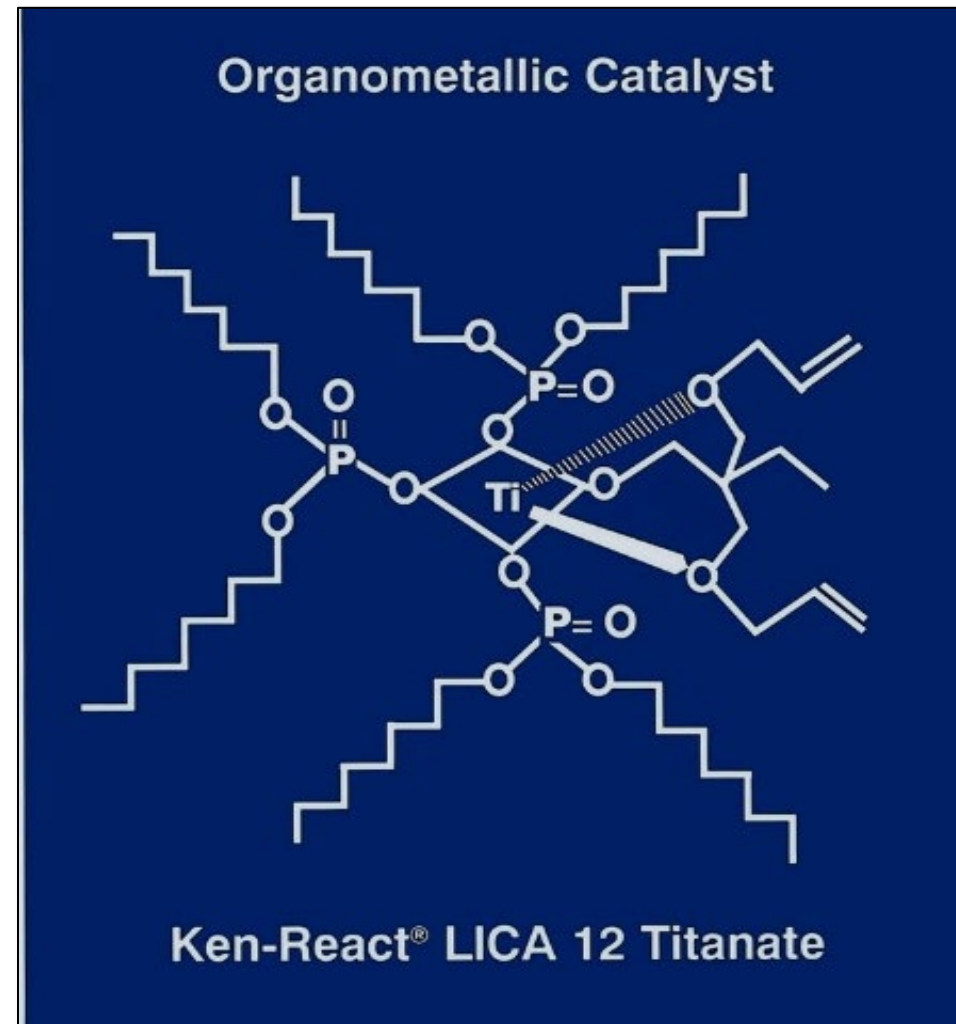
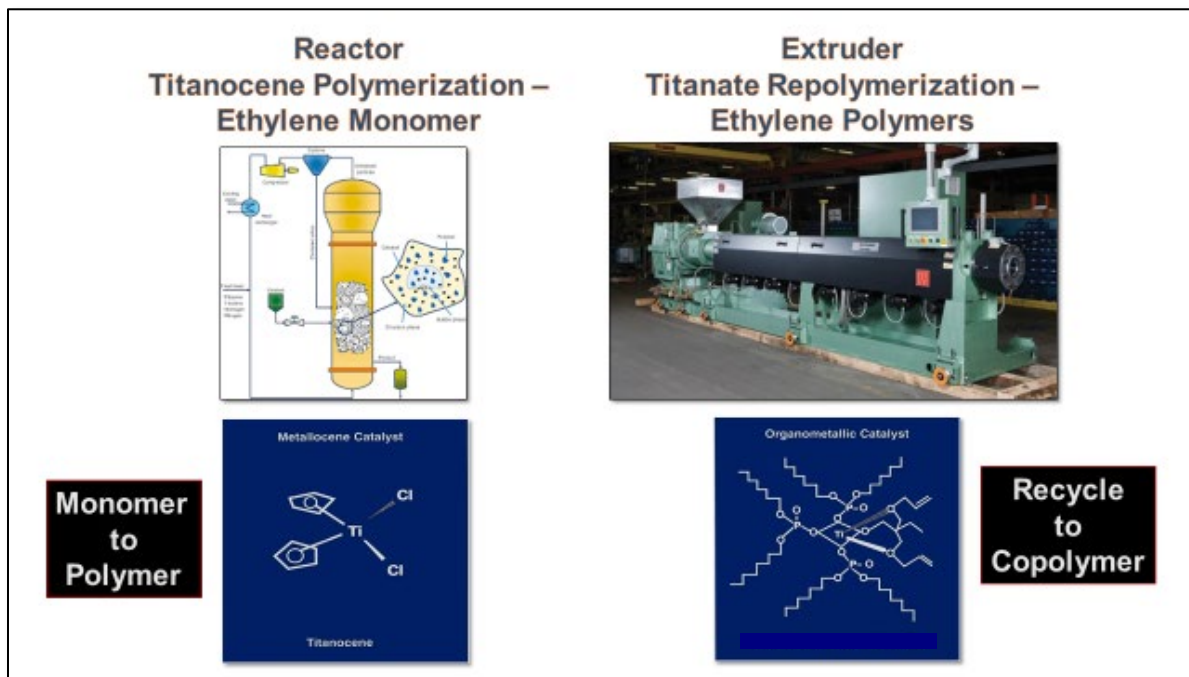
**Titanate:
Recycle
to
Re-Polymer**



50-Year Evolution of Subject Ti-Al Nano-Technology



SIX FUNCTIONS



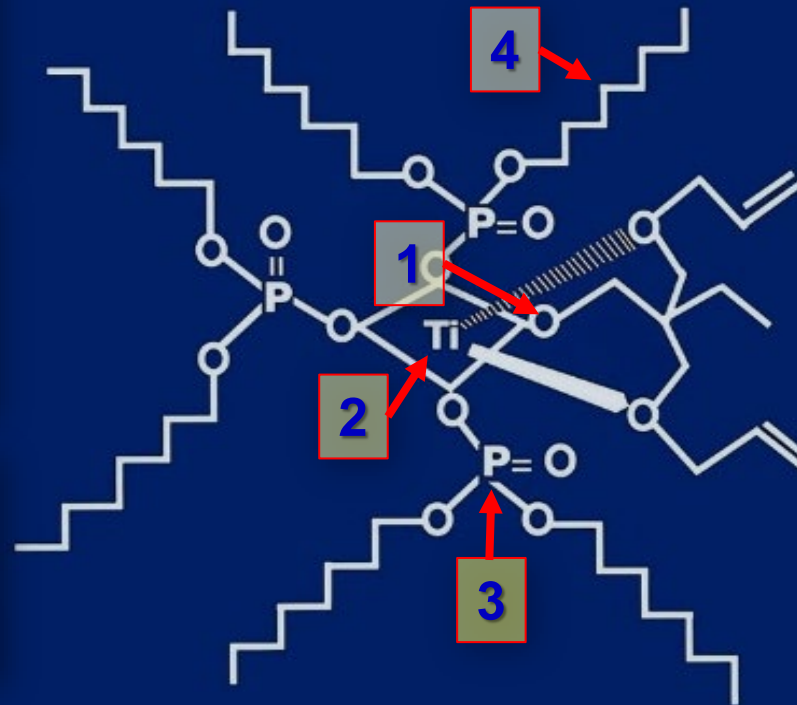
SIX FUNCTIONS

**Function 1 –
Coupling**

**Function 2 –
Catalysis**

**Function 3 -
Phosphatization**

Organometallic Catalyst



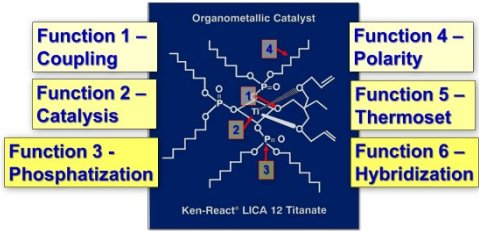
**Function 4 –
Polarity**

**Function 5 –
Thermoset**

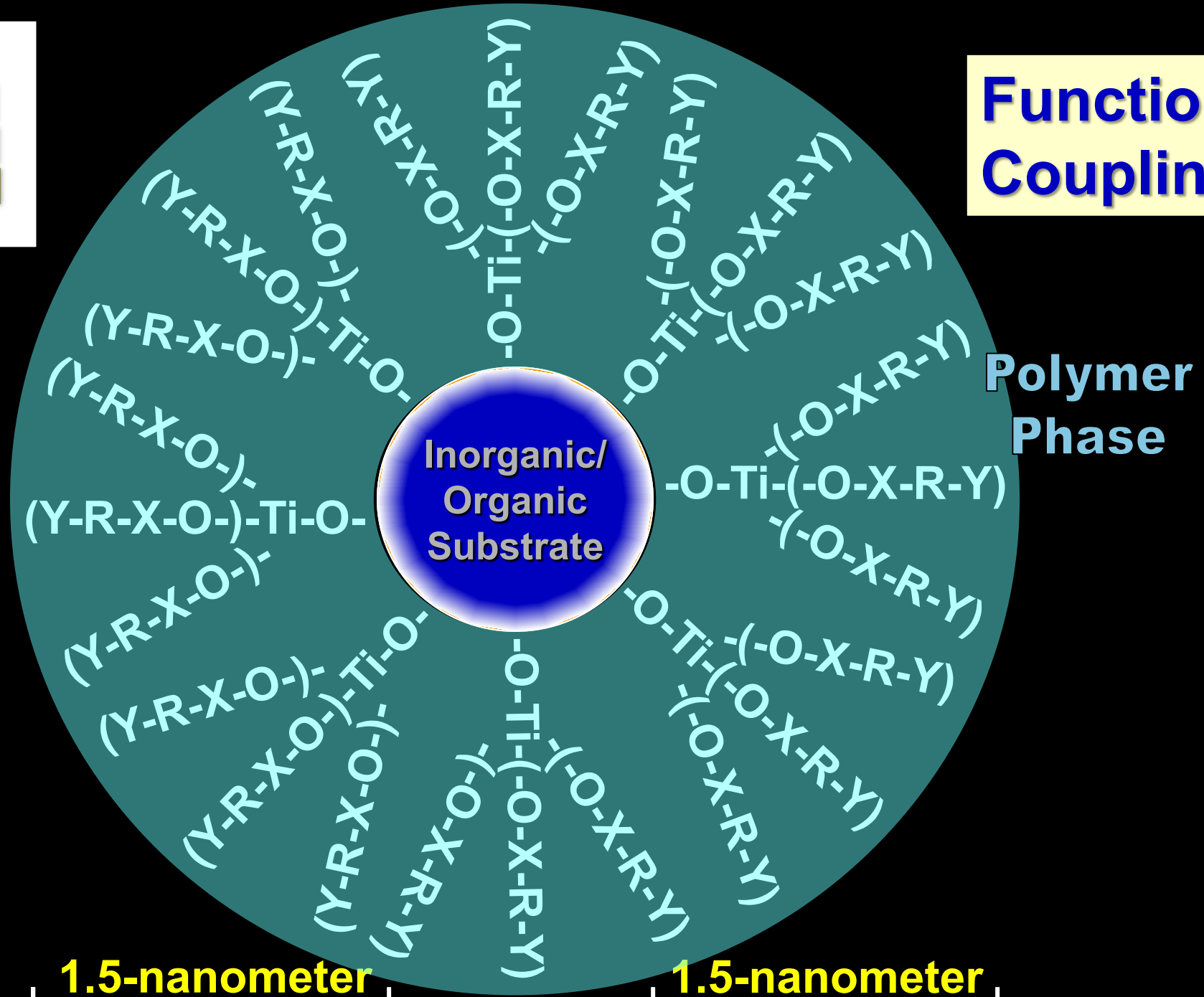
**Function 6 –
Hybridization**

Ken-React® LICA 12 Titanate

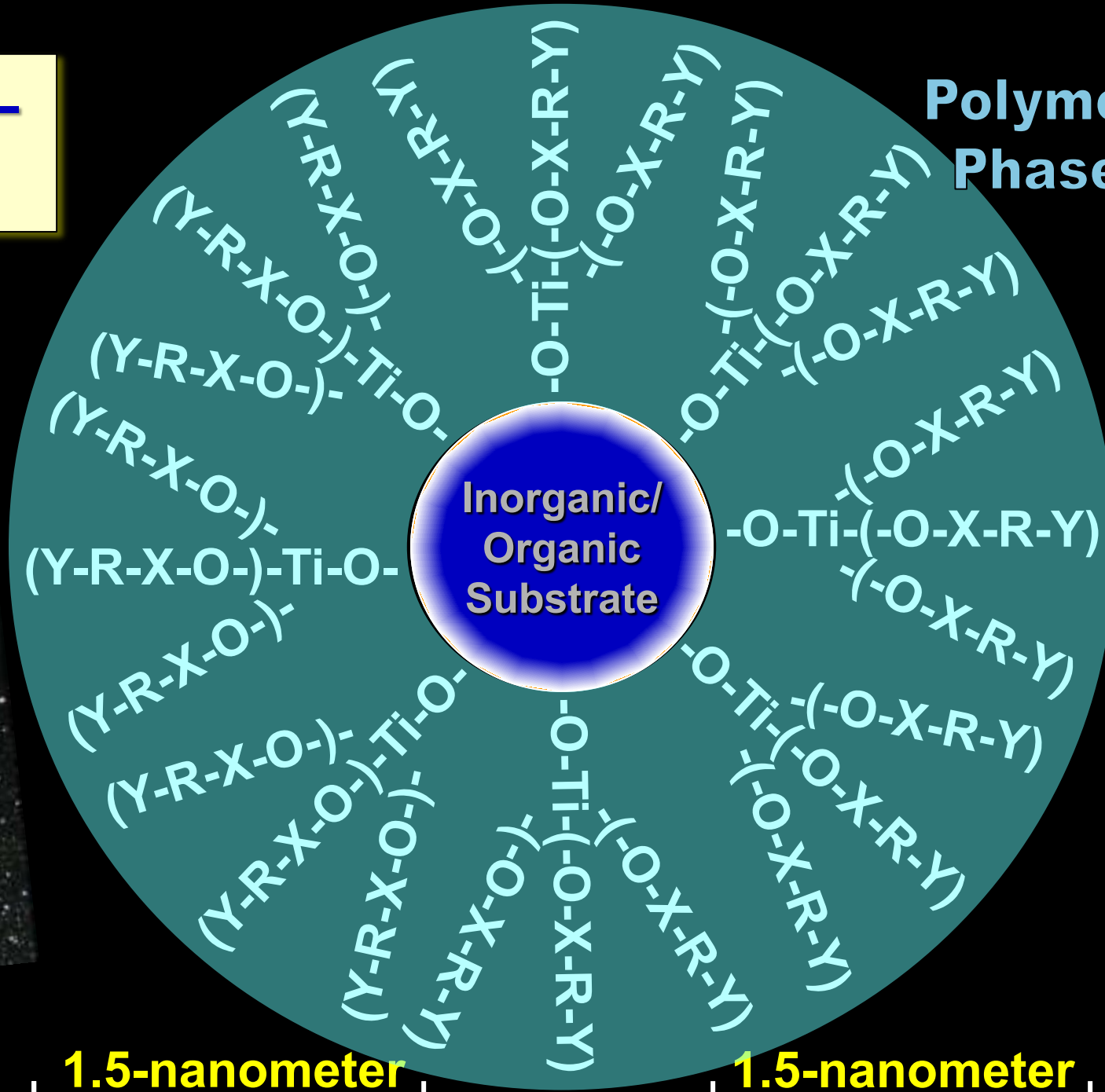
SIX FUNCTIONS



Function 1 – Coupling



Function 1 – Coupling



Polymer
Phase Recycled
Compounds
Contain A
Mixed
Bag of
Polymers
&
Inorganic
and
Organic
Materials

1.5-nanometer

1.5-nanometer



PETE



HDPE



V



LDPE



PP



PS



OTHER



**Recycled
Compounds
Contain A
Mixed
Bag of
Polymers
&
Inorganic
and
Organic
Materials**



PETE



HDPE



V



LDPE



PP



PS



OTHER

32ND ANNUAL VINYL COMPOUNDERS
CONFERENCE & THE VINYL
SUSTAINABILITY SUMMIT
December 16-18, 2022
Marriott Marquis Washington DC, The Wharf

with Titanate Catalysts/Coupling Agents ...
INORGANIC & ORGANIC PIGMENTS,
METAL OXIDES, METAL CARBONATES,
MINERAL FILLERS, CARBON BLACK, etc.
ARE NOT CONTAMINANTS
IN PLASTIC RECYCLE

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Recycled
Compounds
Contain A
Mixed
Bag of
Polymers
&
Inorganic
and
Organic
Materials



Recycle Mix: Polymers #1 to #7 & Fillers, Fibers, Pigments, etc.



PE & PP are ADDITION POLYMERS
PET is a CONDENSATION POLYMER

Incompatibility PE & PP

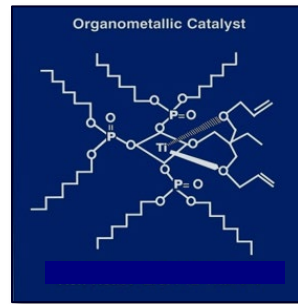


Incompatibility PET & PE

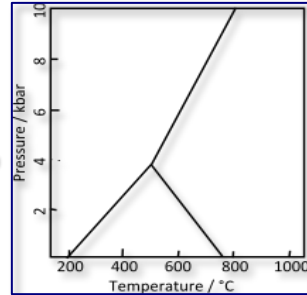


THE FILLER INTERFACE – Function 1 COUPLING

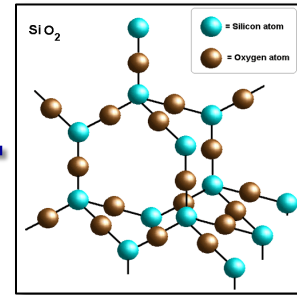
Advanced
Solution
Chemistry



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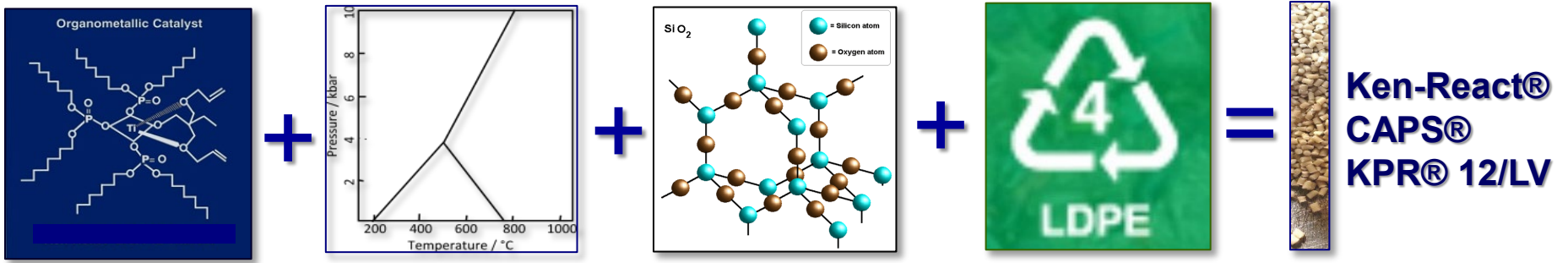


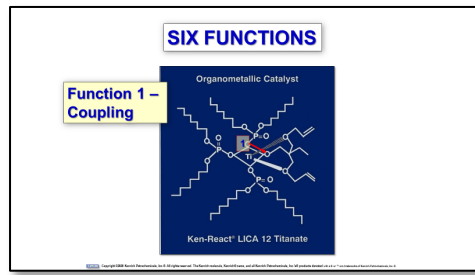
Ken-React®
CAPS®
KPR® 12/LV



THE POLYMER INTERFACE – Function 2 CATALYSIS

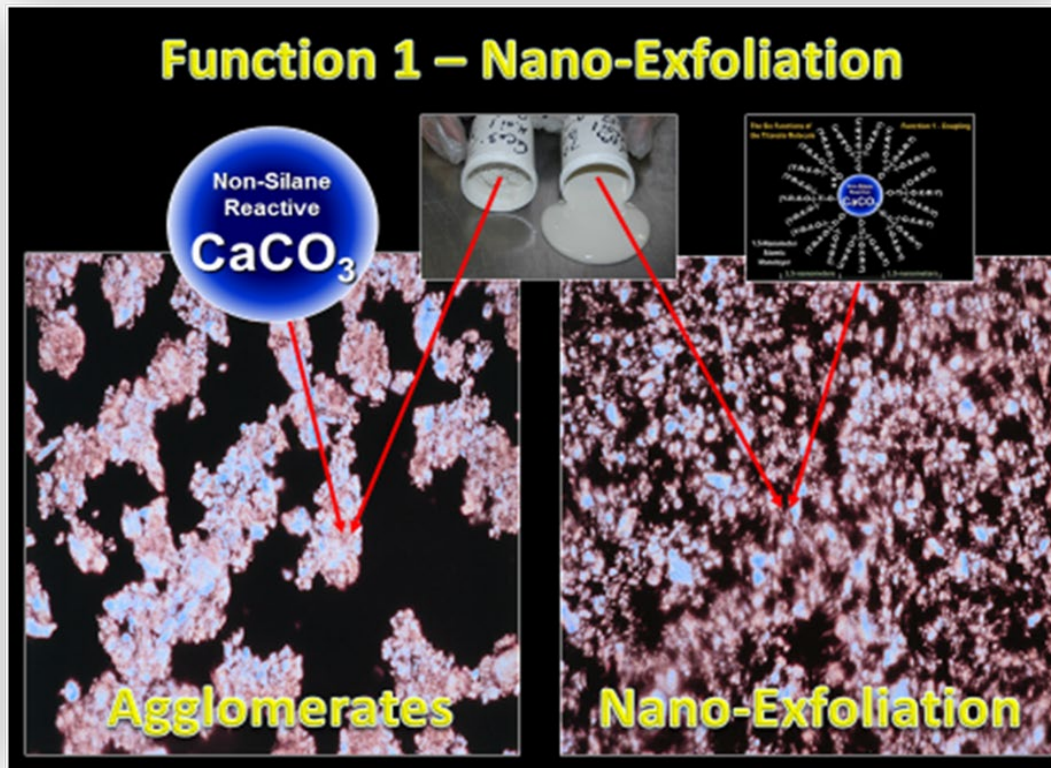
Advanced
Solution
Chemistry

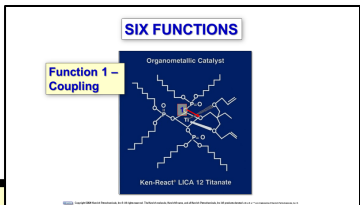




THE FILLER INTERFACE

(1) Couple *in situ* via proton coordination to all fillers, pigments and organics– from CaCO₃ to Carbon to AZO:





**Function 1 Coupling: NO HYDROLYSIS – NO WATER needed –
COUPLES IN THE MELT: Enables the Extruder as a Polymerization
Reactor for Organometallic Coupling & Catalyzing Recycled Polymers**



**Unlike Silanes
– Titanates
Couple to **ALL**
Inorganics &
Organics in
Nano-Atomic
Monolayers**

**Fillers &
Organics are
no longer
contaminants
to be sorted
out before
recycle.**

Sustainable



CaCO₃ is added to the recycled PET fiber for carpet wearability/heft

**Only 2% of
PET Carpet
Fiber Is
Recycled Due
To CaCO₃**



Unsustainable



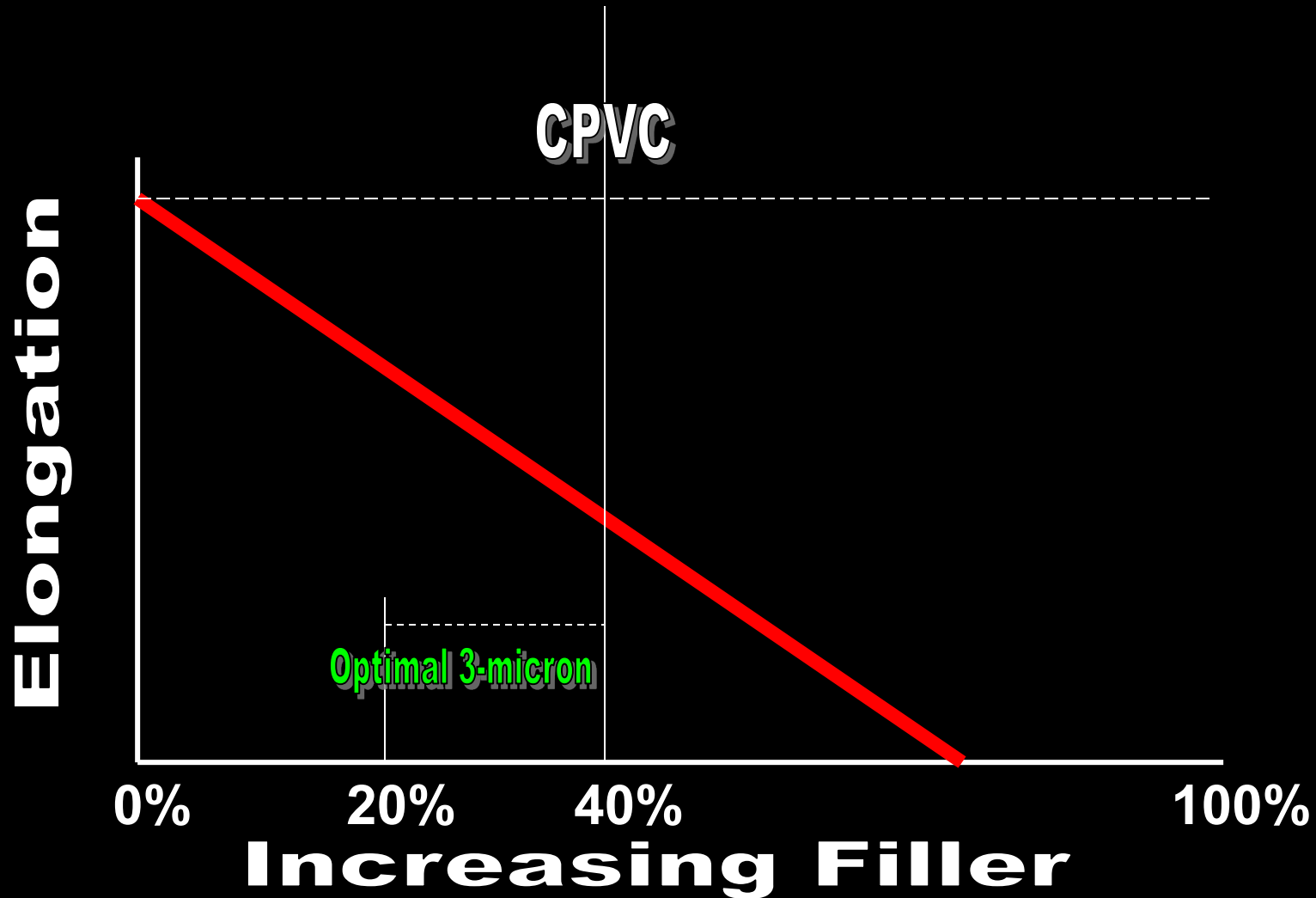
**A Silane Recycle Mindset:
Most fillers are contaminants**



**Not True with Titanates:
Fillers such as BaSO₄
are not contaminants**

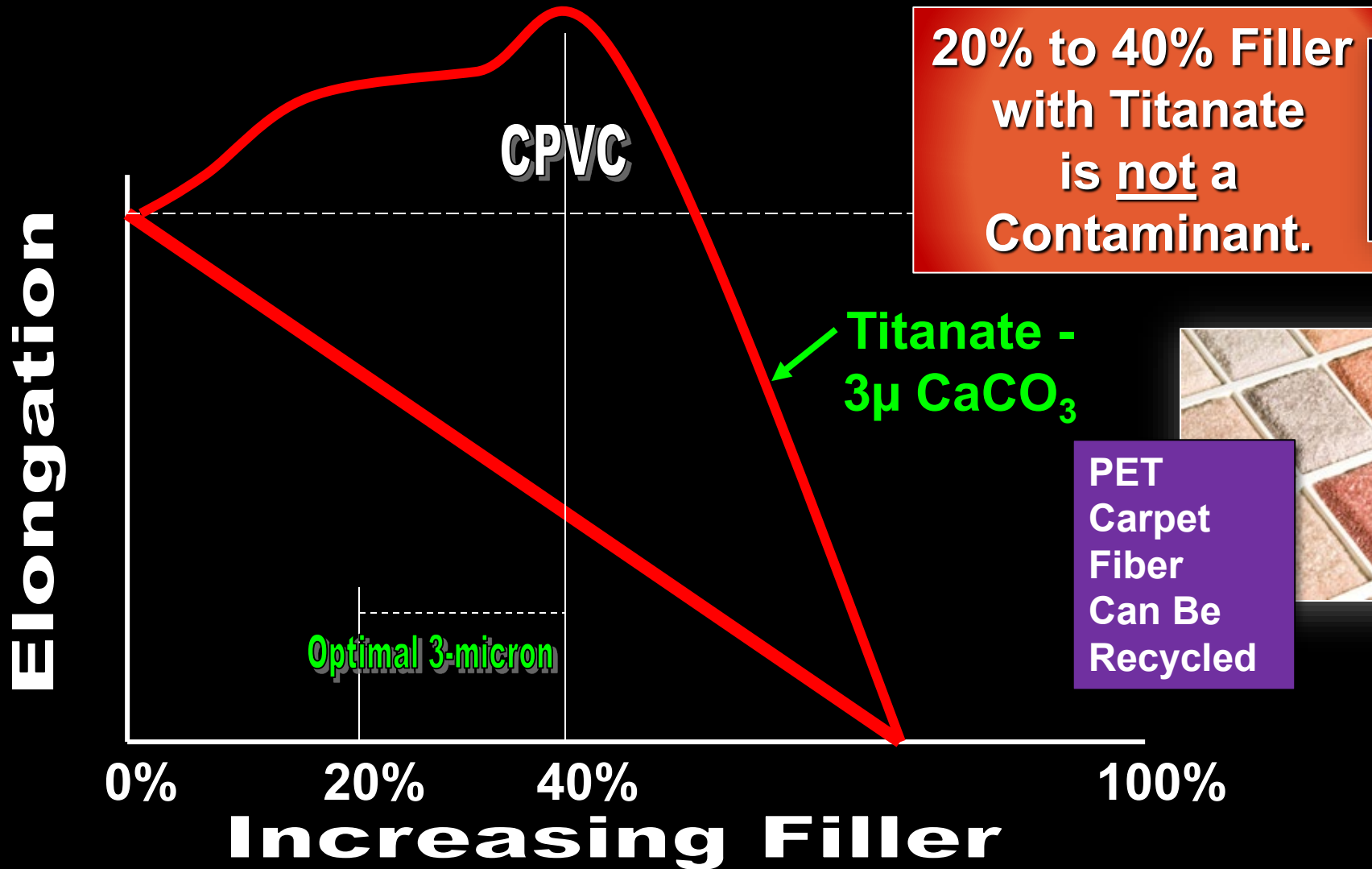
TITANATE Function 1 Coupling & Function 2 Catalysis

Elongation - Shift in Critical Pigment Volume Concentration Point



TITANATE Function 1 Coupling & Function 2 Catalysis

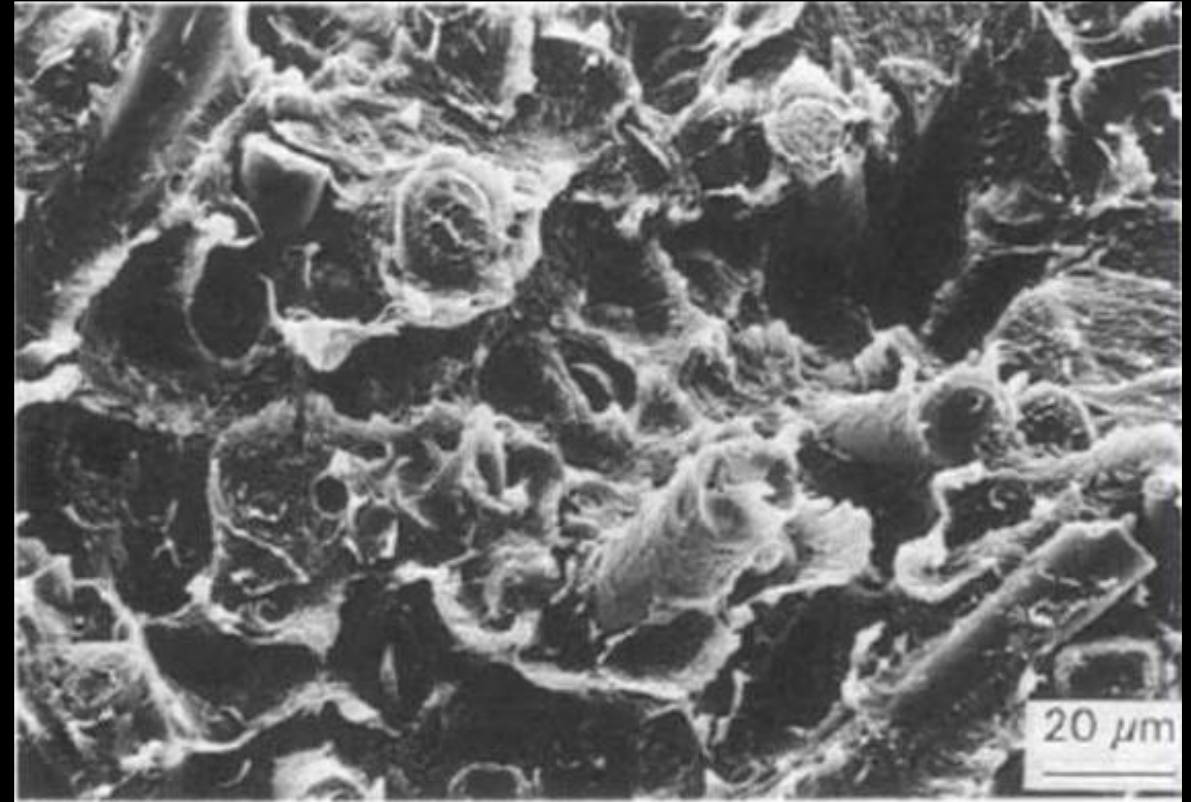
Elongation - Shift in Critical Pigment Volume Concentration Point



Titanates and Zirconates – They Are Different Than Silanes

E-Glass Fiber/ETFE (Ethylene TetraFluoroEthylene)

ETFE (think Teflon®) is extremely non-polar



**No Zirconate: Silane Sized E-Glass
Fiber/ETFE (Ethylene TetraFluoroEthylene)**

**With Zirconate: Silane Sized E-Glass
Fiber/ETFE (Ethylene TetraFluoroEthylene)**

Silane Effectiveness on Inorganics

SUBSTRATES

EXCELLENT


GOOD

SLIGHT

POOR

Silica
Quartz
Glass
Aluminum (AlO(OH))
Alumino-silicates (e.g. clays)
Silicon
Copper
Tin (SnO)
Talc
Inorganic Oxides (e.g. Fe₂O₃, TiO₂, Cr₂O₃)
Steel, Iron
Asbestos
Nickel
Zinc
Lead
Marble, Chalk (CaCO₃)
Gypsum (CaSO₄)
Barytes (BaSO₄)
Graphite
Carbon Black

A Silane Recycle Mindset: Most fillers are contaminants



Not True with Titanates: Fillers such as BaSO₄ are not contaminants

Silane Effectiveness on Inorganics

	SUBSTRATES
EXCELLENT ↑ GOOD ↑ SLIGHT ↑ POOR	Silica
	Quartz
	Glass
	Aluminum (AlO(OH))
	Alumino-silicates (e.g. clays)
	Silicon
	Copper
	Tin (SnO)
	Talc
	Inorganic Oxides (e.g. Fe ₂ O ₃ , TiO ₂ , Cr ₂ O ₃)
	Steel, Iron
	Asbestos
	Nickel
	Zinc
Lead	
SLIGHT ↑ POOR	Marble, Chalk (CaCO ₃)
	Gypsum (CaSO ₄)
	Barytes (BaSO ₄)
	Graphite
	Carbon Black

A Silane Recycle Mindset: Most fillers are contaminants



Not True with Titanates:
Fillers such as BaSO₄
are not contaminants

mineral surface. Silane coupling agents do not exclude water from the interface, but somehow function to retain adhesion in the presence of water.

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.¹² 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 ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$), titanium dioxide, and zinc oxide. Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron.

talc, wollastonite, iron powder, clay, and hydrated aluminum oxide. Only slight improvement was imparted to asbestine, hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$), titanium dioxide, and zinc oxide. Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron.

Although coupling activity of silanes is not universal to all mineral surfaces, response is broad enough to indicate that silanols need not form water-resistant "oxane" bonds with the surface. Even covalent siloxane bonds are hydrolyzed to silanols by water with an activation energy of 23.6 kcal/mol. Hydrolysis catalyzed by benzoic acid has an activation energy of 6 kcal/mol, which is comparable to the strength of a hydrogen bond. Compression set of silicone rubber has been attributed to a stress relaxation involving hydrolytic breaking and remaking of siloxane bonds



“... Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron.”

One Nanometer = 10 Carbons = c - c - c - c - c - c - c - c - c

- 0.5% Titanate
- Disperse in M.O.
- Stir in CaCO₃



mineral surface. Silane coupling agents do not exclude water from the interface, but somehow function to retain adhesion in the presence of water.

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.¹² 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 ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$), titanium dioxide, and zinc oxide. Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron.

ections or microcracks in differential shrinkage would be interface. Once water are capable of hydrolyzing en resin and glass or other id⁷ that glass treated with absorb a molecular layer study of the water resistance ult¹⁰ found no correlation ention of epoxy laminates

turing polymerization has produce intimate contact O-C bond is readily hydro- stance to the composite. ncluded that water cannot and a hydrophilic mineral vary with the nature of the t exclude water from the on in the presence of water.

upling agents form oxane I = Si, Ti, Al, Fe, etc. It is outstanding water resistance on and iron or aluminum, mechanical properties of tion of appropriate silane s.¹² Greatest improvement in carbide, and aluminum onse was observed with

talc, wollastonite, iron powder, clay, and hydrated aluminum oxide. Only slight improvement was imparted to asbestine, hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$), titanium dioxide, and zinc oxide. Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron.

Although coupling activity of silanes is not universal to all mineral surfaces, response is broad enough to indicate that silanols need not form water-resistant "oxane" bonds with the surface. Even covalent siloxane bonds are hydrolyzed to silanols by water with an activation energy of 23.6 kcal/mol. Hydrolysis catalyzed by benzoic acid has an activation energy of 6 kcal/mol, which is comparable to the strength of a hydrogen bond. Compression set of silicone rubber has been attributed to a stress relaxation involving hydrogen bonding and remaking of siloxane bonds

Silane Coupling Agents

Edwin P. Pluedde

“... Only slight improvement was imparted to asbestine, hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$], titanium dioxide and zinc oxide.”



TiO₂

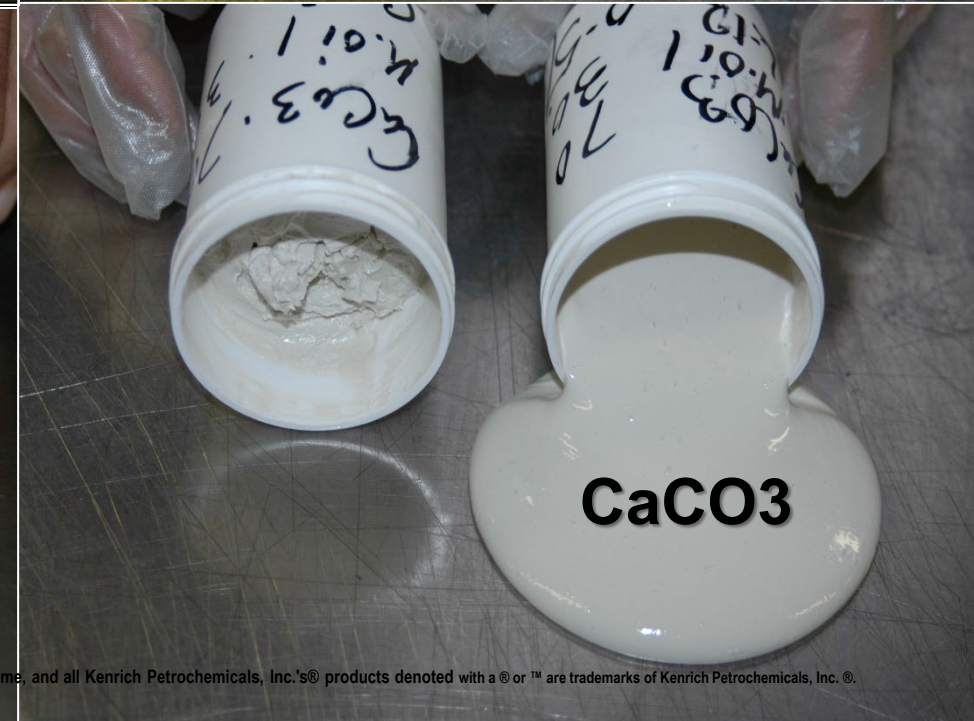


BaSO₄

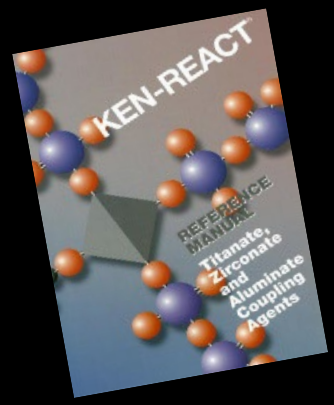
**“Silanes”-Plueddemann:
“... Only slight
improvement was
imparted ...
titanium dioxide and zinc
oxide.”**



ZnO

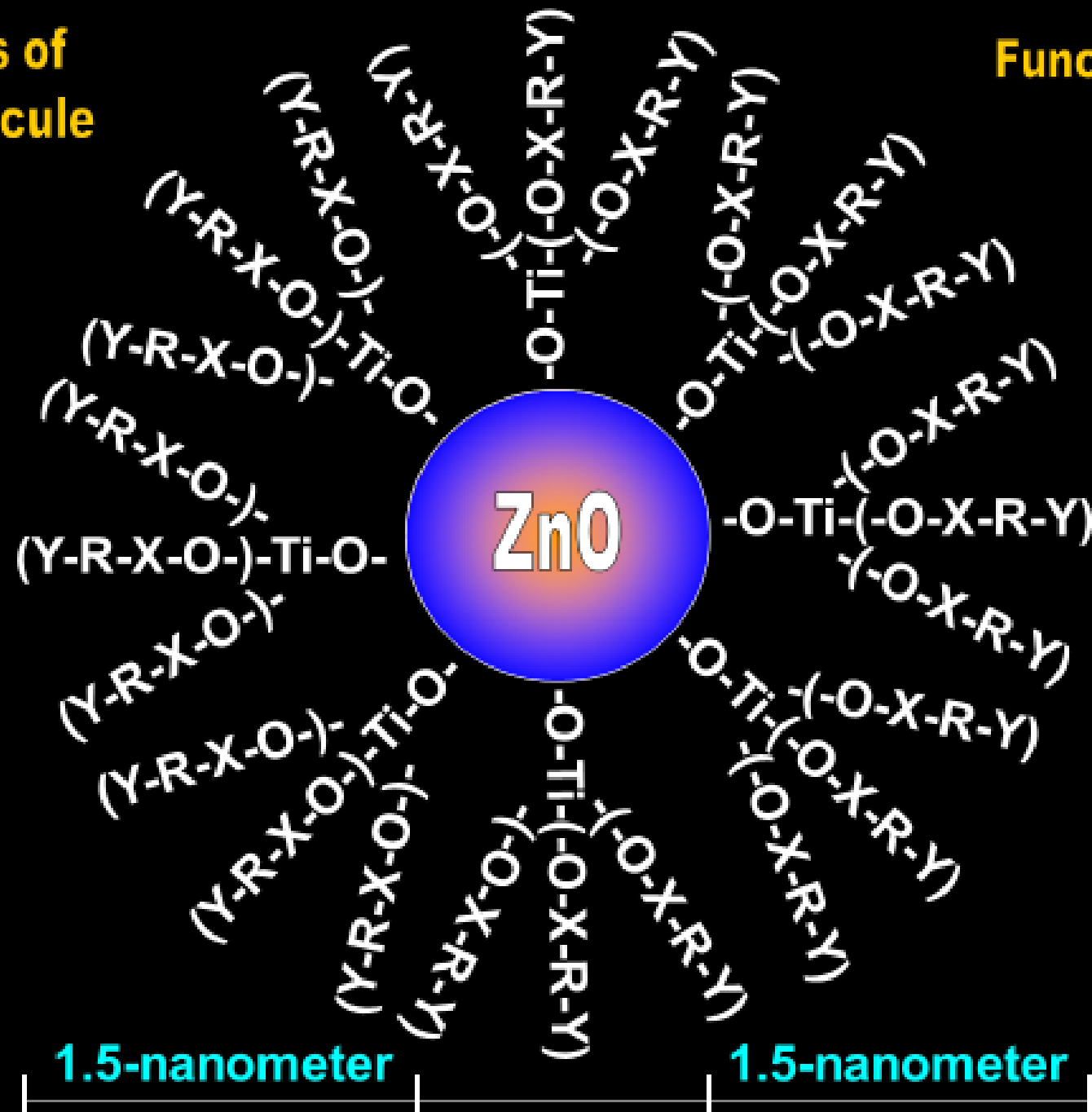


CaCO₃



The Six Functions of the Titanate Molecule

Function 1 - Coupling



1.5-Nanometer
Atomic
Monolayer

1.5-nanometer

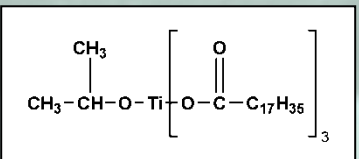
1.5-nanometer



1,600,000 cps

55% ZnO
Dispersed
In Mineral
Oil

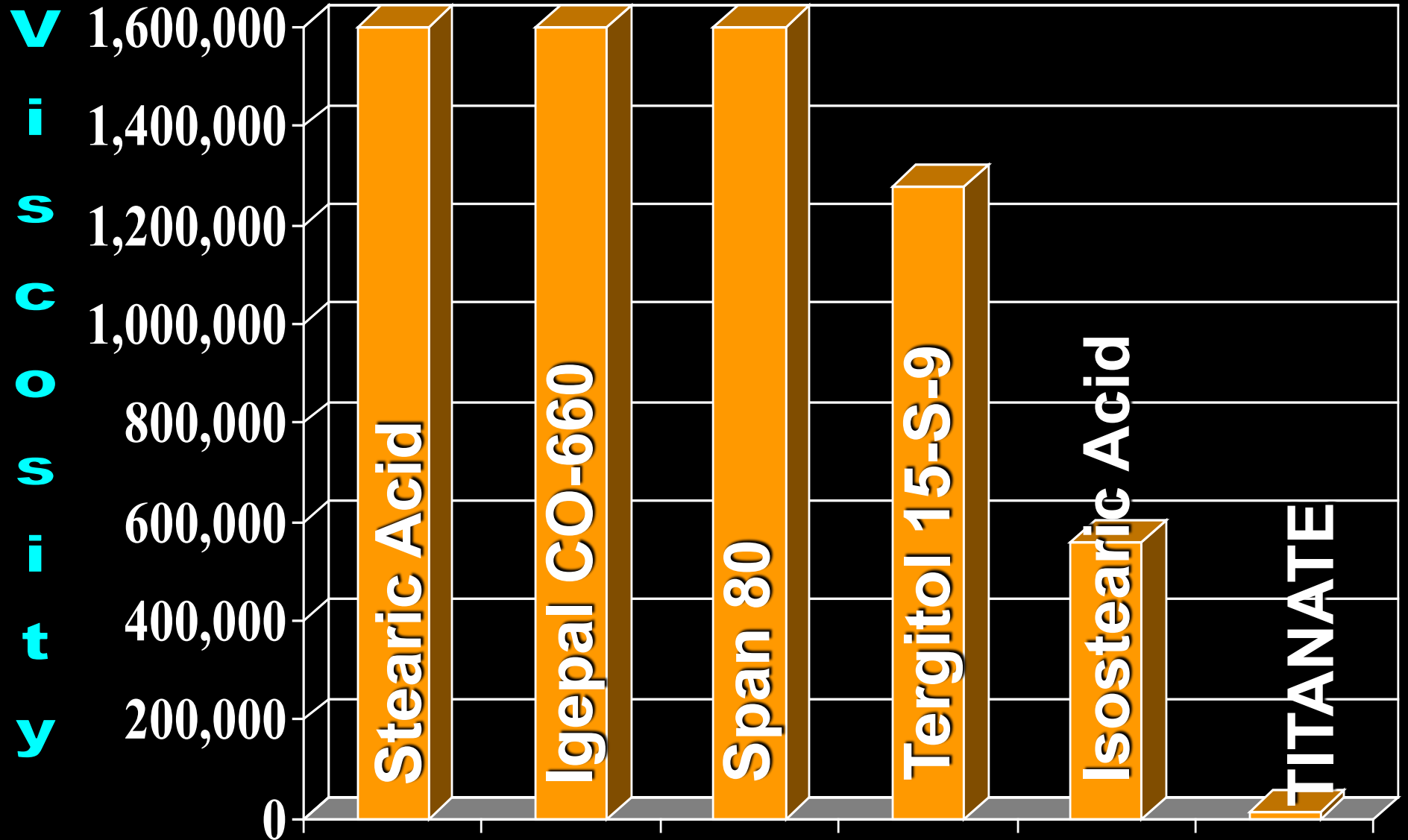
CONTROL



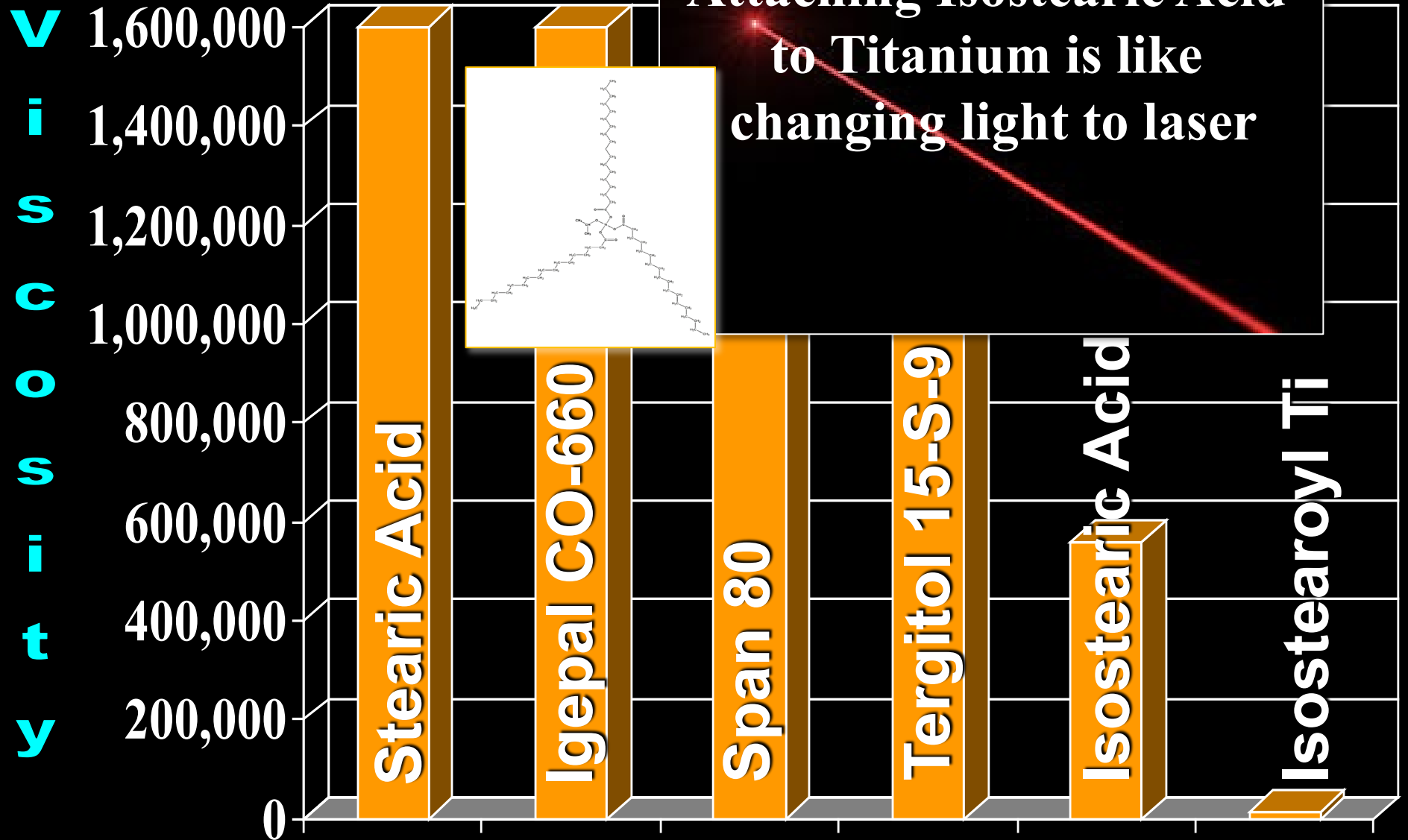
12,800 cps

0.5 wt. %
TITANATE

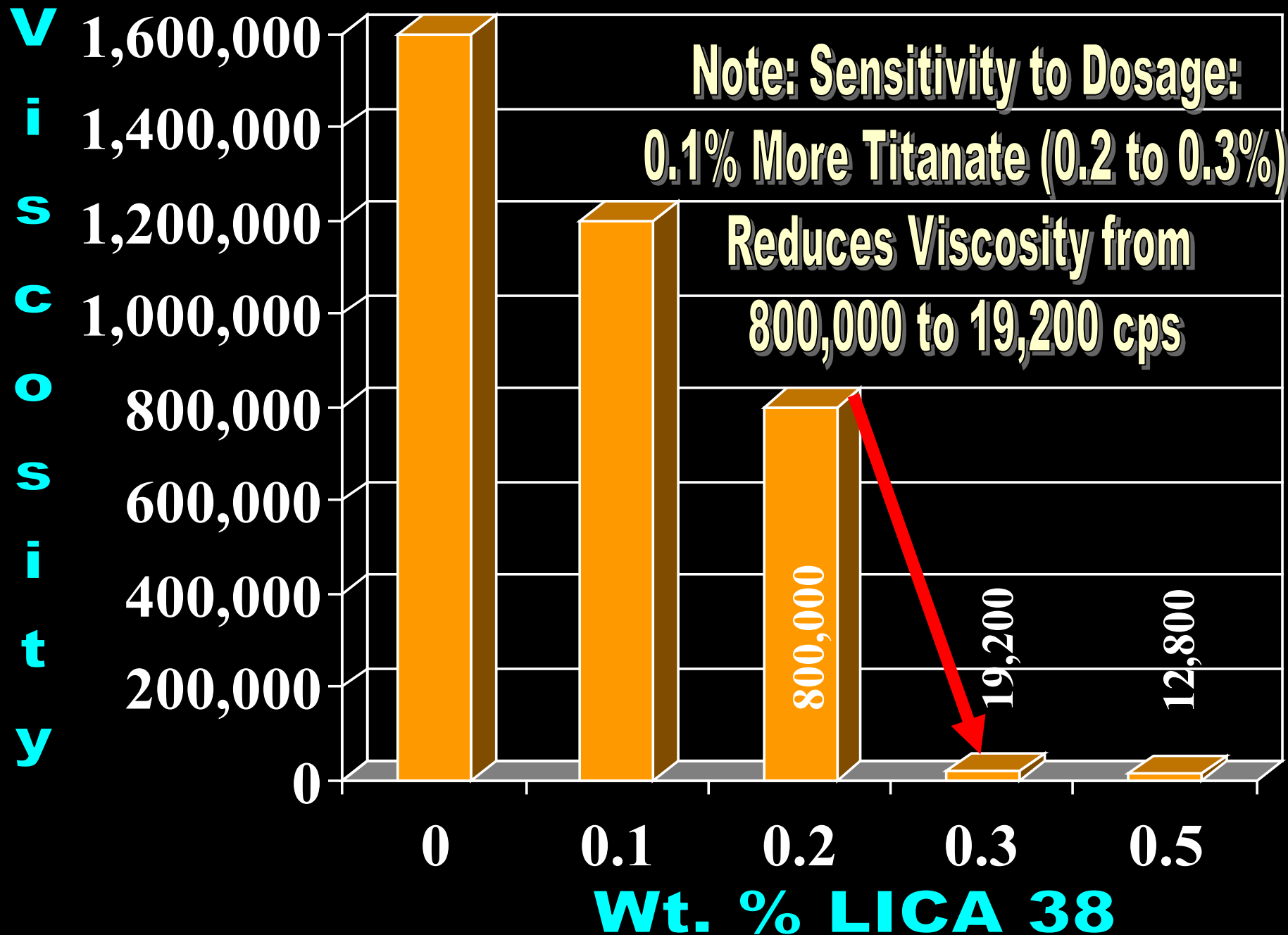
55% ZnO Dispersed In Mineral Oil



55% ZnO Dispersed In Mineral Oil



55% ZnO Dispersed In Mineral Oil



**Dispersion
of
Metal Oxides
and
Conductive
Particulate is
important in
applications
such as
digital copier
toner, polymer
magnets,
smart
coatings, etc.**



Patented ZnO Apps



Order 2435843

Ti or Zr coupling agents
[20071228-20080930/ED]

|
Search Report

Prepared for
Salvatore J. Monte, President
of
Kenrich Petrochemicals, Inc.

September 30, 2008

CONFIDENTIAL

ZnO filled chloroprene and natural rubber

Faculty of Sciences and Engineering Technology, Yemen

ZnO and Metal Hydroxides as Flame Retardants

School of Chem. & Environmental Sci., Hebei U., China

ZnO Sunscreen

Kosei Co., Ltd., Japan

Cosmetic Sunscreen ZnO

L'Oreal, France

TiO₂ and Transparent ZnO

Kobo Products, Inc., USA

Aluminum or ZnO Heat Conductive Composites

Foxconn Technology Co., Ltd., Taiwan

**Nano Functional ZnO, Tourmaline, Alumina,
Zirconia, Magnesium Oxide, Titania, and Maifan**

Stone Filled Polyamide, PET, Polyacrylonitrile, and PU

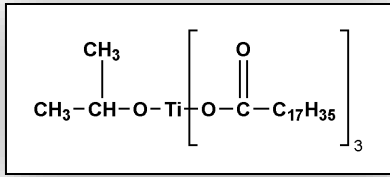
Diamond Polymer Science Co., Ltd., Taiwan

Titanate/Silane ZnO Treatment for Silicone

Kosei Co., Ltd., Japan

Sand-fixing agent w. hi-strength in petroleum recovery

Petrochina Co., Ltd., Peop. Rep. China

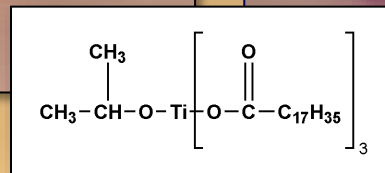


**Isopropyl
Titanium
Triisostearate
is the World
Standard for
Dispersion
of
TiO₂ and ZnO
in Facial
Cosmetics
and Sun Block
Formulations**



COATING LIPS AND EYES

Improving COLOR &
APPEARANCE



FACIAL
COSMETICS

TI Injection molding process for high-strength and large-size modified PVC interior trim parts

IN Xu, Fei

PA Yangzhou Jiakun New Energy Co., Ltd., Peop. Rep. China

SO Faming Zhuanli Shenqing, 6pp.

LA Chinese

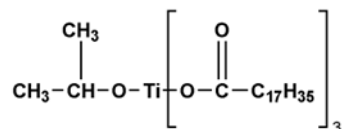
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	CN 113512260	A	2021-10-19	CN 2021-10906120	20210809
PRAI	CN 2021-10906120		20210809		

PSPI

	PATENT NO.	KIND	STATUS	STATUS DATE
	-----	----	-----	-----
AB	CN 113512260	A	Alive	20211028

AB Title PVC interior trim part comprises 100 parts of PVC resin, 10-15 parts of lubricant (paraffin wax, calcium stearate and polyethylene wax), 1-5 parts of filler (calcium carbonate or carbon black), 1-4 parts of coupling agent (iso-Pr triisostearoyl titanate), 30-50 parts of modifier (polyethylene, powd. nitrile rubber and vinyl chloride-acrylonitrile copolymer compounded in the ratio 1:1:1.5) and 2-8 parts of plasticizer (DOS or DOTP). Prepn. method comprises steps: (1) weighing and adding the raw materials into mixer for high-speed mixing, then putting the mixed raw materials into double-screw extruder for extrusion, and cutting and granulating the extruded plastic strips; (2) drying: drying the extruded raw material particles at 85 +/-5° for at least 30 min, and stirring the raw materials continuously in the drying process to fully remove water vapor in the raw materials; (3) injection molding: putting the dried raw materials into injection machine for heating and melting; (4) injection machine injection into a mold, provided with a cooling device, and when the product is formed, the mold is opened and after a product is taken out.

**IT 61417-49-0**

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

(coupling agent; injection molding process of high-strength large-size modified PVC interior trim part)

Safety Assessment of
Titanium Complexes as Used in Cosmetics

Status: Final Report
Release Date: June 5, 2019
Panel Date: April 8-9, 2019



The 2019 Cosmetic Ingredient Review Expert Panel members are: Chair, Wilma F. Bergfeld, M.D., F.A.C.P.; Donald V. Belsito, M.D.; Ronald A. Hill, Ph.D.; Curtis D. Klaassen, Ph.D.; Daniel C. Liebler, Ph.D.; James G. Marks, Jr., M.D.; Ronald C. Shank, Ph.D.; Thomas J. Slaga, Ph.D.; and Paul W. Snyder, D.V.M., Ph.D. The CIR Executive Director is Bart Heldreth, Ph.D. This report was prepared by Wilbur Johnson, Jr., M.S., Senior Scientific Analyst.

© Cosmetic Ingredient Review
1620 L STREET, NW, SUITE 1200 ◊ WASHINGTON, DC 20036-4702 ◊ PH 202.331.0651 ◊ FAX 202.331.0088 ◊ CIRINFO@CIR-SAFETY.ORG

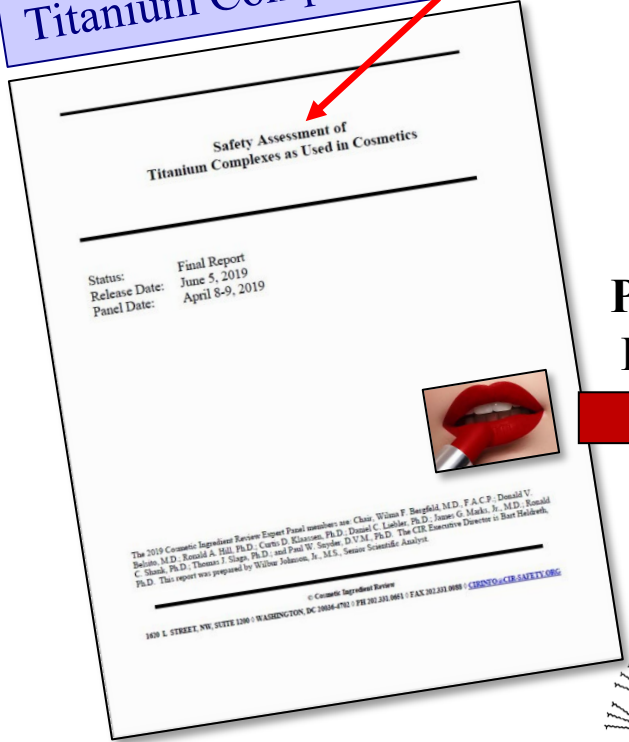
...According to 2019 VCRP data, Isopropyl Titanium Triisostearate is reported as being used in 513 cosmetic products (506 leave-on and 7 rinse-off products); half of the reported uses are in lipstick formulations (253).⁸

...use survey conducted by the Council in 2017 indicate that Isopropyl Titanium Triisostearate is used in leave-on products (eye shadows) and at concentrations up to 0.3% in rinse-off products (eye make-up removers).⁹ ...

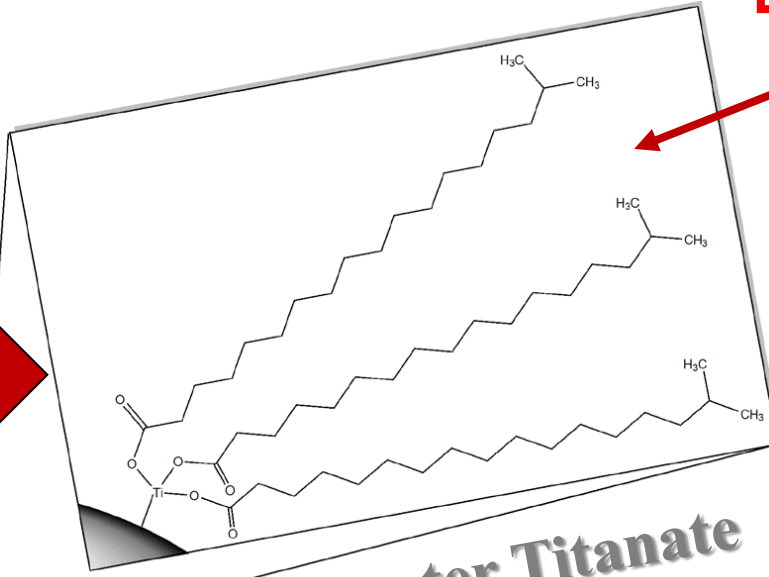


Invention/Technology Evolution – 1973 to 2022

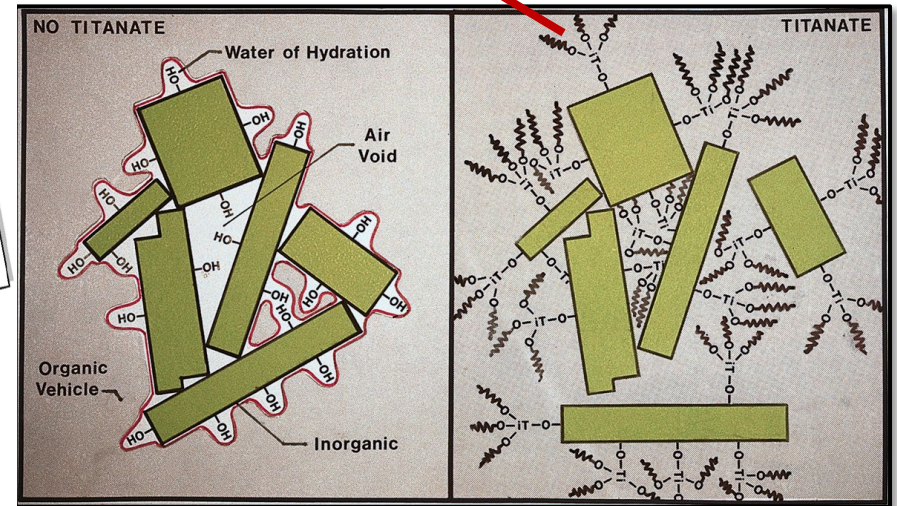
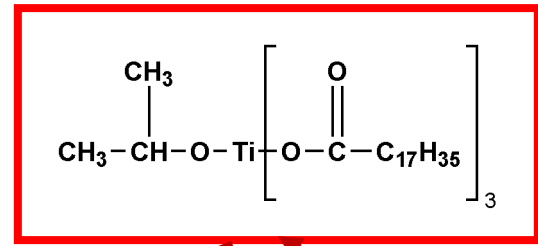
Safety Assessment of Titanium Complexes as Used in Cosmetics



Page 3
Fig. 2

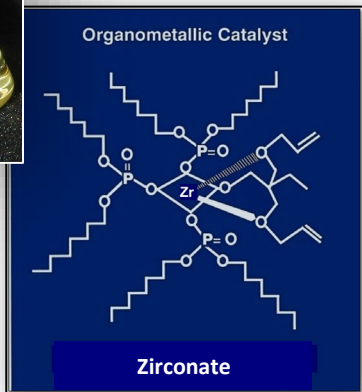
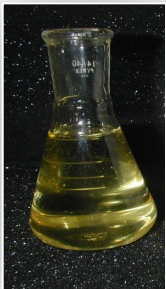


2-Nanometer Titanate Coating on Pigment



1973 Drawing by S. J. Monte
(46-years earlier)

2019 Drawing – Fe₂O₃/Titanate

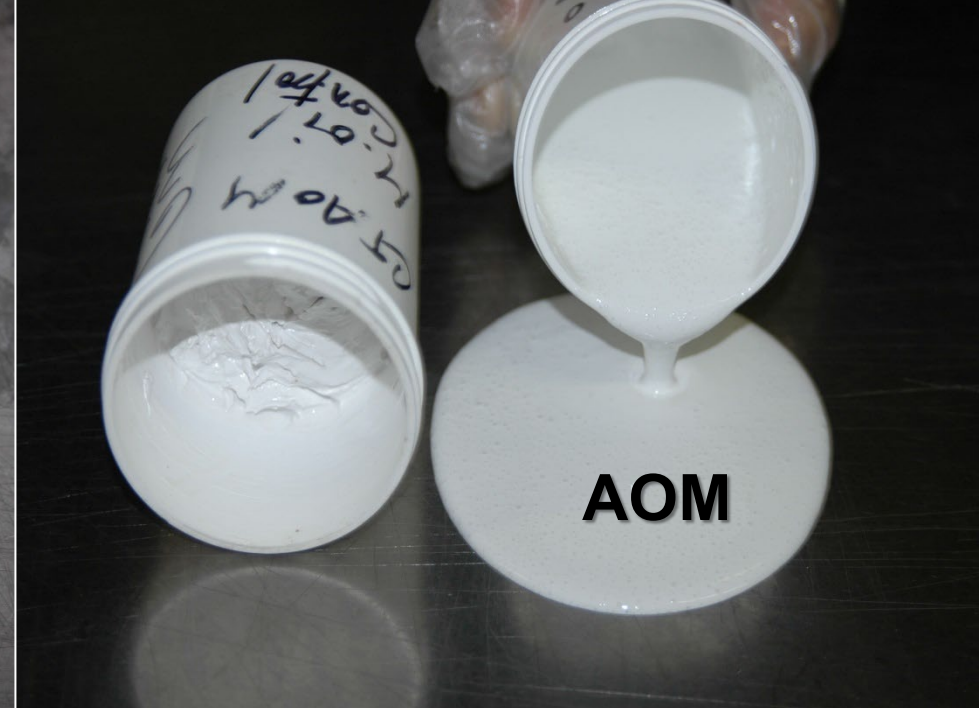


The Liquid Coupling Agent can be added to the liqui-color concentrate and then added at the hopper.



Disperse Organic and Inorganic Pigments

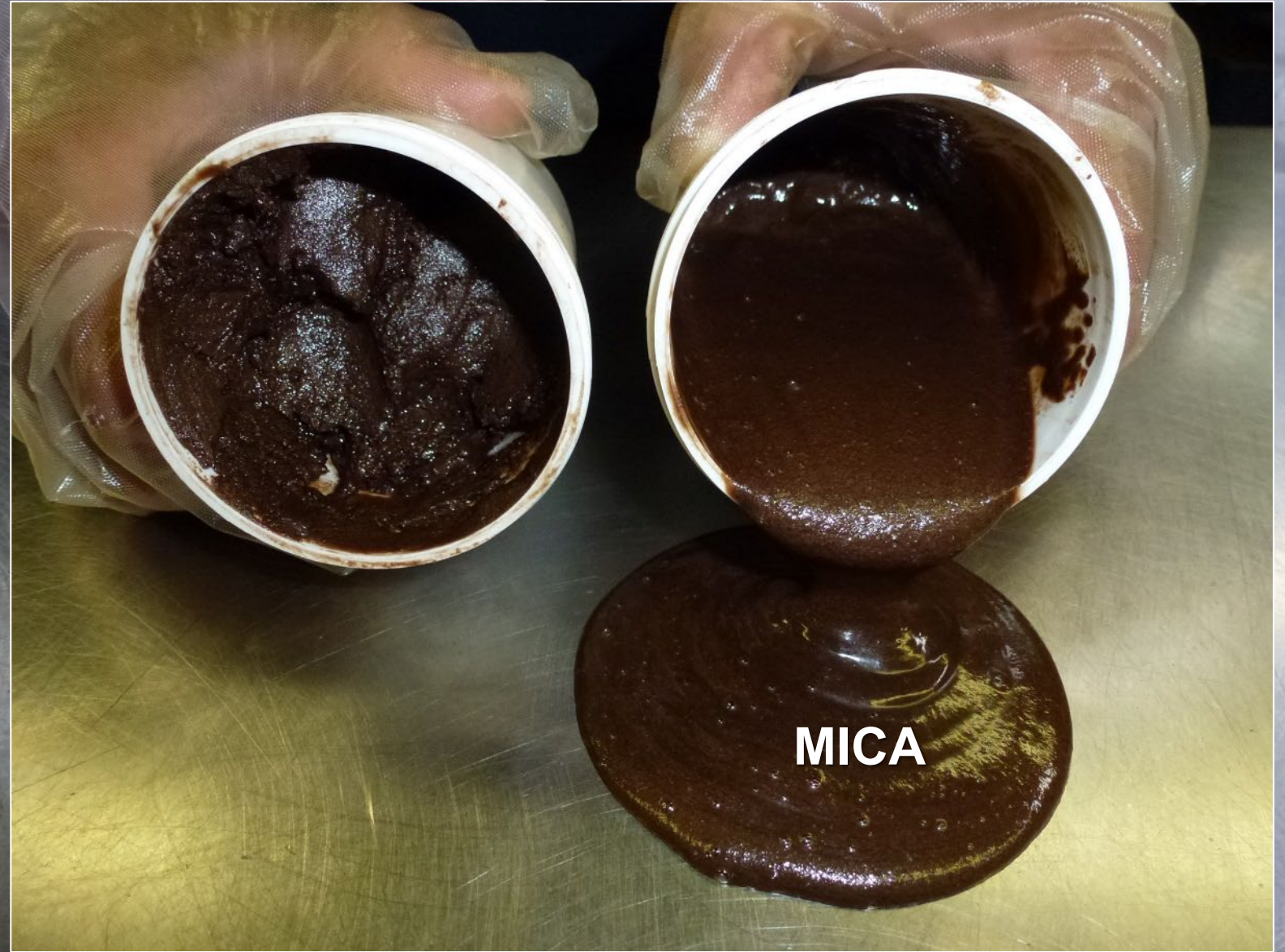
A low dosage of Titanate added in situ into mineral oil followed by filler addition reduces viscosity



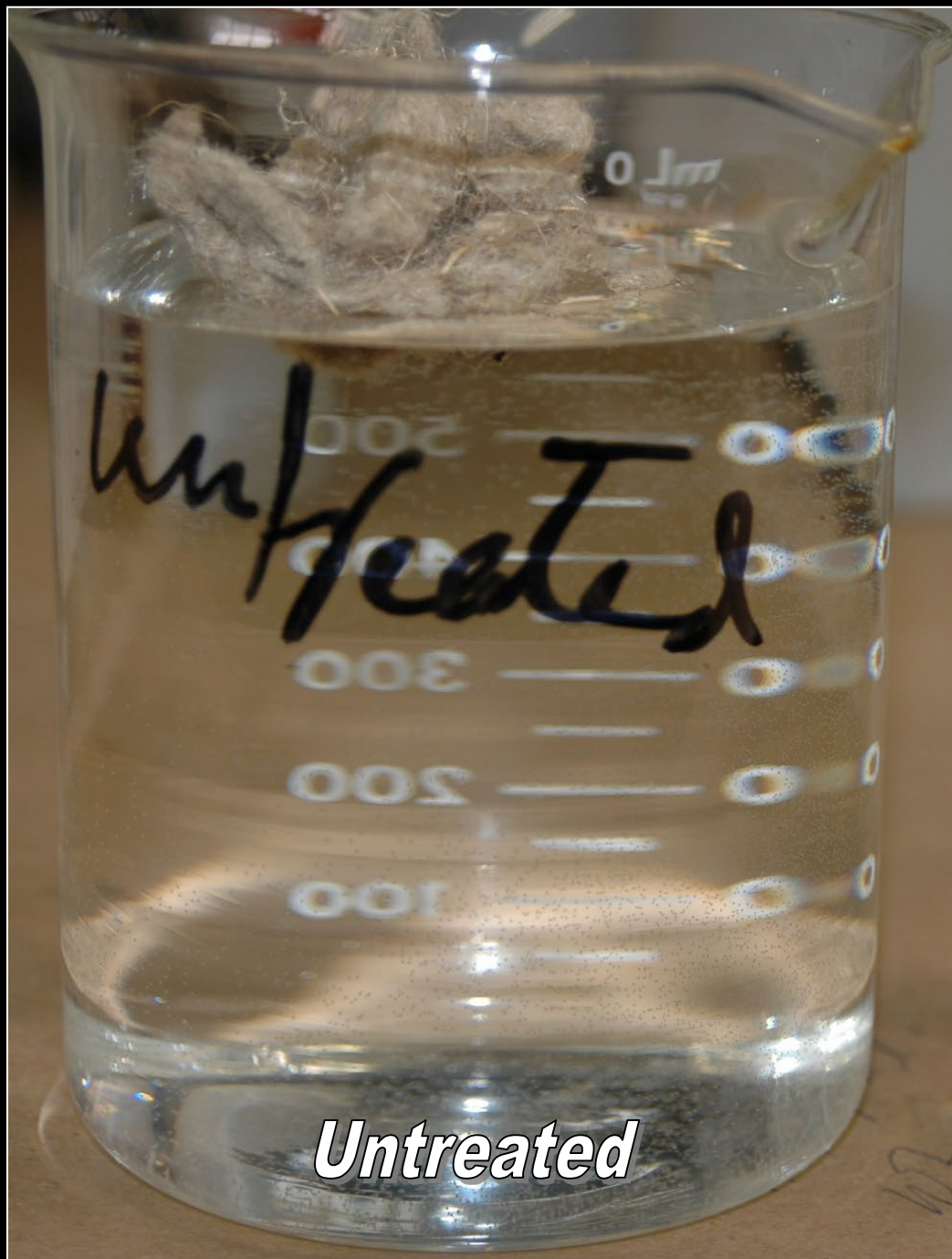
A low dosage of Titanate added in situ into mineral oil followed by filler addition reduces viscosity



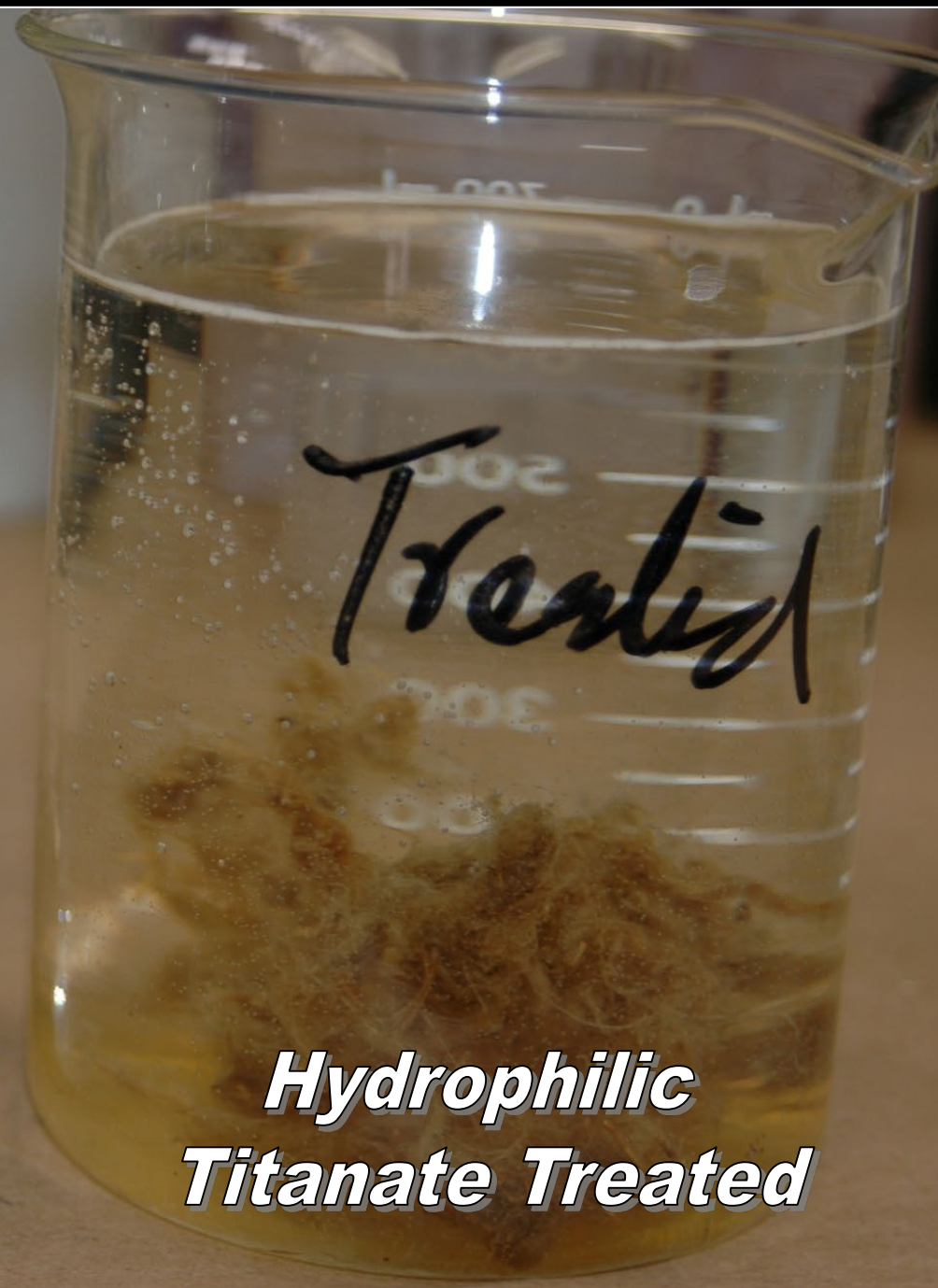
A low dosage of Titanate added in situ into mineral oil followed filler addition reduces viscosity



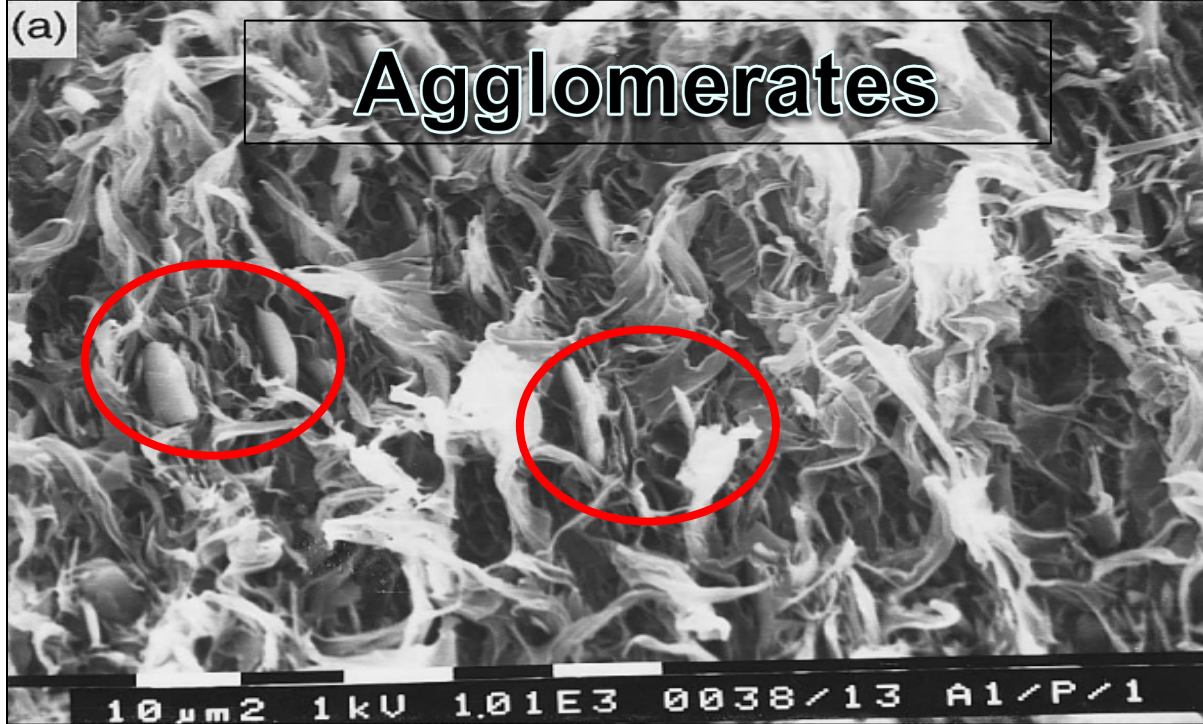
**Reacts
with
Sustainable
Organics
such
as Flax
&
Cellulose**



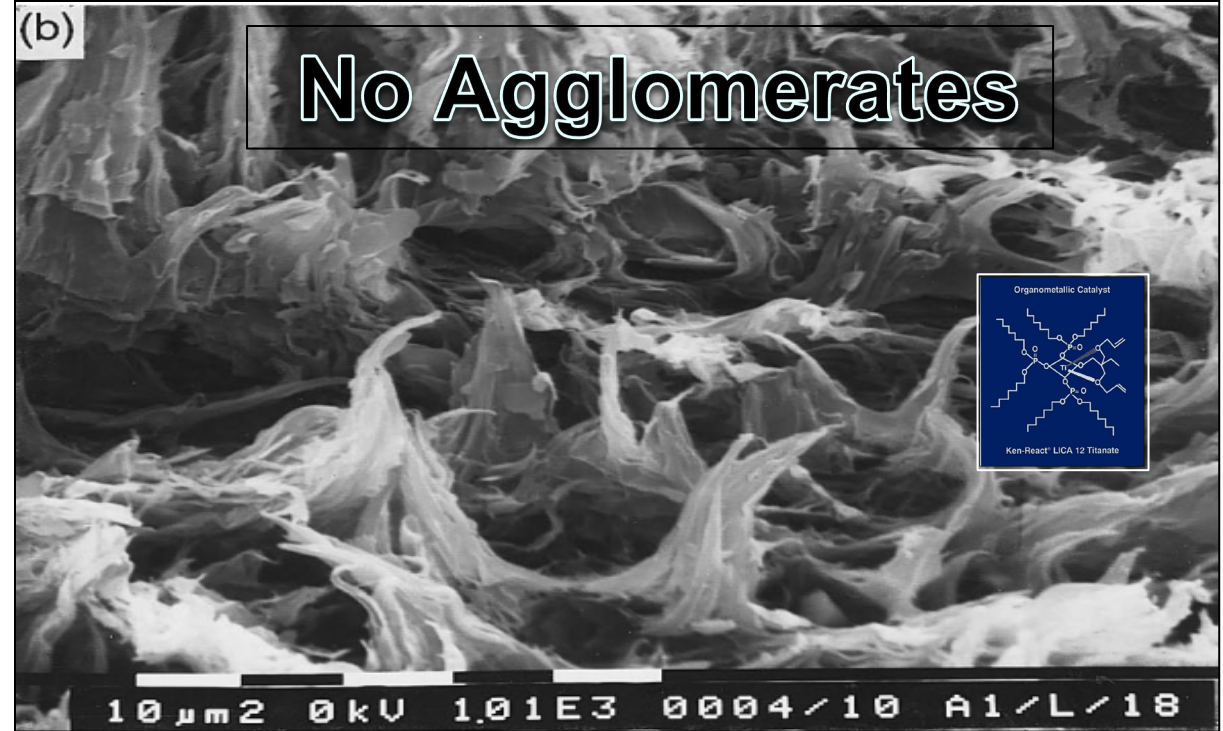
Untreated



***Hydrophilic
Titanate Treated***



30% Talc/PP – No Titanate



30% Talc/PP–0.5% Titanate



ELSEVIER

European Polymer Journal 36 (2000) 789–801

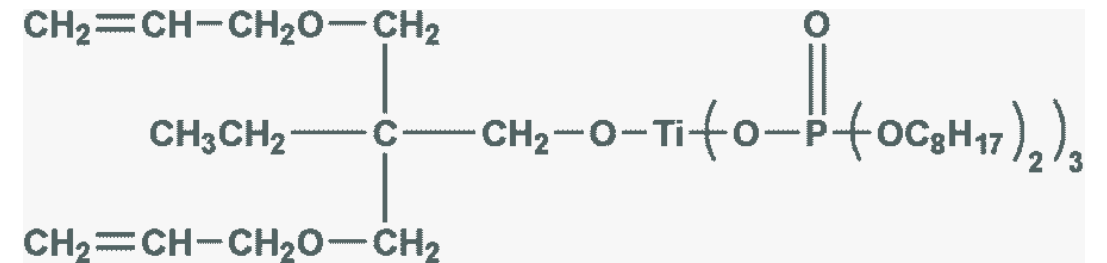
EUROPEAN
POLYMER
JOURNAL

Effects of titanate coupling agent on rheological behaviour, dispersion characteristics and mechanical properties of talc filled polypropylene

Chuah Ai Wah^{a,*}, Leong Yub Choong^b, Gan Seng Neon^b

^aPetronas Research and Scientific Services Sdn. Bhd., Off Jalan Ayer Itam, Kawasan Institusi Bangi, 43000 Kajang, Selangor, Malaysia

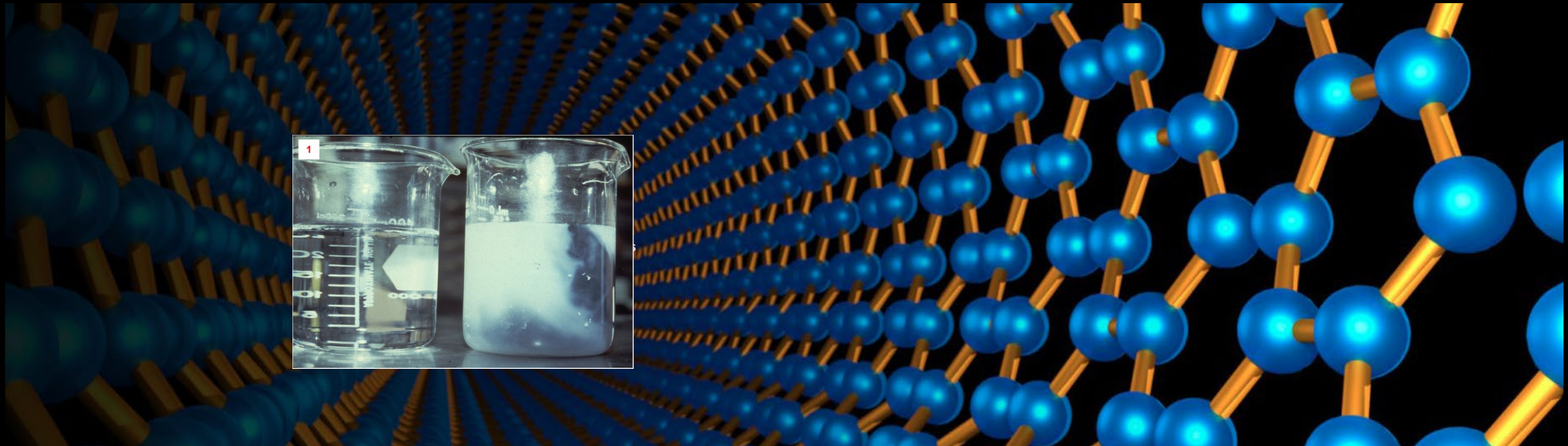
^bDepartment of Chemical Engineering, University of Malaya, 50603, Kuala Lumpur, Selangor, Malaysia



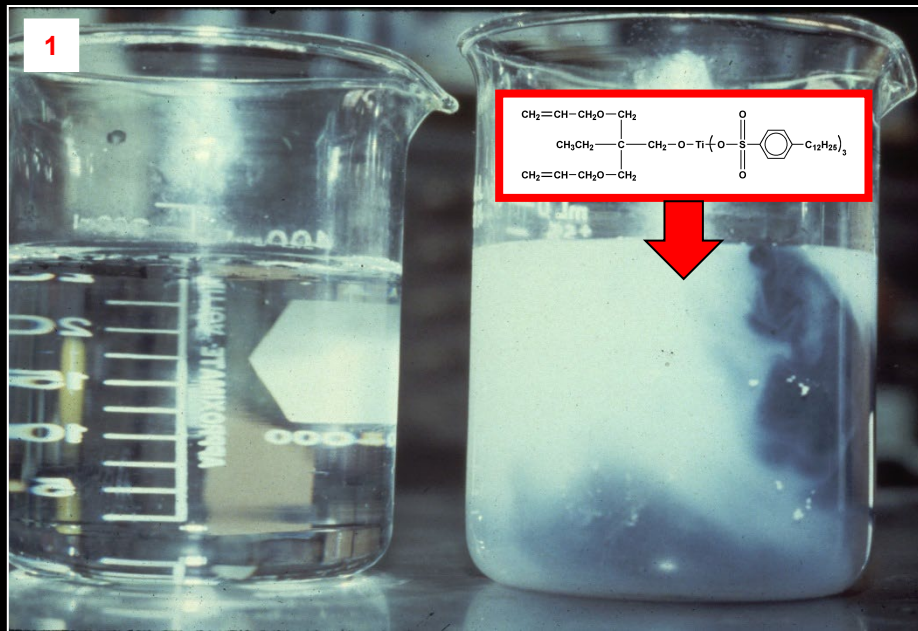
Neoalkoxy Phosphato Titanate

- Different Than Silanes

Silanes do not Nano-Phosphatize or Couple to Carbon

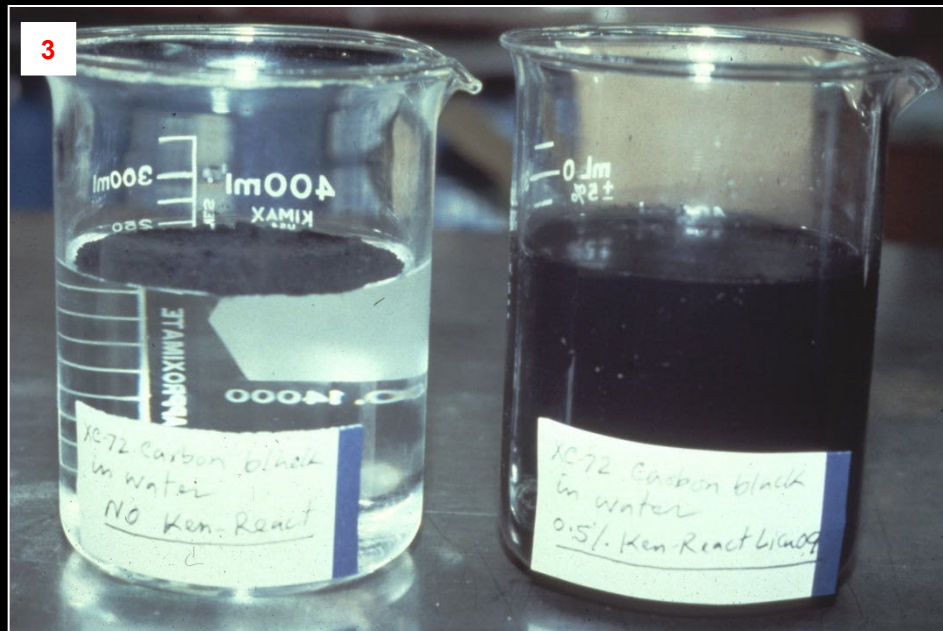


Titanate Coupling to XC-72 Conductive Carbon Black in Water



No Titanate

Titanate



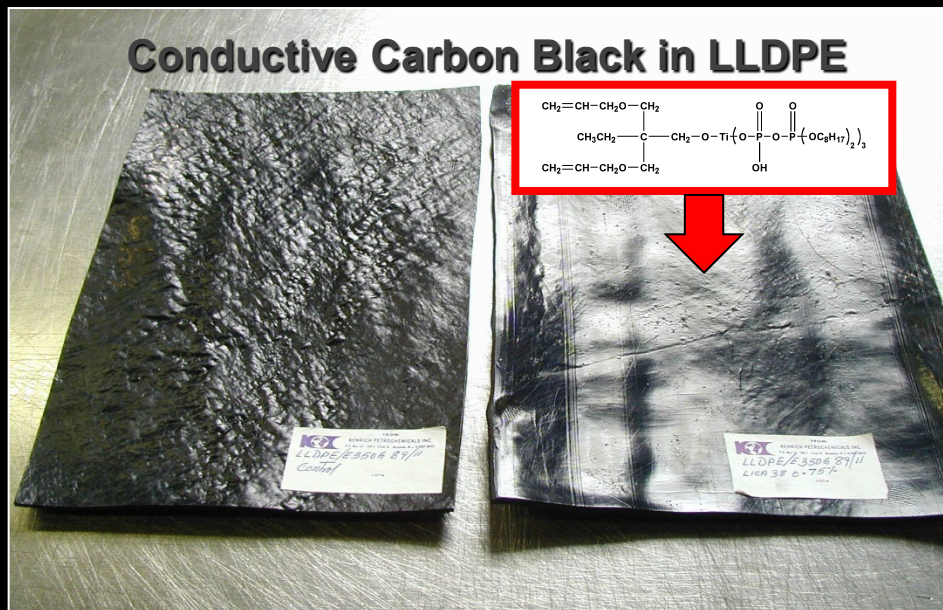
No Titanate

Titanate

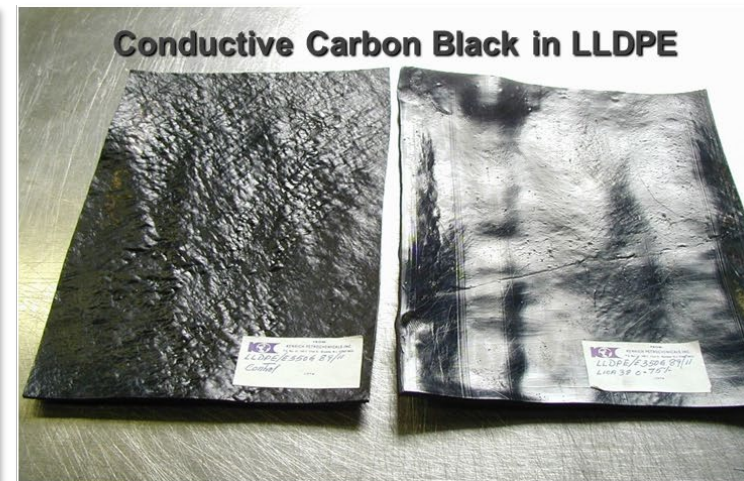
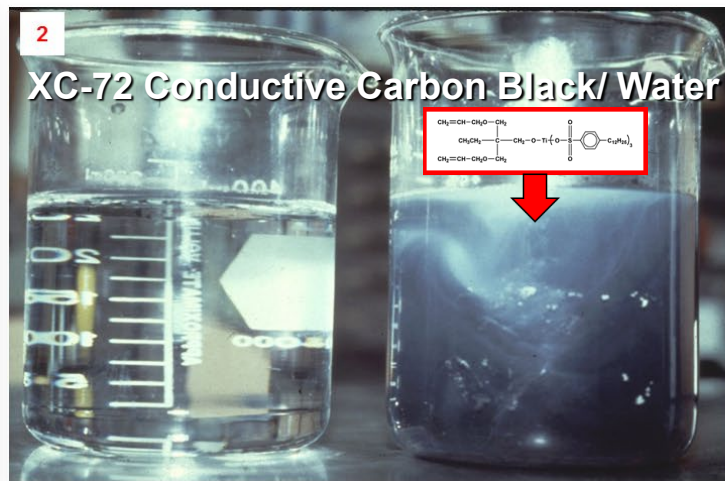
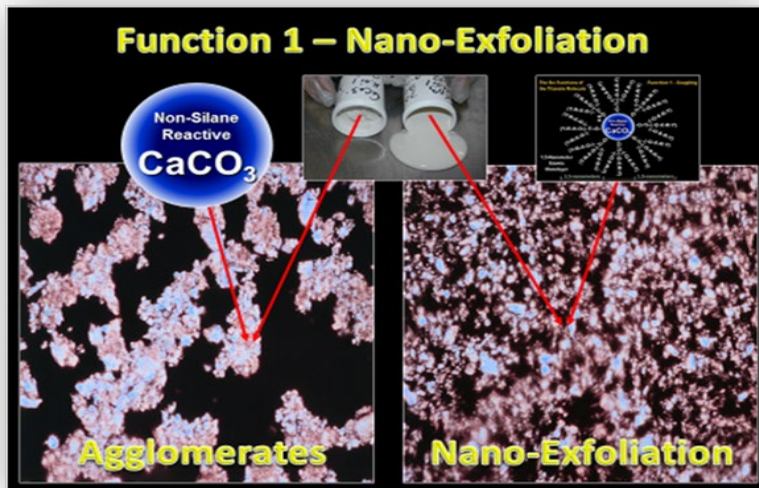


2

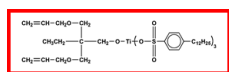
No Mechanical Stirring



Conductive Carbon Black in LLDPE



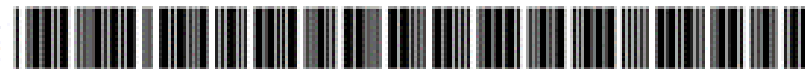
**RESISTIVITY OF 3.75% XC-72R CONDUCTIVE BLACK IN
STYRENE-BUTADIENE BLOCK COPOLYMER/PS
10mm THICK TEST SLAB**



**Wt.% LICA 09
Carbon Black**

**Resistivity
Surface, $\Omega/\text{sq.}$ Volume, $\Omega\cdot\text{cm}$**

Control	$> 10^{16}$	7.8×10^{14}
0.67	1.7×10^{12}	3.0×10^{12}
1.00	2.1×10^8	4.3×10^7
2.00	5.7×10^7	3.7×10^7



US 20200071230A1

(19) **United States**
 (12) **Patent Application Publication** (10) **Pub. No.: US 2020/0071230 A1**
 Monte (43) **Pub. Date: Mar. 5, 2020**

(54) **CONSTRUCTION MATERIALS, COMPOSITIONS AND METHODS OF MAKING SAME** Publication Classification
 (51) **Int. CL. C04B 20/10 (2006.01)**

(71) Applicant: **S&E INNOVAT TECHNOLOGI (US)**

(72) Inventor: **Salvatore J. Monte**

(73) Assignee: **S&E INNOVAT TECHNOLOGI (US)**

**My 32nd
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 Issued
 Mar. 5. 2020**

**Returned
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 Darmstadt
 Mar. 5. 2020**



 **Praxisforum
 Kunststoffrezyklate**

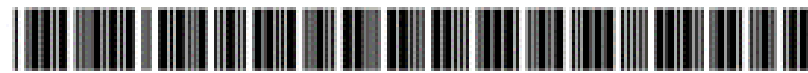
Salvatore J. Monte – Kenrich Petrochemicals, Inc.



3-4 March 2020 in Darmstadt

**Forum Plastic Recyclates 2020
 Quality Increase of Material & Processing**

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(71) Applicant: S&E / TECI (US)
 (72) Inventor: Salvat
 (73) Assignee: S&E / TECI (US)
 (21) Appl. No.: 1

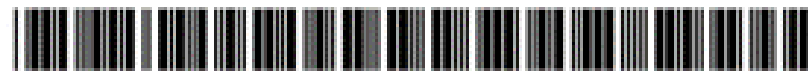
My 32nd Patent Issued Mar. 5. 2020

Returned From Darmstadt Mar. 5. 2020



Compatibilize Oil Soaked Seawater Sand with OPC





US 20200071230A1

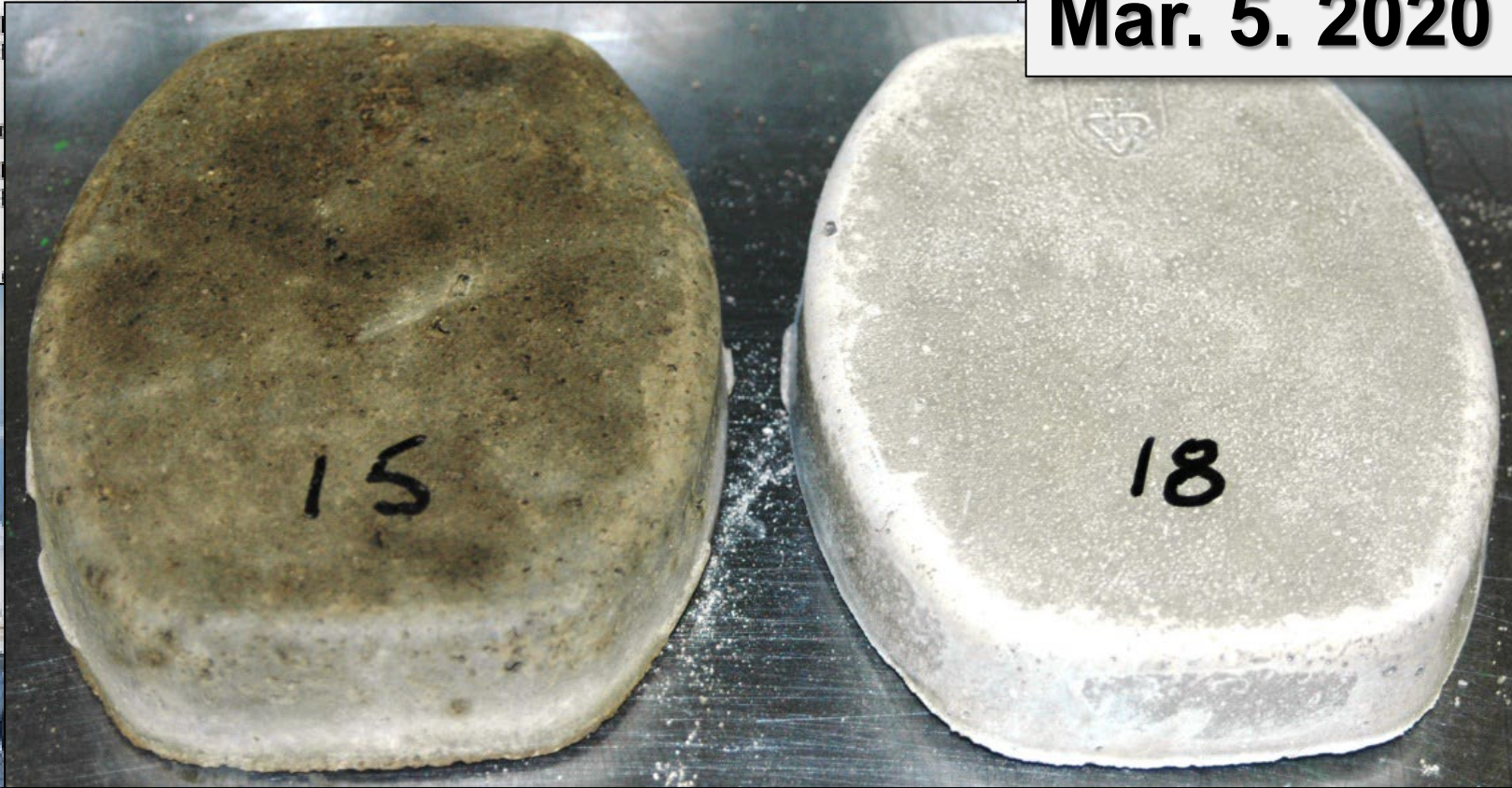
(19) **United States**
 (12) **Patent Application Publication** (10) **Pub. No.: US 2020/0071230 A1**
 Monte (43) **Pub. Date: Mar. 5, 2020**

(54) **CONSTRUCTION MATERIALS, COMPOSITIONS AND METHODS OF MAKING SAME** Publication Classification
 (51) **Int. Cl. C08B 20/10 (2006.01)**

(71) Applicant: S&E I
 TECH
 (US)
 (72) Inventor: Salvat
 (73) Assignee: S&E I
 TECH
 (US)
 (21) Appl. No.: 1

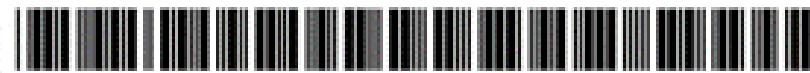
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 Mar. 5, 2020**

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 Darmstadt
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Compatibilize Oil Soaked Seawater Sand with OPC





US 20200071230A1

(19) **United States**
 (12) **Patent Application Publication**
 Monte

(10) **Pub. No.: US 2020/0071230 A1**
 (43) **Pub. Date: Mar. 5, 2020**

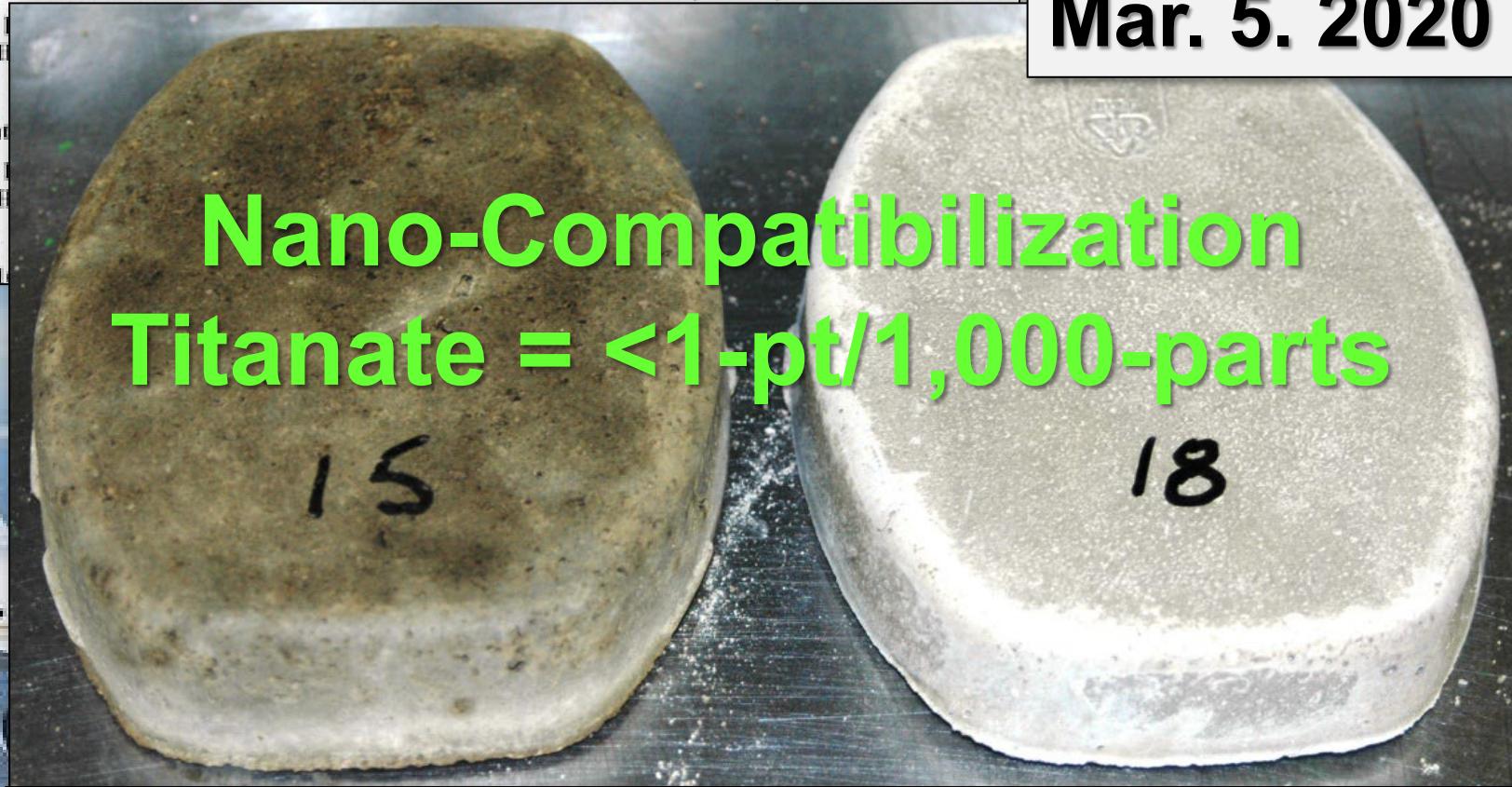
(54) **CONSTRUCTION MATERIALS, COMPOSITIONS AND METHODS OF MAKING SAME**

Publication Classification
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 (US)
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 (73) Assignee: S&E I
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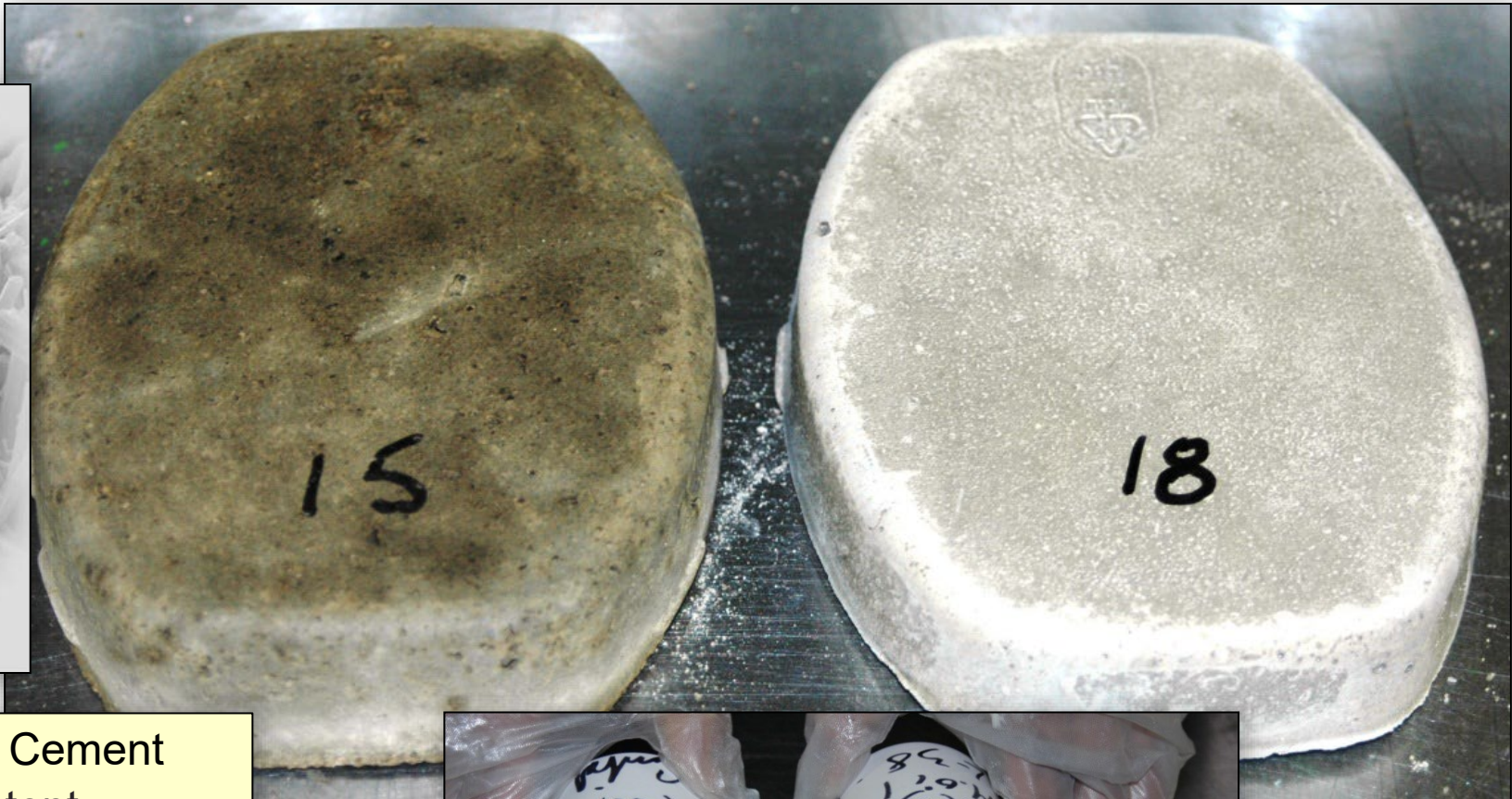
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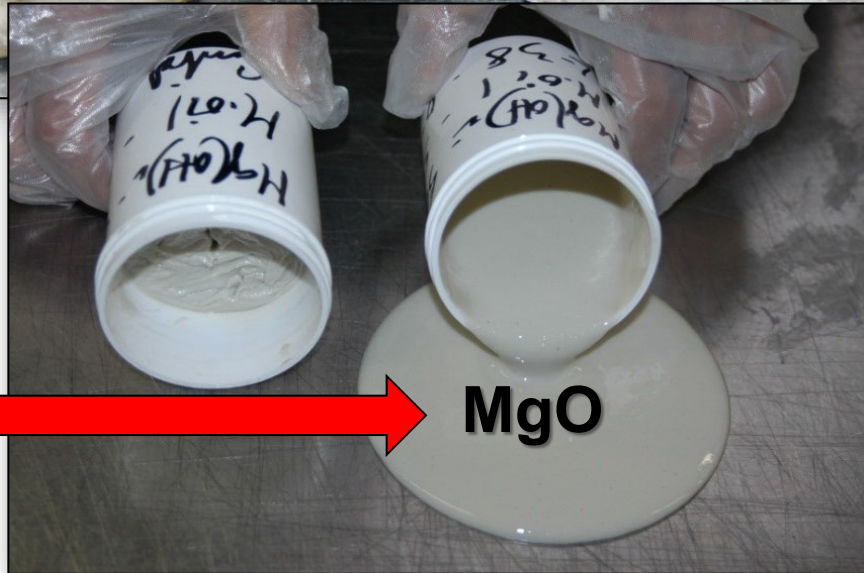
Compatibilize Oil Soaked Seawater Sand with OPC



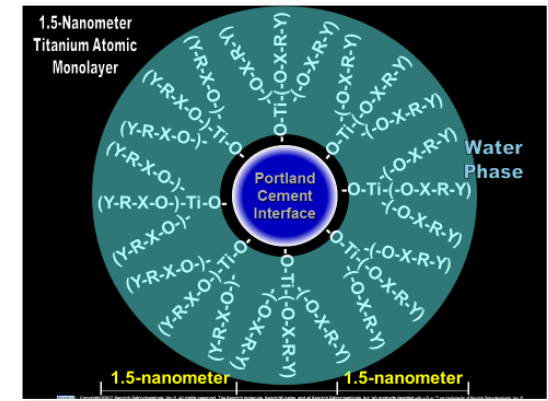


~ Oxide Composition Ordinary Portland Cement

<u>Oxide</u>	<u>Per cent content</u>
CaO (non-silane reactive)	60.0–67.0
SiO ₂	17.0–25.0
Al ₂ O ₃ (aluminum oxide in cement)	3.0–8.0
Fe ₂ O ₃	0.5–6.0
MgO	0.1–4.0
Alkalies (K ₂ O, Na ₂ O)	0.4–1.3
SO ₃ (non-silane reactive)	1.3–3.0



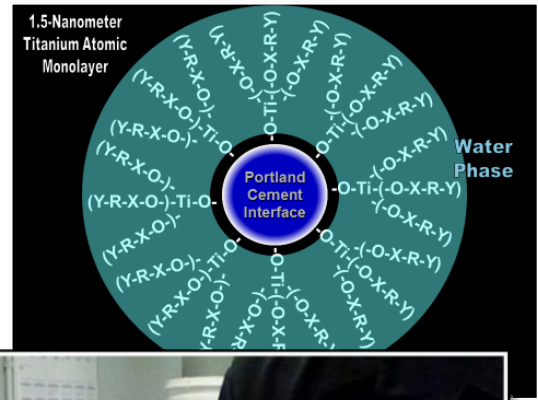
A New 1.5-Nanometer Titanium Treated Portland Cement (ASTM C150 – Type I) reduces the cement water ratio by 31% to equivalent slump (flow).



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

The effects of nano-titanium organo-functionality on the Portland Cement interface provides a technology for new & novel concrete structures.

A New 1.5-Nanometer Titanium Treated Portland Cement (ASTM C150 – Type I) reduces the cement water ratio by 31% to equivalent slump (flow).

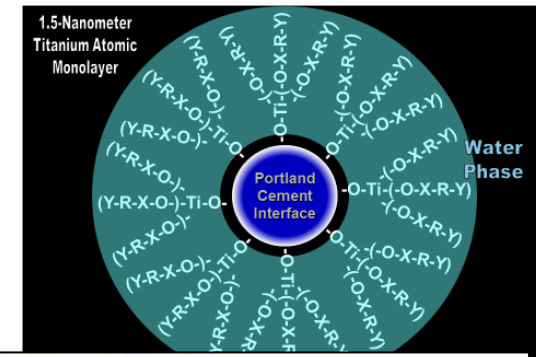


Portland Cement	
<u>Oxide</u>	<u>% content</u>
CaO	60.0–67.0
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Fe ₂ O ₃	0.5–6.0
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Alkalies (K ₂ O, Na ₂ O)	0.4–1.3
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The effects of nano-titanium organo-functionality on the Portland Cement interface provides a technology for new & novel concrete structures.

A New 1.5-Nanometer Titanium Treated Portland Cement (ASTM C150 – Type I) reduces the cement water ratio by 31% to equivalent slump (flow).



Compound	Ultramarine Blue	Meta Kaolin	Portland Cement
SiO ₂	39.180	51.150	17.0 – 25.0
Al ₂ O ₃	25.330	42.110	3.0 – 8.0
Fe ₂ O ₃	1.489	1.180	0.5 – 6.0
CaO	0.390	0.030	60.0 – 67.0
MgO	0.314	0.590	0.1 – 4.0
SO ₃	5.724	0.070	1.3 – 3.0
Na ₂ O	18.735	0.220	0.4 – 1.3
K ₂ O	0.815	0.480	

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 (K ₂ O, Na ₂ O)	0.4–1.3
SO ₃	1.3–3.0



The effects of nano-titanium organo-functionality on the Ultramarine Blue Pigment or Kaolin interface provides a technology for new & novel coatings.

EVALUATION OF 0.35% LICA 38ENP TITANATE BY WEIGHT OF ULTRAMARINE BLUE PIGMENT (Grade 5008 - 2.14µm) IN TOLUENE AND MINERAL OIL

**50% UB 5008
In Toluene**

**50% UB 5008
In Mineral Oil**

**0.35%
EPP Titanate**

**0.35%
EPP Titanate**

**In
Situ Pre-
treat**

**In
Situ Pre-
treat**

**Control
80,000**

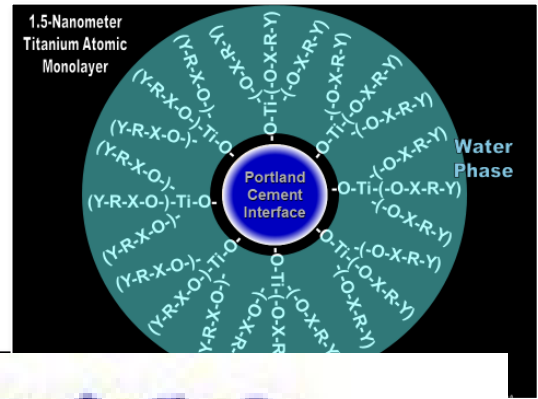
25

45

**Control
150,400**

16,000

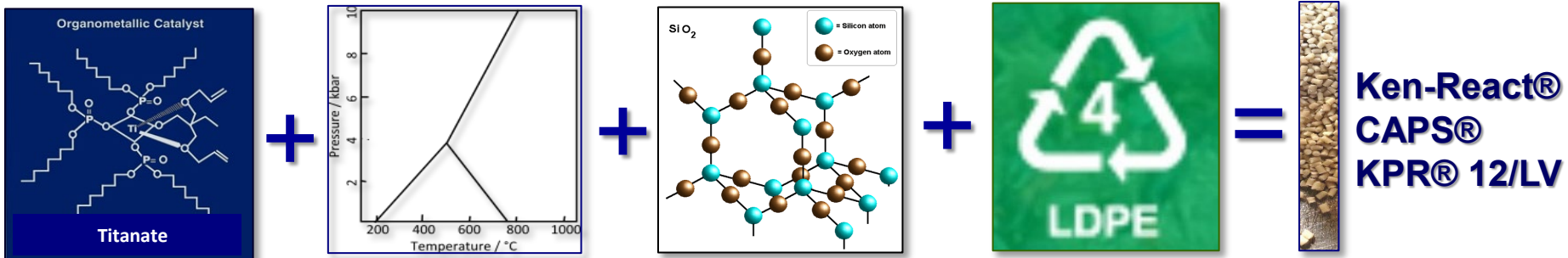
1,700



The effects of nano-titanium organo-functionality on the Ultramarine Blue Pigment or Kaolin interface provides a technology for new & novel coatings.

THE POLYMER INTERFACE – Function 2 CATALYSIS

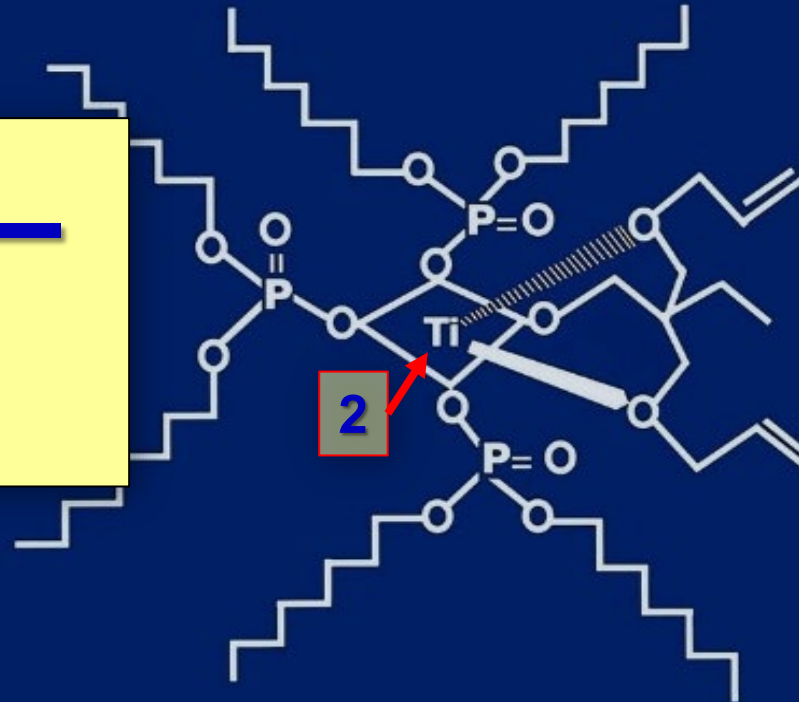
Advanced
Solution
Chemistry



SIX FUNCTIONS

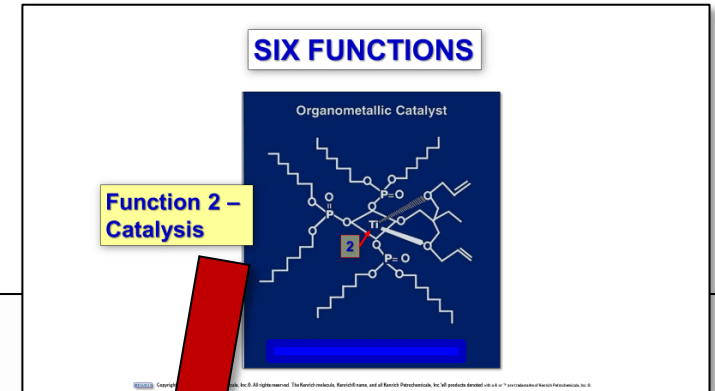
Function 2 – Catalysis

Organometallic Catalyst



Ken-React® LICA 12 Titanate

Advanced Solutions in Mechanical Recycling with 1.5-Nanometer Titanate Catalysts/Coupling Agents



**(2) Titanium, Zirconium & Aluminum
Polymer Catalysis –without or with filler:
Polymer Mechanical Properties Are Increased.**

**Provides Nano-Titanium Technology for
RECYCLING of Polymers #1 to #7**

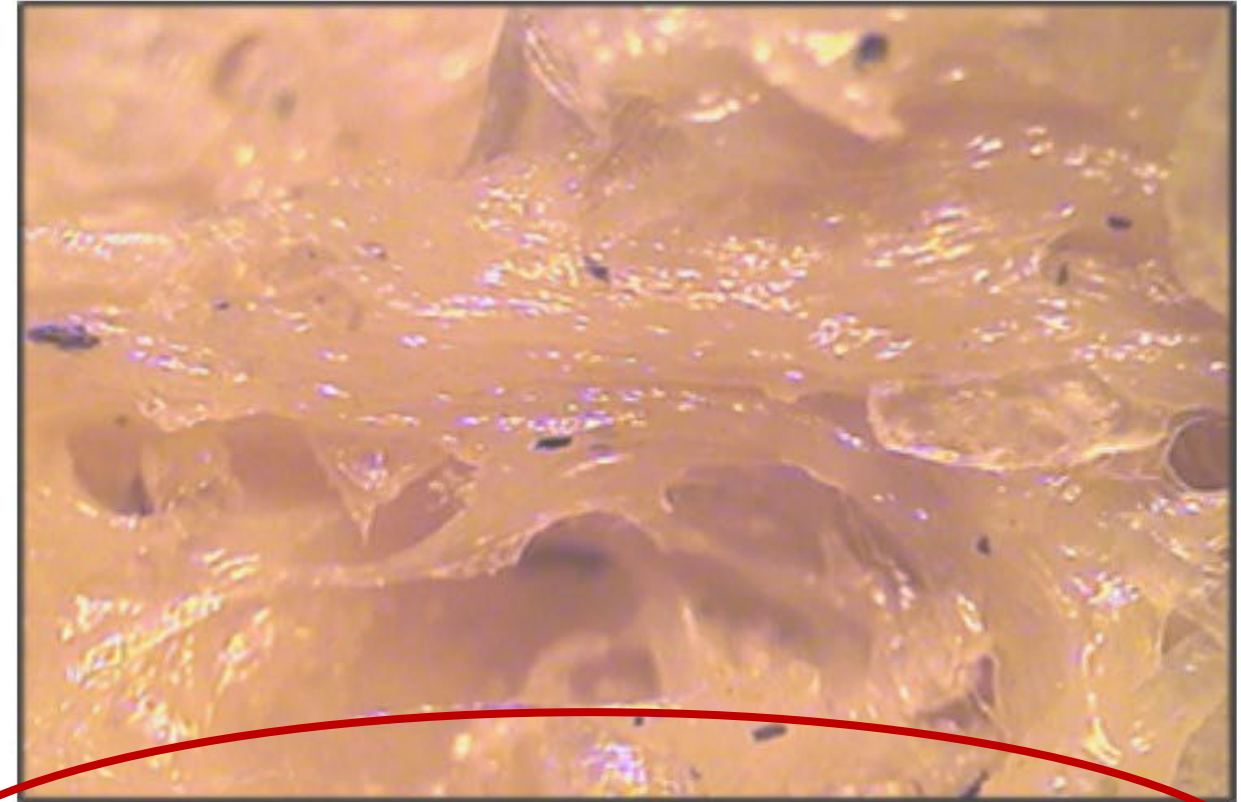
Function 2 Titanium Catalysis for Compatibilization of Addition & Condensation Polymers

Brabender Plasticorder Blends of Three Recycled Polymers: PP/PET/PE



Incompatible PP/PET/PE—

No Additive

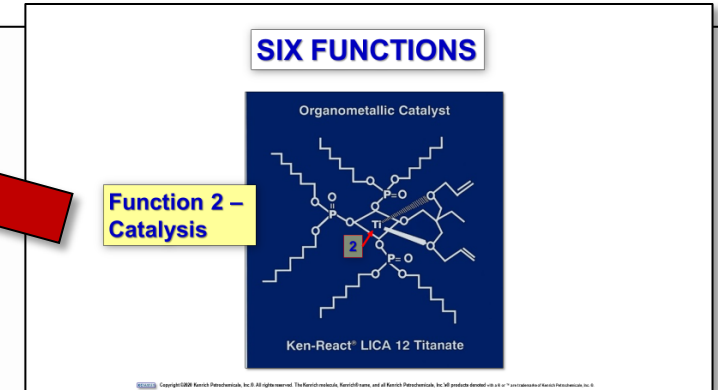


Compatibilized PP/PET/PE—

1.5% Ken-React® CAPS® KPR® 12/LV Pellets

Advanced Solutions in Mechanical Recycling with 1.5-Nanometer Titanate Catalysts/Coupling Agents

(2) Titanium, Zirconium & Aluminum Polymer Catalysis –without or with filler allows:



- Significant increase in unfilled polymer flow @ 0.2% additive.
- Lower polymer process temperatures from 10 to 40%.
- In situ copolymerization of dissimilar polymers #1 to #7.
- Reduce PVC plasticizer up to 18% to equal elongation.
- Reduced monomer in UV+EB coatings.
- **Repolymerization:** Regenerate regrind to virgin properties.

Recycle Mix: Polymers #1 to #7 & Fillers, Fibers, Pigments, etc.

SUSTAINABILITY

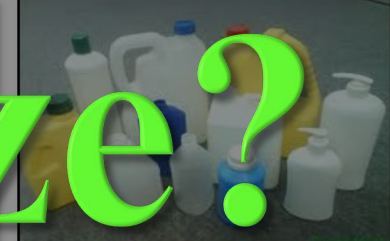


Technology Challenge

PE & PP are ADDITION POLYMERS
PET is a CONDENSATION POLYMER

Incompatibility PE & PP

Incompatibility PET & PE



How to

Compatibilize?

Recycle Mix: Polymers #1 to #7 & Fillers, Fibers, Pigments, etc.



PE & PP are ADDITION POLYMERS
PET is a CONDENSATION POLYMER

Incompatibility PE & PP



Incompatibility PET & PE



RECYCLE Technology Challenge: Incompatibility of Fillers & Polymers



PE & PP are ADDITION POLYMERS

PET is a CONDENSATION POLYMER

Incompatibility PE & PP



Trouble Shooting for Injection Molding Process

- Black Spots, Brown streaks.
- Blisters (Air Entrapment).
- Brittleness.
- Bubbles.
- Burn Marks, Dieseling.
- Cracking, Crazing.
- **Delamination.**
- Discoloration.
- Excessive Flash.
- Flow, Halo, Blush Marks.
- Gate Stringing, Drooling.
- Gels.
- Jetting.
- Material Leakage.
- Oversized Part.
- Part Sticking.
- Short Shot (Incomplete Filled Parts).
- Sink Marks.
- Splay Marks, Silver Streaks.
- Sprue Sticking.
- Surface Finish (Low Gloss).
- Surface Finish (Scars, Wrinkles).
- Undersized Part.
- Valve Pin Does Not Close.
- Voids.
- Warping, Part Distortion.
- Weld Lines.

Injection Molding Delamination
5% PP (Tupperware) in 95% HDPE (Milk Jug) = part reject

RECYCLE Technology Challenge: Incompatibility of Fillers & Polymers



PE & PP are ADDITION POLYMERS

PET is a CONDENSATION POLYMER

Incompatibility PE & PP



Trouble Shooting for Injection Molding Process

- Black Spots, Brown streaks.
- Blisters (Air Entrapment).
- Brittleness.
- Bubbles.
- Burn Marks, Dieseling.
- Cracking, Crazing.
- **Delamination.**
- Discoloration.
- Excessive Flash.
- Flow, Halo, Blush Marks.
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Injection Molding Delamination
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PP & HDPE are incompatible

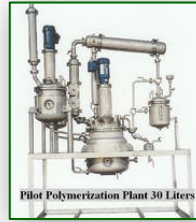


Mark Twain: "It ain't what you don't know that gets you in trouble. It's what you know that ain't so."

**It ain't so:
PP & HDPE
are
incompatible**



Reactor Titanocene Polymerization - Ethylene Monomer

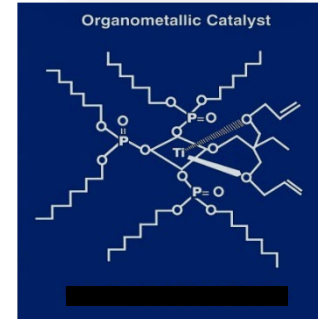
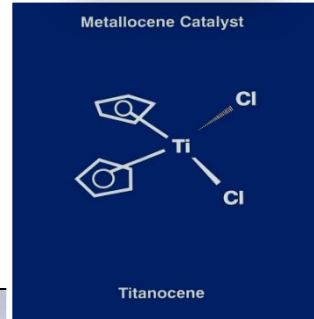


Pilot Polymerization Plant 30 Liters



Extruder Titanate Copolymerization - Ethylene Polymers

Injection Molding Delamination
5% PP (Tupperware) in 95%
HDPE (Milk Jug) = part reject

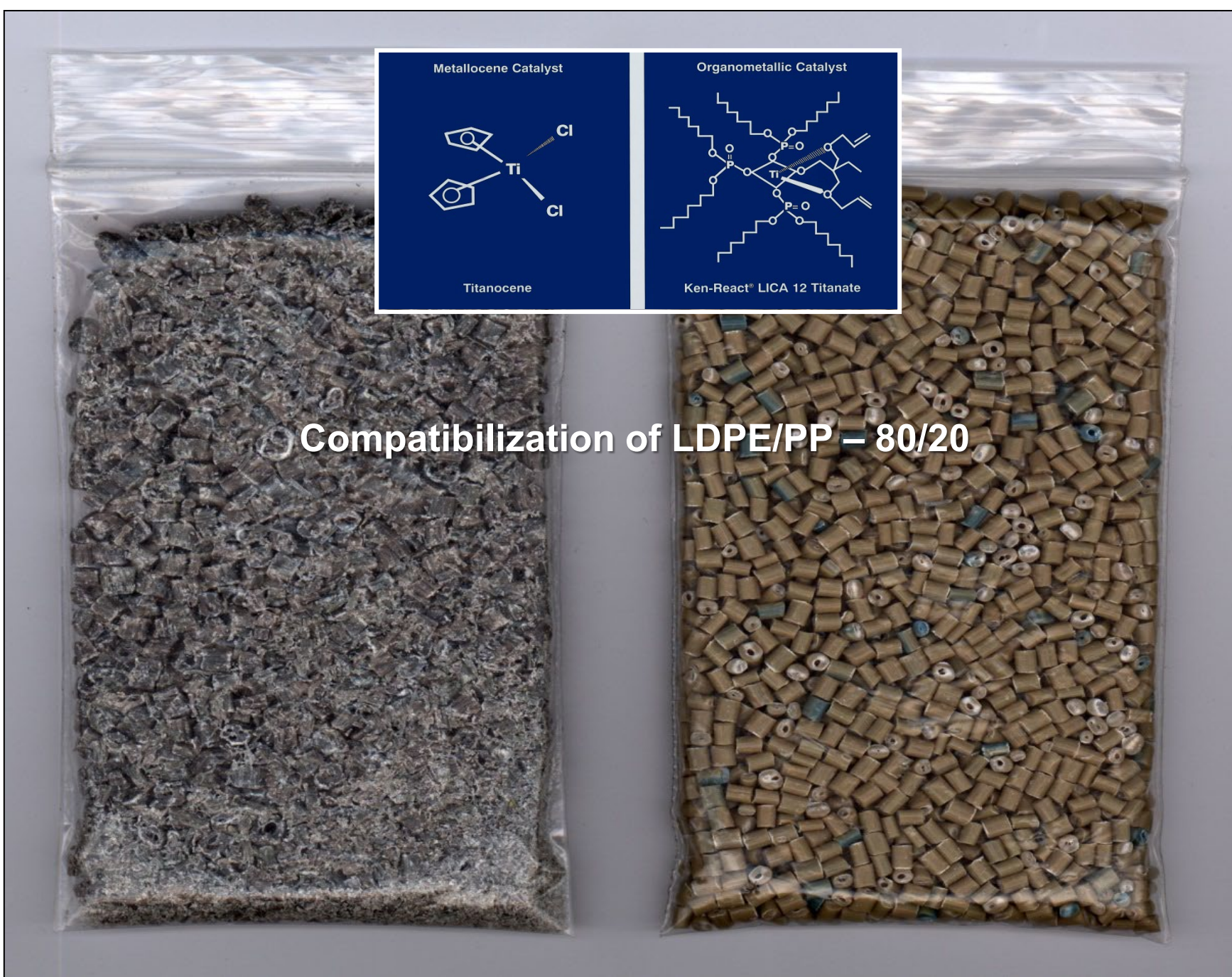


Compatibilization of LDPE/PP – 80/20 Regrind Using 0.2% Titanate Catalyst



PP & HDPE
are
Compatible

PE
&
PP
are
C
O
M
P
A
T
I
B
L
E



○ Compatibilization of LDPE/PP – 80/20

**CHAIN SCISSORING DURING MELT PROCESSING
IS WHAT MAKES RECYCLE & REGRIND
WEAKER THAN VIRGIN**



REPOLYMERIZATION of LDPE/PP – 50/50 Regrind

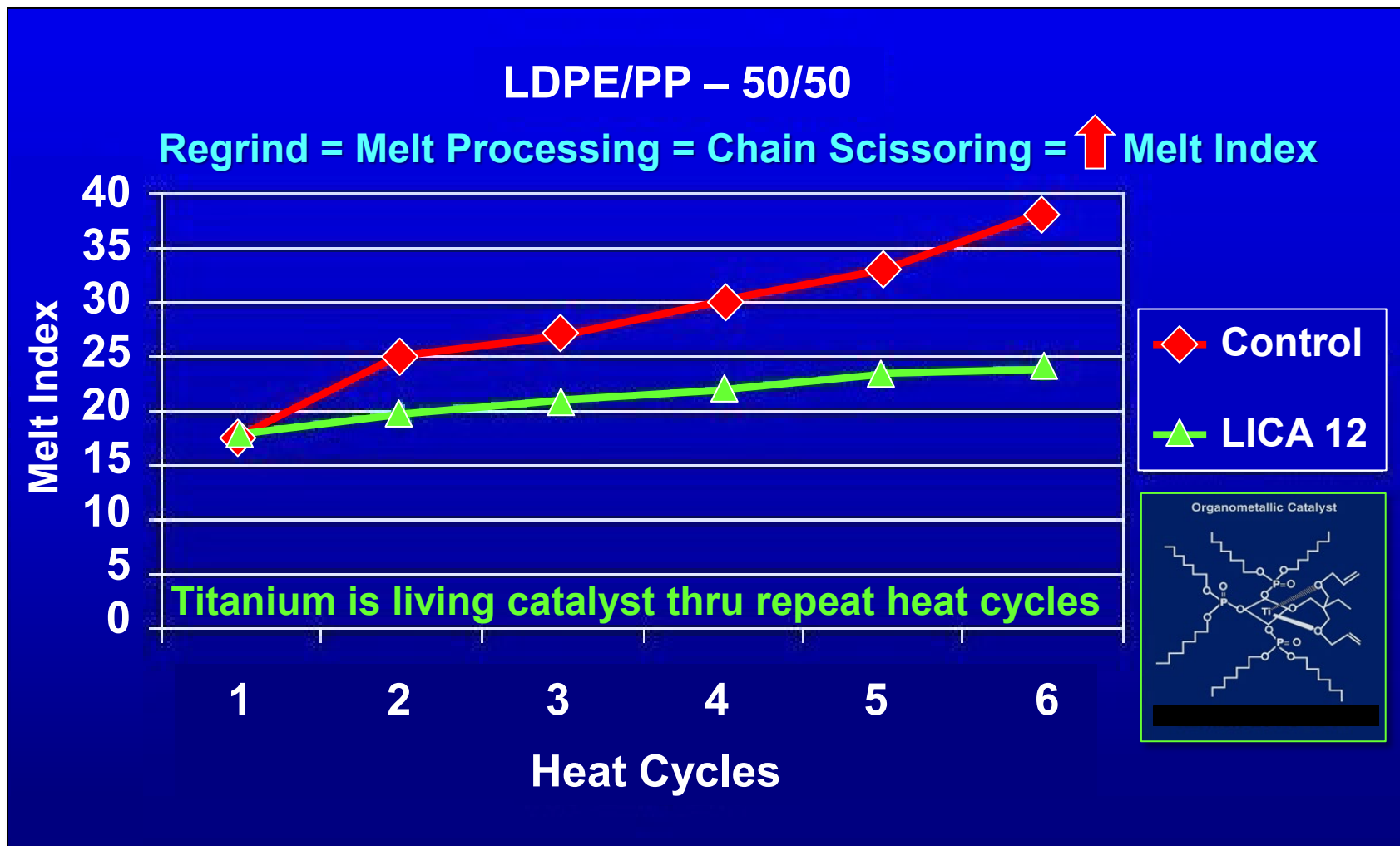
Using 1% Titanate Catalyst Pellet = 2 parts per thousand Titanate



**Chain Scissoring Effect - 6 Heat Cycles
on LDPE/PP – 50/50 Regrind
Without and With Titanium Catalysis**

REPOLYMERIZATION of LDPE/PP – 50/50 Regrind

Using 1% Titanate Catalyst Pellet = 2 parts per thousand Titanate





Mark Twain: "It ain't what you don't know that gets you in trouble. It's what you know that ain't so."



You can't plasticize without losing tensile

Titanate Catalysis Unfilled Ethylene Propylene Rubber (EPR)

0.2phr Titanate: It's like adding
15phr plasticizer to PVC while
increasing both
Tensile Strength & Elongation



1000g off 2-roll mill



0.2% Titanate

It's like adding
15phr plasticizer while
increasing both
Tensile Strength & Elongation



Titanium Catalysis Is How You Increase the COR of a Golf Ball

1000g off 2-roll mill

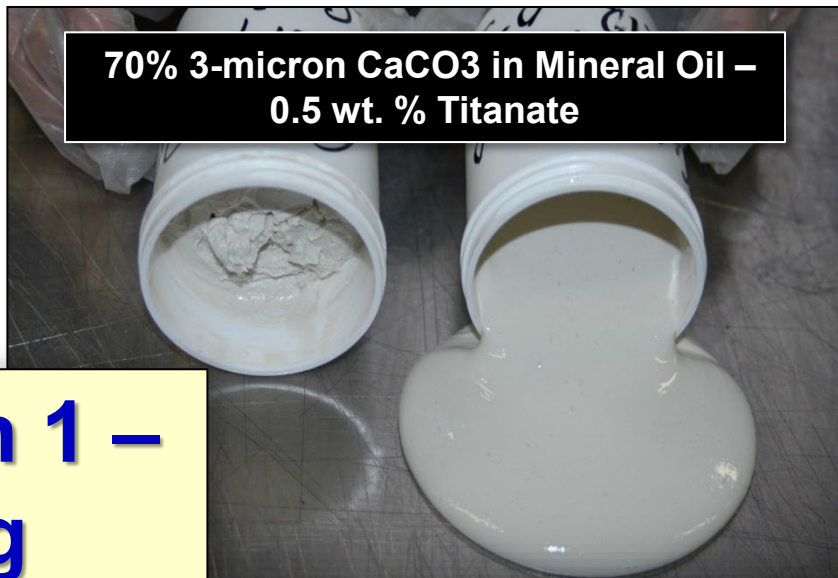
0.2% Titanate

**70%
3-micron
CaCO₃
Filled
PP
Homo-
Polymer
-
No White
Stress
Cracking**



Filler Coupling and Polymer Catalysis = Compatibility

70% 3-micron CaCO₃ in Mineral Oil –
0.5 wt. % Titanate



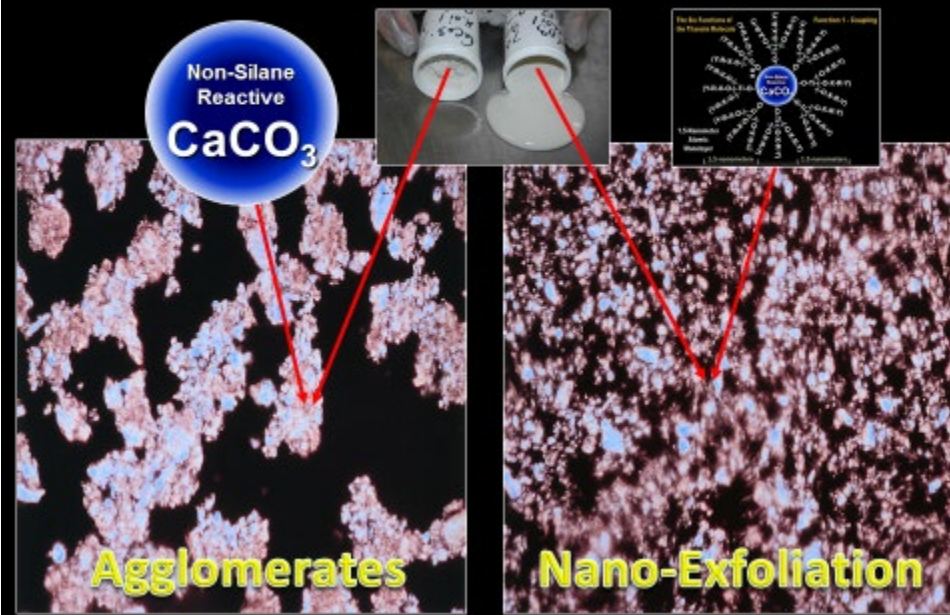
**Function 1 –
Coupling**

70% 3-micron CaCO₃ in PP
Homopolymer – 0.5 wt. % Titanate

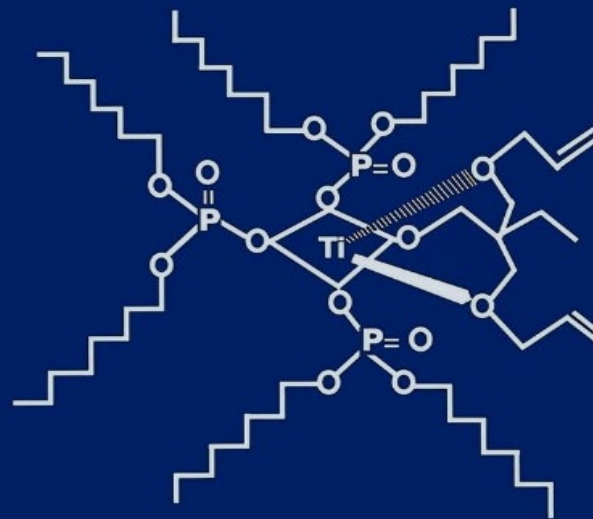


**Function 2 -
Catalysis**

Function 1 – Nano-Exfoliation



Organometallic Catalyst



Ken-React® LICA 12 Titanate
Function 2 - Catalysis

SPE VINYLTEC 2004 Technical Paper

The Application of Titanates in PVC

by
Salvatore J. Monte



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PETROCHEMICALS, INC.

140 East 22nd Street / P.O. Box 32
Bayonne, NJ 07002-0032 USA
Tel: 201-823-0000 Fax: 201-823-0091
Email: kenreact@kenrich.com
Web: www.kenrich.com

Function 2 - Catalysis

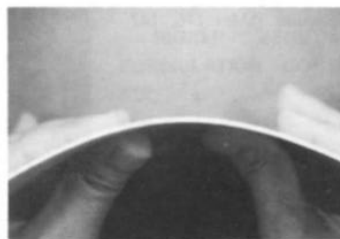


Figure 43 – A 50 phr CaCO_3 (5 micron), 1.0% KR 38S filled rigid PVC compression molded sheet showing excellent flexibility.

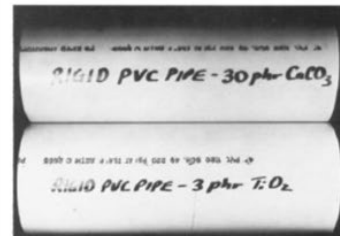


Figure 44 – Compare equivalent impact strength 3 phr CaCO_3 (marked as TiO_2) filled pipe titanate to a pipe containing 30 phr CaCO_3 (2.5 micron), 0.5% KR 38S.



Figure 45 – Extruded flexible PVC (Geon 86337) gray tubing as discussed in Table 38. of 1.0 percent CAPS (KR 55/PVC pellet) permitted a line-speed increase from 46.8 to 63.5 with zone temperatures: 20 to 40 °F lower.



Figure 32 – Flexible PVC washing machine tub splash ring containing 100 parts of CaCO_3 pretreated with 0.3% KR 44 shows lack of white stress cracking when subjected to 180° bend.



Figure 33 – Both azodicarbonamide foamed PVC plastisol luggage covering samples represent a successful reduction in the PVC: CaCO_3 ratio from 8:1 to 2:1 (increase in CaCO_3 from 12.5 to 33.3%) while maintaining excellent film strength using KR 138S. The sample on the left exhibited a reduction in “hand” or feel caused by a tighter cell structure induced by the titanate. The problem was resolved by quick quenching the titanate containing film (left) at 260°C as compared to 210°C (right). Film integrity was maintained and sponginess and the hand of the highly filled composite was better than the (lesser loaded) prior art control.



Figure 34 – 0.2% KZ TPP by weight of CaCO_3 allows increase in filler loading from 30 to 60 phr.

Function 2 - Catalysis

SPE VINYLTEC 2004 Technical Paper
The Application of Titanates in PVC
 by
 Salvatore J. Miano

Flexible
 Rigid
 Plastisols
 Foams

KENRICH
 PETROCHEMICALS

1401 East 12th Street P.O. Box 32
 Englewood, CO 80155-0032 USA
 Tel: 303-652-6000 Fax: 303-652-0851
 Email: ksmiano@kenrich.com
 www.kenrich.com

Figure 41 - A 50 phr CaCO₃ (5 micron), 1.0% K2 S2 O8 filled rigid PVC compression molded sheet showing excellent flexibility.

Figure 42 - Flexible PVC working machine roll which ring containing 100 parts of CaCO₃ processed with 0.2% K2 S2 O8 shows lack of white stress cracking when subjected to 180° bend.

Figure 43 - Bulk azodicarbonamide foamed PVC plasticol baggie covering sample represents a successful reduction in the PVC:CaCO₃ ratio from 2:1 to 1:1 increase in CaCO₃ while maintaining excellent film strength using 2.0 phr. The sample on left represents a "bad" film created by a lighter cell structure induced by the use was resulted by quick switching the streamer containing film data at 200°C in (right). This sample is unannealed and transparent and the head of the baggie was better than the three loaded prior are created.

Figure 44 - Compare extruded impact strength 2 phr CaCO₃ (loaded in TO) filled pipe streamer to a pipe containing 10 phr CaCO₃ (5 micron), 0.4% K2 S2 O8.

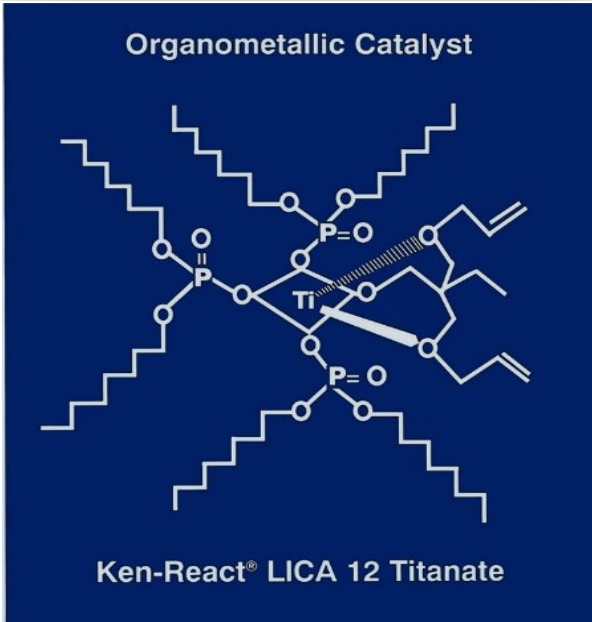
Figure 45 - Extruded flexible PVC (Genex 8017) pipe tubing as directed in Table 10, percent CAPS (2.5 phr PVC pellet) pretreated + line speed increase from 46.8 to 63.4 line temperature 21 to 41 °F lower.

Figure 24 - 6.2% K2 TPP by weight of CaCO₃ shows increase in film loading.

FINER FOAM CELL STRUCTURE

Titanate Increases Strength of AZO Foamed PVC Plastisol

No Titanate **With Titanate**



UNFILLED WB ACRYLIC / Automotive Tin Plate

Function 1 – ADHESION

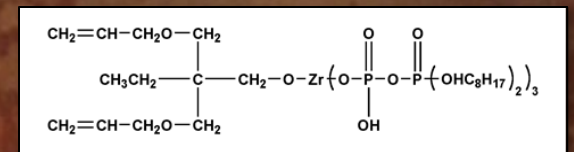
Proton Coordination to metal

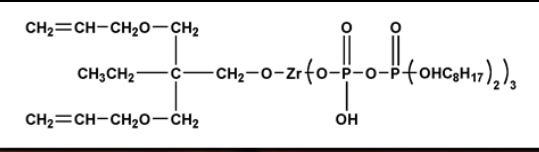
Function 2 – CATALYSIS

Flexibilize – 1" to 1/4" Mandrel Bend

Function 3 – PHOSPHATIZE

Anti-Corrosion at the scribe





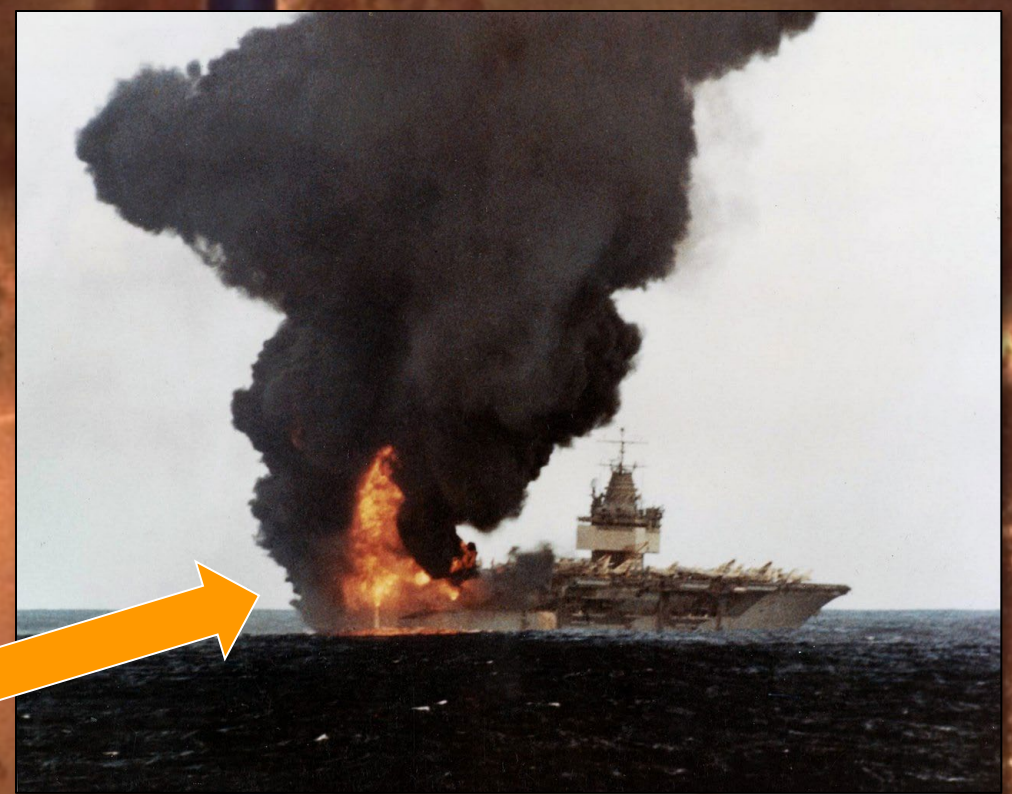
UNFILLED WB ACRYLIC Automotive Tin Plate

Function 1 – ADHESION

Function 2 – CATALYSIS

Function 3 – PHOSPHATIZE
for nano-Ti-Phosphorus

Intumescence – Flame Retardance



- **Nano-Titanium Phosphatize for Flame Retardance.**



Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents



Salvatore J. Monte – Kenrich Petrochemicals, Inc.

July 20, 2021 – 2:00-4:00pm



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**PROBLEM SOLVING
RECYCLE IS A
COMPLEX
MATERIALS CHALLENGE**



Insensitive Munitions & Energetic Materials (IMEM) Technology Symposium



April 7-8, 2021
Virtual Conference

**PROBLEM SOLVING
INSENSITIVE MUNITIONS
IS A COMPLEX
MATERIALS CHALLENGE**

Advanced Insensitive Munitions & Energetic Materials Concepts Using 1.5-Nanometer Titanates & Zirconates

Salvatore J. Monte

simonte@4kenrich.com · www.4kenrich.com



Distribution Statement A, Approved for public release. Distribution Unlimited

Solved The 2-Decade Problem of Unplanned Detonation

Nano-Titanium Phosphatize for Flame Retardance



Classified TOP SECRET for DOD IM Program



RDX/CAB & Plastic Bound Explosives

Issued Mar 6, 2001

(12) **United States Patent**
Monte et al.

(10) Patent No.: **US 6,197,135 B1**
(45) Date of Patent: ***Mar. 6, 2001**

(54) **ENHANCED ENERGETIC COMPOSITES**

(75) Inventors: **Salvatore J. Monte**, Staten Island, NY (US); **Gerald Sugerman**, Allendale, NJ (US)

(73) Assignee: **Kenrich Petrochemicals, Inc.**, Hudson, NJ (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **06/841,471**

(22) Filed: **Feb. 18, 1986**



US006197135B1

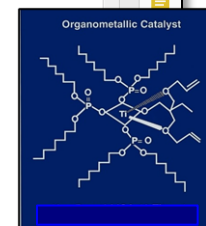
3,932,353	*	1/1976	Mastrolia et al.	149/19.2
4,050,968	*	9/1977	Goldhagen et al.	149/19.1
4,051,207	*	9/1977	Brachert et al.	149/100
4,139,404	*	2/1979	Goddard et al.	149/19.2
4,260,437	*	4/1981	Nakagawa et al.	149/19.9
4,352,700	*	10/1982	Hoffman	149/19.2
4,354,884	*	10/1982	Williams	149/10
4,597,924	*	7/1986	Allen et al.	149/19.1
4,713,127	*	12/1987	Muller et al.	149/98
4,985,094	*	1/1991	Nahlovsky et al.	149/19.9

* cited by examiner

Primary Examiner—Edward A. Miller
(74) Attorney, Agent, or Firm—Darby & Darby

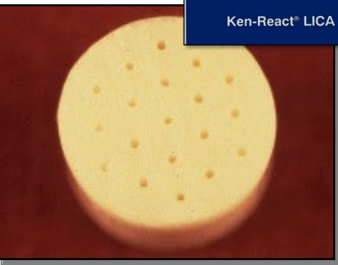
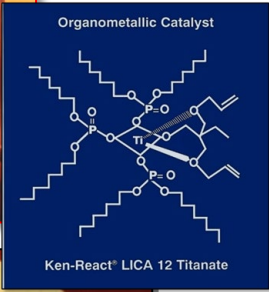
(52)

The instant invention relates to the use of certain selected neoalkoxy organo-titanates and organo-zirconates in energetic compositions to improve their processability, physical



Held under DoD
Secrecy Orders
for
15-years-1-month

Filed Feb. 18, 1986



0.5% LICA-12 Titanate on Vulnerability of 85% HMX / Al Filled CAB Explosive US Army Patent – “Insensitive Explosive Composition”

Control

Sensitive

0.25%
LICA 12

Brittle
Extrudate

0.50%
LICA 12

Patentable
Insensitive

0.75%
LICA 12

“ Too Inert ”



US005472531A

United States Patent [19]
Turci et al.

[11] **Patent Number:** 5,472,531
[45] **Date of Patent:** Dec. 5, 1995

[54] **INSENSITIVE EXPLOSIVE COMPOSITION**

Distribution Statement A, Approved for public release. Distribution Unlimited
4,853,051 8/1989 Bennett et al. 149/19.4
5,240,523 8/1993 Willer 149/19.4

[75] Inventors: **Joseph Turci**, Long Valley, N.J.; **Mark Mezger**, Mt. Bethel, Pa.; **Bernard Strauss**, Rockaway; **Thelma Manning**, Montville, both of N.J.

Primary Examiner—Donald P. Walsh
Assistant Examiner—Anthony R. Chi
Attorney, Agent, or Firm—Anthony T. Lane; Edward Goldberg; John E. Callaghan

[73] Assignee: **The United States of America** as represented by the Secretary of the Army, Washington, D.C.

[57] **ABSTRACT**

The explosive blasting composition in this invention contains 1 to 40 percent Aluminum powder, 40 to 80 percent Cyclotetramethylene Tetranitramine, 4 to 15 percent Cellulose Acetate Buterate, 5 to 20 percent of 1:1 mixture of bis 2,2-dinitropropyl acetate and bis 2,2-dinitropropyl formal, and, and 0.25 to 0.75 percent Tri (dioctyl Phosphato) Titanate.

[21] Appl. No.: 385,843

[22] Filed: Feb. 1, 1995

Related U.S. Application Data

[63] Continuation of Ser. No. 983,954, Dec. 1, 1992, abandoned.

[51] Int. Cl.⁶ C06B 25/34

[52] U.S. Cl. 149/92; 149/88; 149/109.6

[58] Field of Search 149/92, 88, 109.6

The method of making the above composition consists of combining Cyclotetramethylene Tetranitramine, Cellulose Acetate Buterate, 1:1 bis 2,2-dinitropropyl acetate and bis 2,2-dinitropropyl formal, and tri (dioctyl phosphato) titanate, mixed at an elevated temperature for a period of time. Prior to blowdown, the Aluminum powder is added. to

Function 1 – Dosage; Function 2 - Catalysis
Function 3 – Nano- Ti-Phosphatization



US005472531A

United States Patent [19]

Turci et al.

[11] Patent Number: 5,472,531

[45] Date of Patent: Dec. 5, 1995

Distribution Statement A, Approved for public release. Distribution Unlimited

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Primary Examiner—Donald P. Walsh
Assistant Examiner—Anthony R. Chi
Attorney, Agent, or Firm—Anthony T. Lane; Edward Goldberg; John E. Callaghan

[73] Assignee: The United States of America as represented by the Secretary of the Army, Washington, D.C.

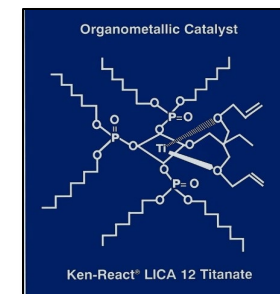
[57] ABSTRACT

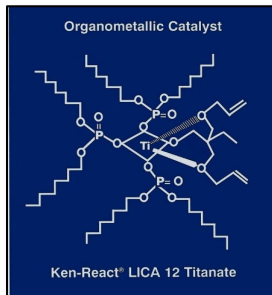
Issued Dec. 5, 1995

- [21] • Aluminum Powder
- [22] • (HMX)
- [63] • Cellulose Acetate Butyrate
- [51] • Bis 2,2-dinitropropyl acetate
- [52] • Bis 2,2-dinitropropyl formal
- [58] • Tri(dioctyl Phosphato) Titanate
@ 0.25 to 0.75 percent

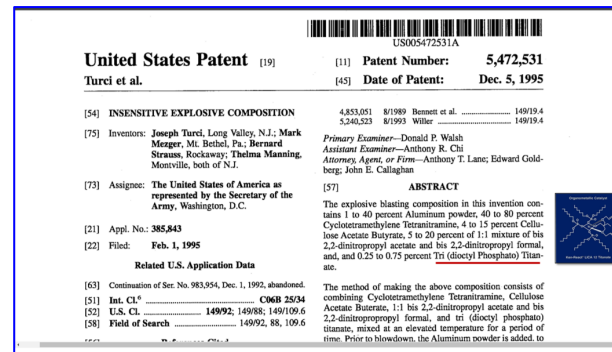
The explosive blasting composition in this invention contains 1 to 40 percent Aluminum powder, 40 to 80 percent Cyclotetramethylene Tetranitramine, 4 to 15 percent Cellulose Acetate Butyrate, 5 to 20 percent of 1:1 mixture of bis 2,2-dinitropropyl acetate and bis 2,2-dinitropropyl formal, and, and 0.25 to 0.75 percent Tri (dioctyl Phosphato) Titanate.

The method of making the above composition consists of combining Cyclotetramethylene Tetranitramine, Cellulose Acetate Butyrate, 1:1 bis 2,2-dinitropropyl acetate and bis 2,2-dinitropropyl formal, and tri (dioctyl phosphato) titanate, mixed at an elevated temperature for a period of time. Prior to blowdown, the Aluminum powder is added. to





BACKGROUND



...Safety is the uppermost in the minds of the military when fielding such compositions.

...We have found that our composition (based on 0.5% LICA 12) is the only composition at present, that can meet safety requirements. Various tests have shown that our composition performs as well or even better than any experimental blasting composition known to date. In fact our tests have shown that it performs ten percent better than the compositions of the art.



METHOD OF MAKING PREFERRED EMBODIMENT OF THE INVENTION

Nano-Titanium Phosphatize for Flame Retardance

Column 2, Line 18. Optionally LICA-12 may be used but not below 0.25% because it does not have the structural integrity to be able to cut. However, again, above 0.75% the composition is too inert.

Titanium Catalysis

REPOLYMERIZATION

Hosted VINYLTEC 2010 as President

Voting Member & Recycle Supporter

SPE Fellow & Honored Service Member

PPA Board of Governors – Nominating Member

450- ACS CAS Abstracted Worldwide

32-US Patents Filed Worldwide

Classified TOP SECRET for DOD IM

Salvatore J. Monte, President

Kenrich Petrochemicals, Inc.

United States Patent [19] [11] **Patent Number:** 4,657,988
 [45] **Date of Patent:** Apr. 14, 1987

[54] **REPOLYMERIZATION**

[75] **Inventors:** Gerald Sugerman, Allendale, N.J.; Salvatore J. Monte, Staten Island, N.Y.

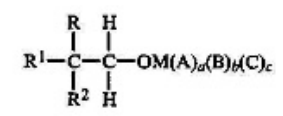
[73] **Assignee:** Kenrich Petrochemicals, Inc., Bayonne, N.J.

[21] **Appl. No.:** 834,794

[22] **Filed:** Feb. 28, 1986

Primary Examiner—Lucille M. Phynes
Attorney, Agent, or Firm—Bert J. Lewen; Henry Sternberg

[57] **ABSTRACT**
 Polymeric materials are repolymerized by intensely admixing the polymer with an additive having the formula:



wherein M is titanium or zirconium, R, R¹ and R² are each a monovalent alkyl, alkenyl, alkynyl, aralkyl, aryl or alkaryl group having up to 20 carbon atoms or a halogen or ether substituted derivative thereof, and, in addition, R² may also be an oxy derivative or an ether substituted oxy derivative of said groups; A, B, and C are each a monovalent aroxy, thioaroxy, diester phosphate, diester pyrophosphate, oxyalkylamino, sulfonyl or carboxyl containing up to 30 carbon atoms; and a+b+c=3. The repolymerized polymers have improved physical properties and higher heat distortion temperatures, experience less thermal degradation and show greater solvolysis resistance than the polymers prior to the repolymerization.

Publication Data

[63] Continuation-in-part of Ser. No. 725,437, Apr. 22, 1985, which is a continuation-in-part of Ser. No. 609,727, May 14, 1984, abandoned.

[51] **Int. Cl.⁴** C08G 63/76

[52] **U.S. CL.** 525/437; 525/390; 525/444; 525/453; 525/534; 528/17; 528/56; 528/207; 528/279; 528/286; 528/288

[58] **Field of Search** 525/390, 437, 444, 453, 525/534; 528/17, 56, 207, 279, 286, 288

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,036,796	7/1977	Sugiyama et al.	525/437	X
4,115,371	9/1978	Bier et al.	528/286	X
4,148,989	4/1979	Tews et al.	525/437	
4,452,970	6/1984	Brunelle	528/279	
4,454,312	6/1984	Kuze et al.	528/279	X
4,482,700	11/1984	Kühnrich et al.	528/279	

5 Claims, No Drawings

**One of 32-US Patents:
 "REPOLYMERIZATION"
 Mechanical Properties
 of 11 – Unfilled Plastics**

6-Ti/Zr @ 4 dosages

REPOLYMERIZATION 11 – Unfilled Plastics *** 6-Ti/Zr @ 4 dosages

Unfilled Plastics Data

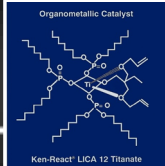
 ABS	 Acetal	 Acrylic	 CAB	 Nylon6	 PC
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The Extruder acts as a Polymerization Reactor for Organometallic Catalysis

 PP	 HDPE	 PBT	 PPO	 PS
 PP	 PE-HD	 PET	 PPO	 PS

UNFILLED PP

EFFECT OF NEOALKOXY TITANATE
CAPOW L 12/H ON THE PROPERTIES
OF INJECTION MOLDED UNFILLED PP



Coupling Agent Additive	Weight % of Resin	Tensile Yield K psi	% Elong. @ Break	Flexural Modulus psi x 10 ⁴	Notched Izod (R.T.) ft.lb./in.
Control	0.00	4.9	120	21	0.7
L 12/H	0.10	5.4	127	24	0.9
L 12/H	0.30	5.7	142	26	1.1
L 12/H	0.50	5.6	148	22	1.4
L 12/H	0.75	5.2	139	21	1.1

Titanium Catalysis

Catalytic dosages:
2 to 3 pts titanate /
1,000 pts polymer

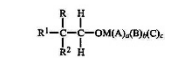
United States Patent [19] Patent Number: **4,657,988**
Date of Patent: **Apr. 24, 1988**

[54] **REPOLYMERIZATION**
[73] Inventors: Salvatore J. Monte, Staten Island, N.Y.

Primary Examiner—Lucille M. Phynes
Attorney, Agent or Firm—Rost, L...
Sternberg

[73] Assignee: Kenrich Petrochemicals, Inc., Bayonne, N.J.
[21] Appl. No.: 834,794
[22] Filed: Feb. 28, 1986

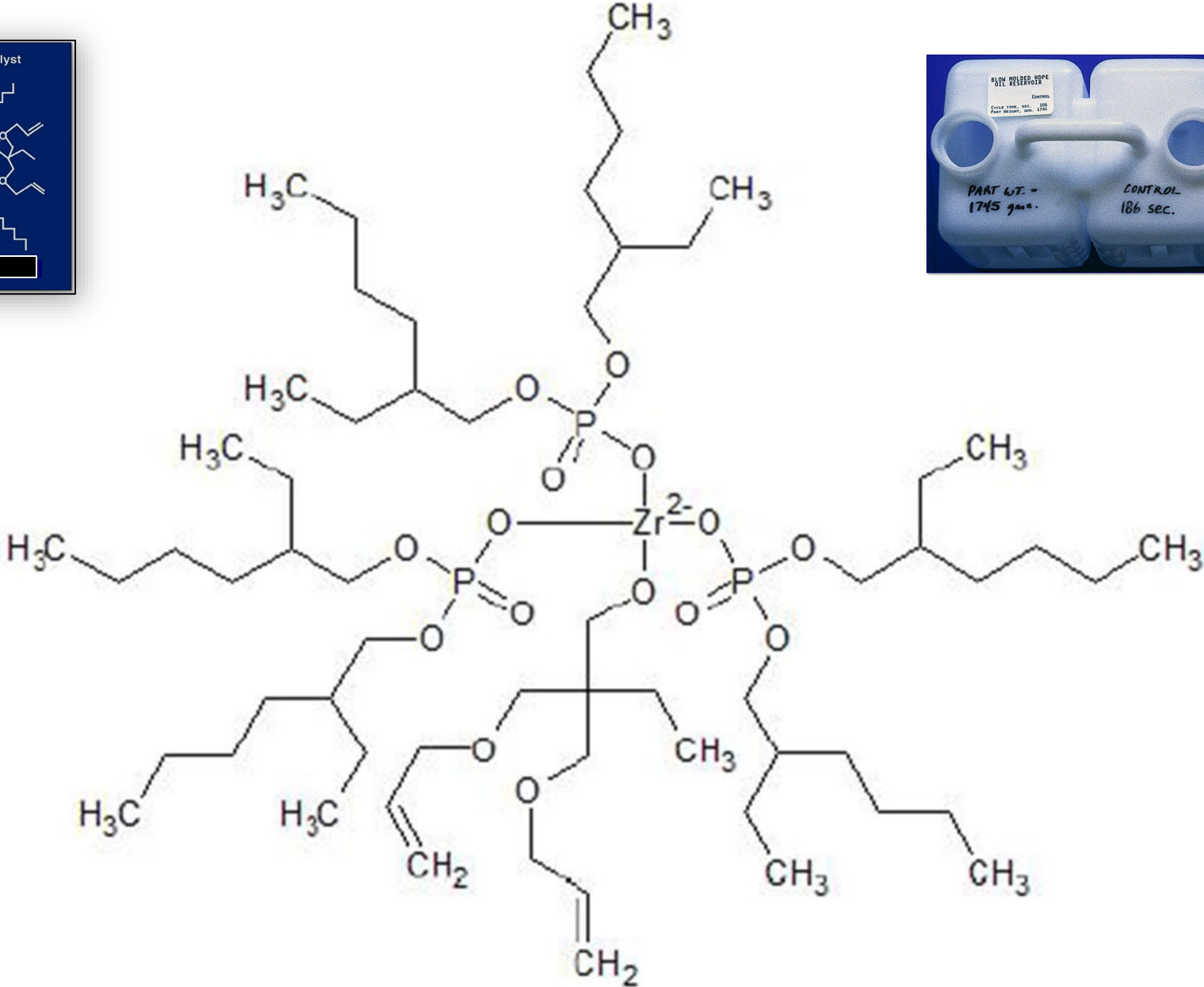
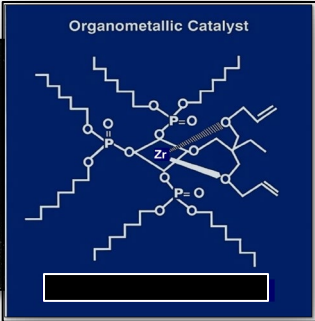
[57] **ABSTRACT**
Polymeric materials are repolymerized by intensely admixing the polymer with an additive having the formula:



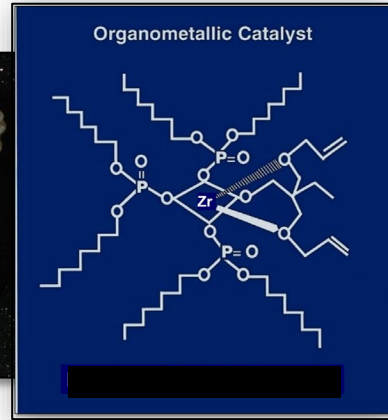
wherein M is titanium or zirconium, R, R¹ and R² are each a monovalent alkyl, alkenyl, alkynyl, aralkyl, aryl or alkaryl group having up to 20 carbon atoms or a halogen or other substituted derivative thereof, and, in addition, R² may also be an oxy derivative or an ether substituted oxy derivative of said groups; A, B, and C are each a monovalent aroxy, thioaroxy, diester phosphate, diester pyrophosphate, oxyalkylamino, sulfonyl or carbonyl containing up to 30 carbon atoms; and n + m = 3. The repolymerized polymers have improved physical properties and higher heat distortion temperatures, experience less thermal degradation and show greater solvolysis resistance than the polymers prior to the repolymerization.

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[63] Continuation-in-part of Ser. No. 725,437, Apr. 22, 1985, which is a continuation-in-part of Ser. No. 609,727, May 14, 1984, abandoned.
[51] Int. Cl.⁴ C08G 63/76
[52] U.S. Cl. 525/444; 525/453; 525/534; 528/17; 528/56; 528/207; 528/279; 528/286; 528/288
[58] Field of Search 525/390, 437, 444, 453, 525/534; 528/17, 56, 207, 279, 286, 288
[56] **References Cited**
U.S. PATENT DOCUMENTS
4,036,796 7/1977 Sugiyama et al. 525/437 X
4,115,371 9/1978 Bier et al. 528/286 X
4,148,989 4/1979 Tevis et al. 525/437
4,452,970 6/1984 Brunelle 528/279
4,454,312 6/1984 Kuze et al. 528/279 X
4,482,700 11/1984 Kühnrich et al. 528/279

HDPE Re grind Using 0.2% Zirconate Catalyst as Pellet Masterbatch



HDPE Regrind Using 0.2% Zirconate Catalyst as Pellet Masterbatch



- Used 100% Regrind.
- Reduced Part Wt. from **1745g** to **1500g** to equivalent drop weight impact strength.
- Reduced Cycle Time **156** to **116 seconds**.



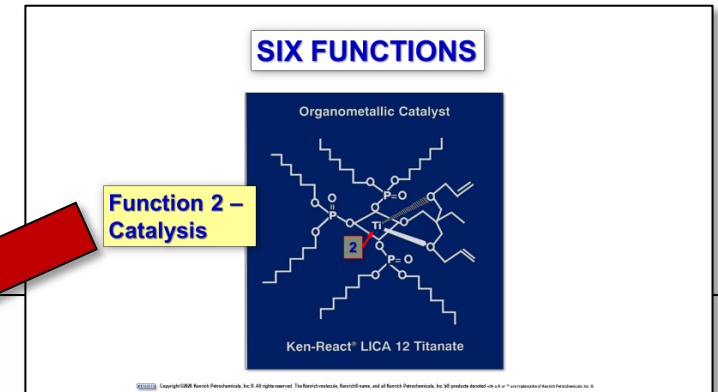


**New thinking in
Compatibilization &
Polymer Regeneration via Ti / Zr
Coupling & Catalysis**

**to reduce the need & cost to sort materials so as to broaden
Mechanical Recycling Compounding
Capability**

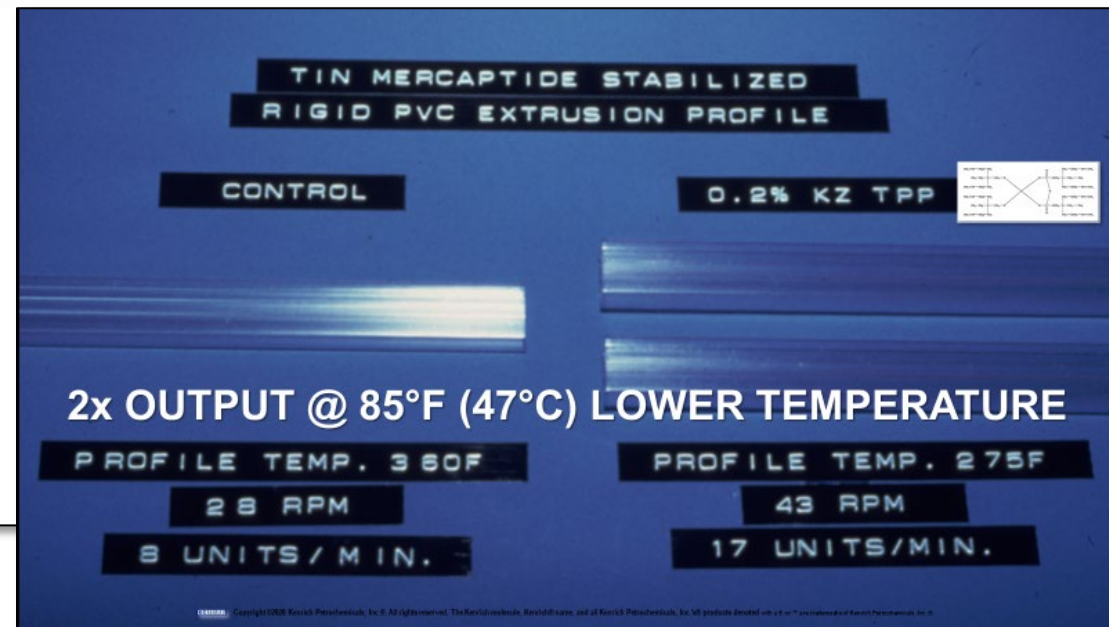
**PVC, PC & PA6 & other Engineering Plastics can be
processed at much lower temperatures.**

Advanced Solutions in Mechanical Recycling with 1.5-Nanometer Titanate Catalysts/Coupling Agents



(2) Titanium, Zirconium & Aluminum Polymer Catalysis – without or with filler allows:

0.2% Zirconate in recycled unfilled / transparent rigid PVC to extrude twice as fast as the control @ 24% lower temp.



Advanced Solutions in Mechanical Recycling with
1.5-Nanometer Titanate Catalysts/Coupling Agents

Transparent Recycled PVC Extrusion

TIN MERCAPTIDE STABILIZED
RIGID PVC EXTRUSION PROFILE

CONTROL

0.2% KZ TPP



360°F

275°F

2x OUTPUT @ 85°F (47°C) LOWER TEMPERATURE

PROFILE TEMP. 360F

PROFILE TEMP. 275F

28 RPM

43 RPM

8 UNITS/MIN.

17 UNITS/MIN.

Advanced Solutions in Mechanical Recycling with 1.5-Nanometer Titanate Catalysts/Coupling Agents

Transparent Recycled PVC Extrusion

The image shows a screenshot of a web browser displaying a search result for "PVC heat sensitivity in recycle". The search results are from omnexus.specialchem.com and plasticsrecycling.org. Large red and yellow callouts are overlaid on the page, indicating "360°F" and "275°F".

360°F

275°F

The window of PVC RECYCLE processing temperatures is made wider.

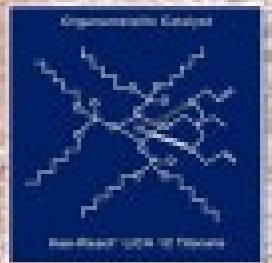
PC IS A CONDENSATION POLYMER

Molded @100°C lower Temp. (188°C vs. 304°C)

- Maleated polymer compatibilizers work on Addition Polymers but depolymerize Condensation Polymers.
- Maleated polymers couple polymers but not fillers.


40% FG/PC Control – Injection Molded @ 304°C (580°F)

1% Ken-React® CAPS® – Injection Molded @ 188°C (370°F)





**TIN MERCAPTIDE STABILIZED
RIGID PVC EXTRUSION PROFILE**

CONTROL **0.2% KZ TPP** 

2x OUTPUT @ 85°F (47°C) LOWER TEMPERATURE

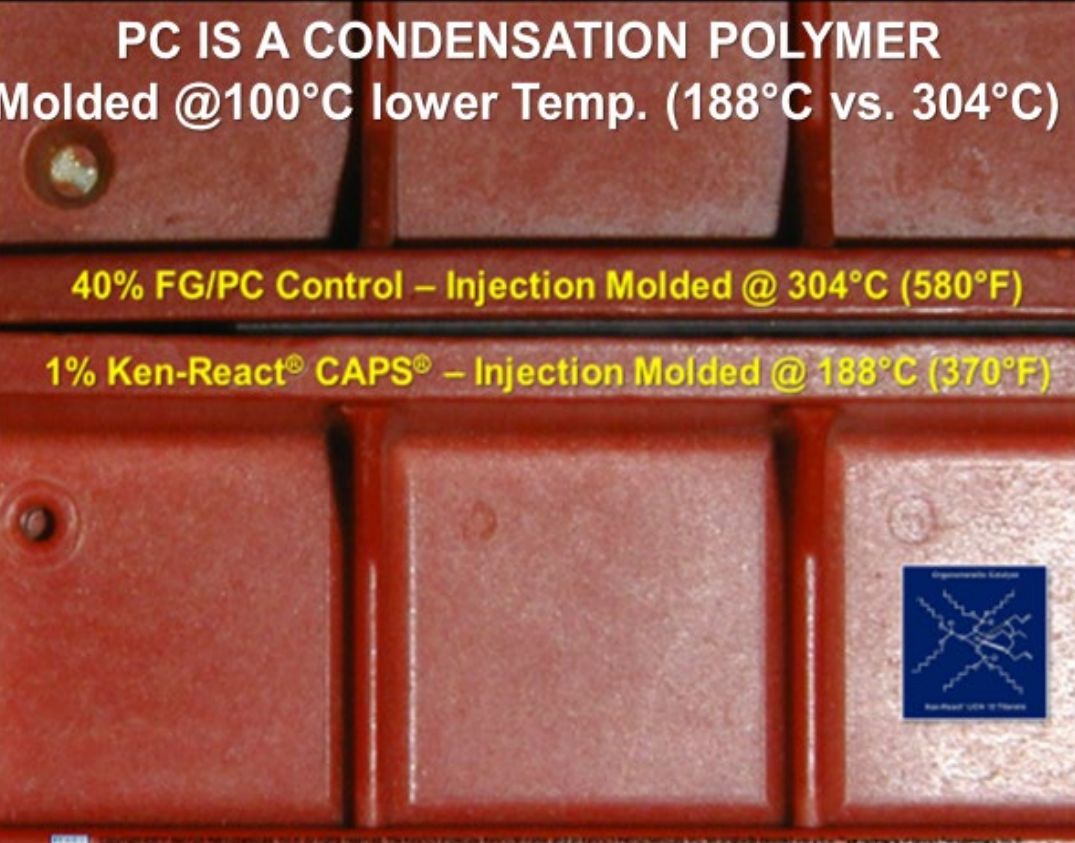
Parameter	Control	0.2% KZ TPP
PROFILE TEMP.	360F	275F
RPM	28 RPM	43 RPM
Output	8 UNITS / MIN.	17 UNITS / MIN.


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PC IS A CONDENSATION POLYMER
Molded @100°C lower Temp. (188°C vs. 304°C)

40% FG/PC Control – Injection Molded @ 304°C (580°F)

1% Ken-React® CAPS® – Injection Molded @ 188°C (370°F)

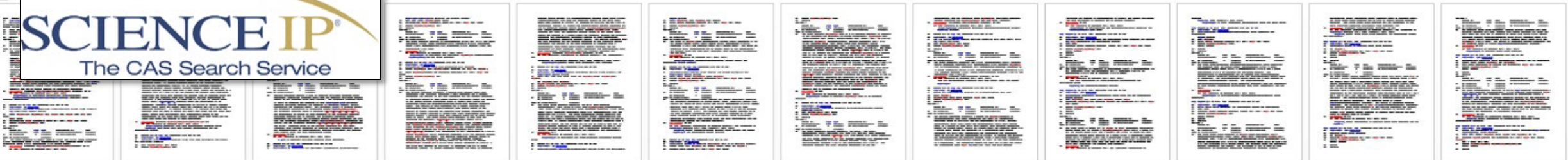




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71-ABSTRACTS on POLYBLENDs – sjmonte@4kenrich.com



TIN MERCAPTIDE STABILIZED RIGID PVC EXTRUSION PROFILE

CONTROL **0.2% KZ TPP**



2x OUTPUT @ 85°F (47°C) LOWER TEMPERATURE

PROFILE TEMP. 360F **PROFILE TEMP. 275F**

28 RPM **43 RPM**


8 UNITS/MIN. **17 UNITS/MIN.**

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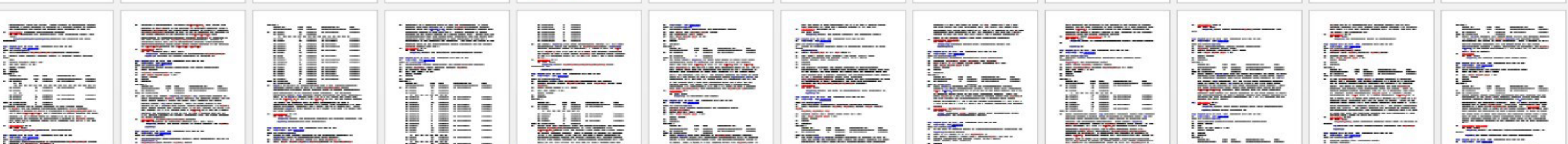
PC IS A CONDENSATION POLYMER
Molded @100°C lower Temp. (188°C vs. 304°C)

40% FG/PC Control – Injection Molded @ 304°C (580°F)

1% Ken-React® CAPS® – Injection Molded @ 188°C (370°F)



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71-ABSTRACTS on POLYBLENDs – sjmonte@4kenrich.com

KEY SEARCH WORD: “BLEND”
44 References to “PVC”

PVC 45-55, polycarbonate 20-25

TI Polyvinyl chloride-polycarbonate alloy with good weathering resistance and antistatic property

PA Yin, Peihua, Peop. Rep. China
SO Faming Zhuanli Shenqing, 4pp.
LA Chinese
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 104861378	A	20150826	CN 2014-10847633	20141229
PRAI	CN 2014-10847633		20141229		

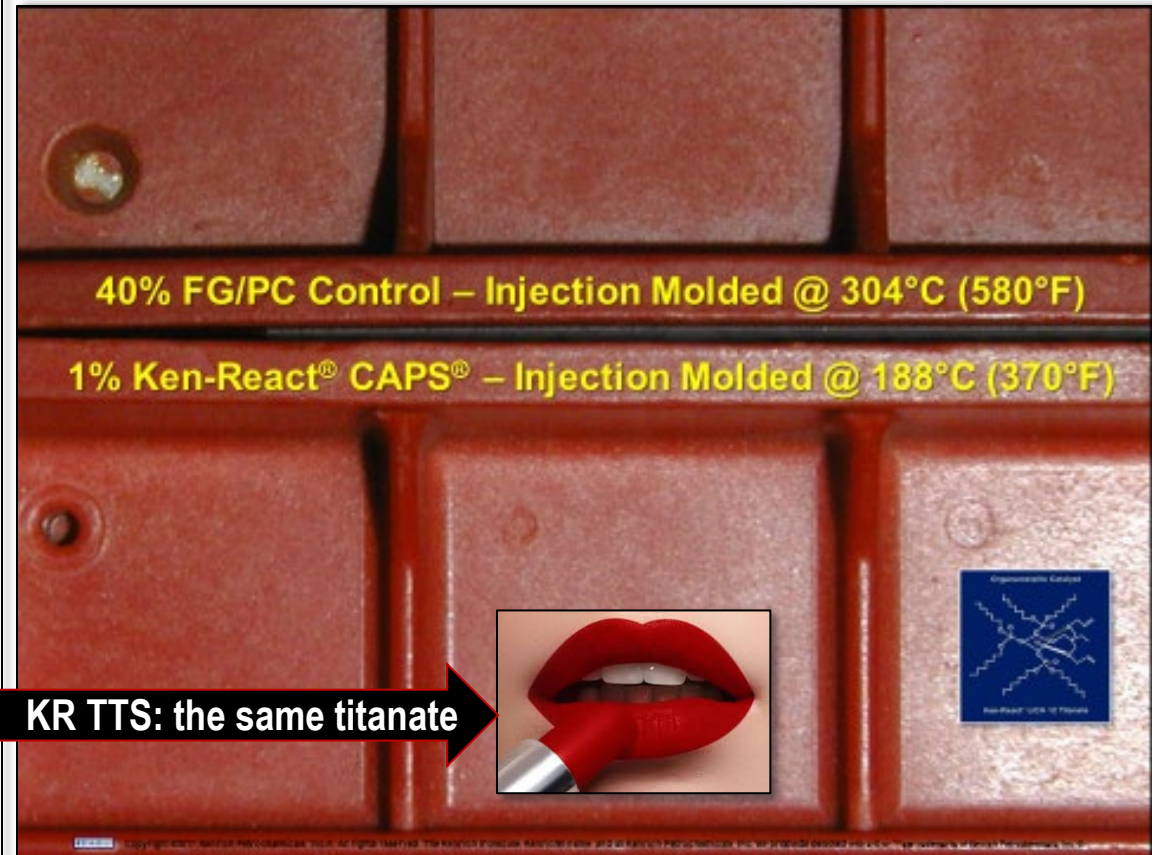
AB The present invention provides polyvinyl chloride (PVC)-polycarbonate alloy with good weathering resistance and antistatic property, comprising the following components by mass percentages: PVC 45-55, polycarbonate 20-25, SMA 2-4, ACR 3-6, attapulgite 2-8, melamine cyanurate 4-7, dioctyl phthalate 3-6, antistatic agent 1-3, UV absorber 1-2, calcium-zinc composite stabilizer 0.1-1, pentaerythritol stearate 0.5-1, and antioxidant 1010 0.1-0.5. The described PVC has average d.p. of 800-1,200, and weight average mol. weight of 50,000-120,000.

IT 61417-49-0, KR TTS

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

(polyvinyl chloride-polycarbonate alloy with good weathering resistance and antistatic property)

PVC temperatures range from:
500°F (260°C) to 212°F (100°C);
PC temperatures reduced from:
580°F (304°C) to 370°F (188°C);



PVC 45-55, polycarbonate 20-25

TI Polyvinyl chloride-
polycarbonate alloy with good
weathering resistance and
antistatic property

PA Yin Beihua Beon Ben China

Lower Temps.
Opens the
Innovation
Window to PVC
Copolymerization

PVC temperatures range from:
500°F (260°C) to 212°F (100°C);
PC temperatures reduced from:
580°F (304°C) to 370°F (188°C);





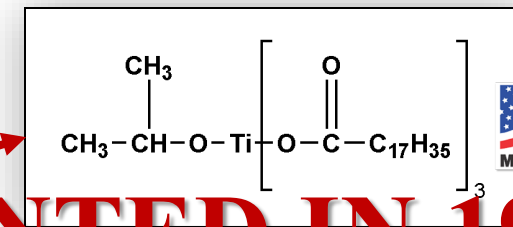
L5 ANSWER 152 OF 439 CA COPYRIGHT 2016 ACS on STN
AN 163:386826 CA Full-text <<LOGINID::20160920>>

TI Flame-retardant anti-aging polyvinyl chloride-polyethylene blended composite plastic

PA Yin, Peihua, Peop. Rep. China
SO Faming Zhuanli Shenqing, 5pp.
LA Chinese
FAN.CNT 1

INVENTED IN 2014

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	---	-----	-----	-----
PI CN 104861353	A	20150826	CN 2014-10838685	20141230
PRAI CN 2014-10838685		20141230		



INVENTED IN 1973

AB The title composite plastic comprises (by mass%): PVC 35-50, polyethylene 20-25, GMA-St-AN 2-4, SEBS 4-6, ACR 2-4, nano aluminum hydroxide 3-8, melamine cyanurate 4-7, zinc borate 1-4, light stabilizer 622 1-2, light stabilizer 944 1-2, dioctyl phthalate 5-8, calcium-zinc composite stabilizer 0.5-1.5, calcium stearate 0.5-1, iso-Pr triisostearoyl titanate 0.1-0.5, and antioxidant 1010 0.1-0.5. **The**

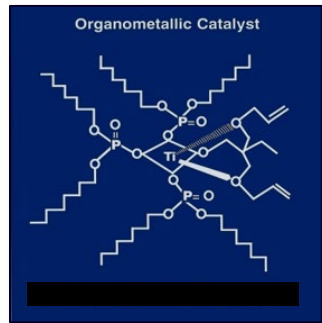
invention combines the resp. original advantages of PVC and polyethylene, and has excellent flame retardancy, anti-aging property, thermal stability and processability, and good mech. strength.

IT 61417-49-0, Iso-propyl triisostearoyl titanate, KR TTS

RL: MOA (Modifier or additive use); USES (Uses)
(flame-retardant anti-aging polyvinyl chloride-polyethylene blended composite plastic)

Compatibilizing Recycled PET/PC – 80/20 Blend Using 0.3% CAPOW[®] Titanate Catalyst – 100°C lower Temp.

Copolymerization of Two Dissimilar Condensation Polymers



Extruded@ 180°C using
0.3%  Titanate Catalyst
vs. 280°C without the Additive



Regrind: Compatibilizing HDPE / Nylon Film Using 0.2% Titanate Catalyst



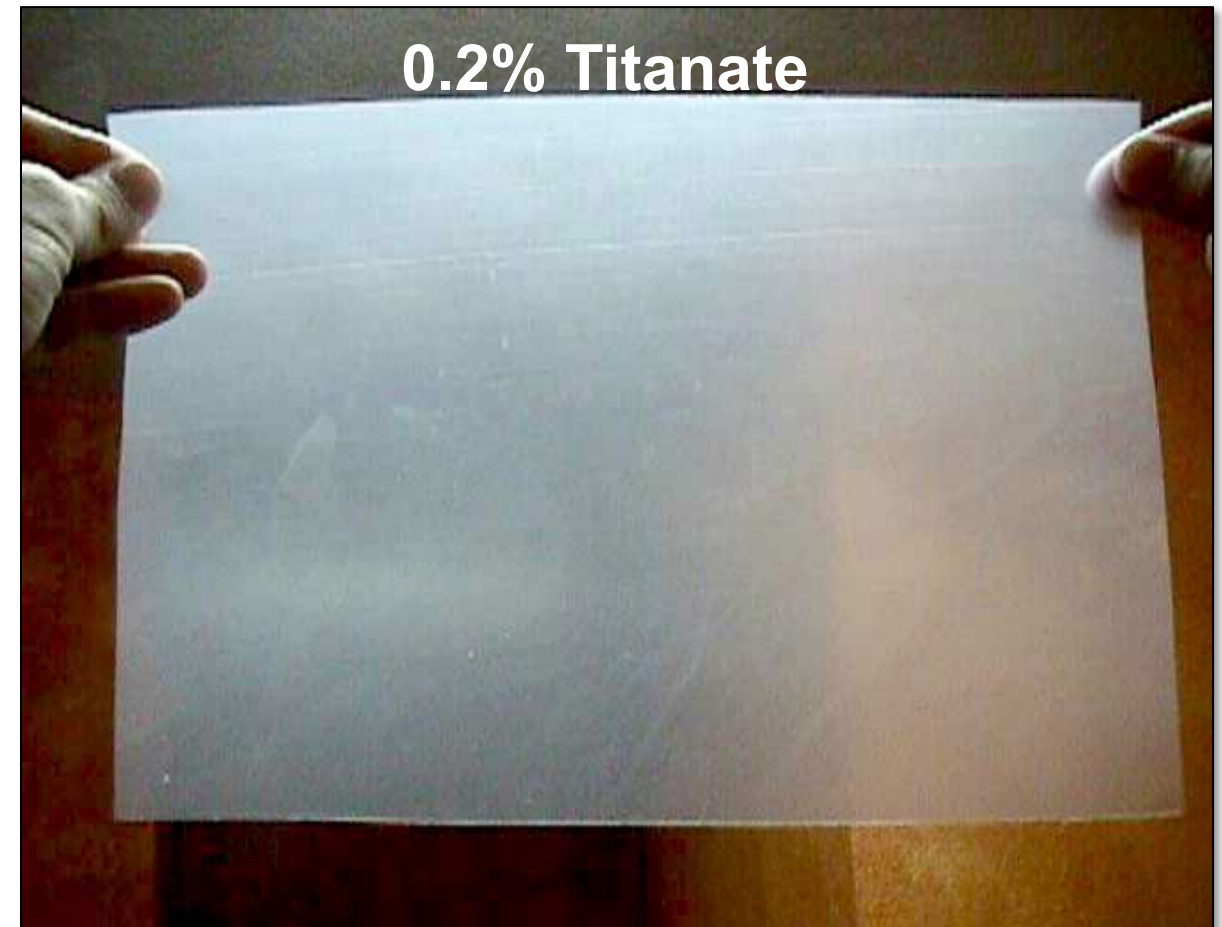
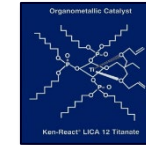
HDPE – Addition
Polymer

+

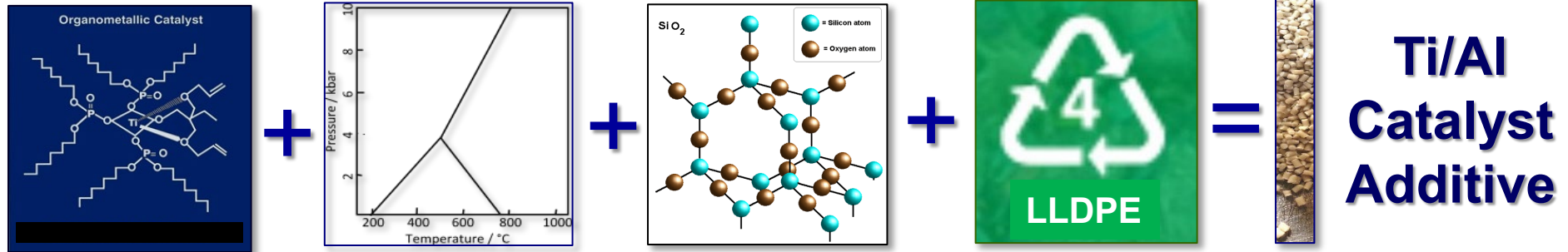


NYLON – Condensation
Polymer

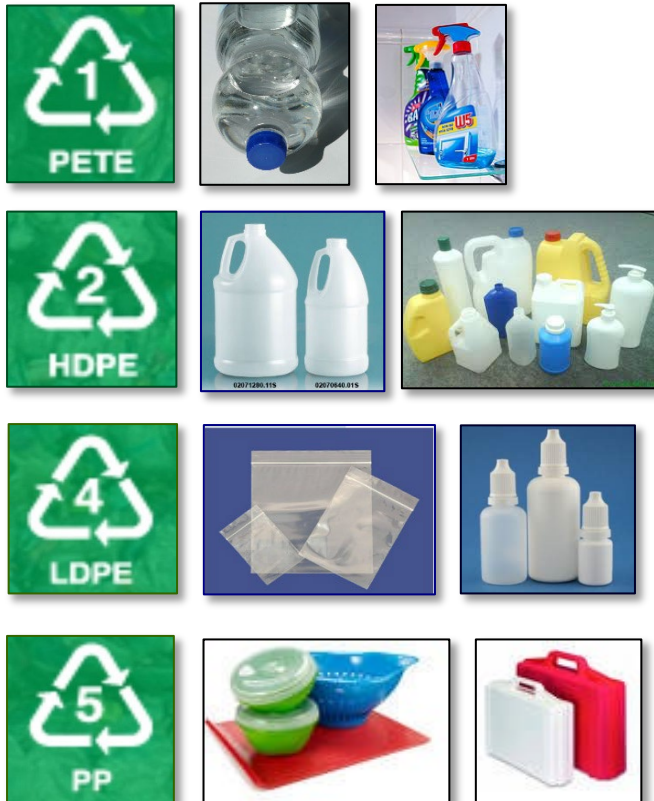
+



Compatibilization of Addition & Condensation Polymers



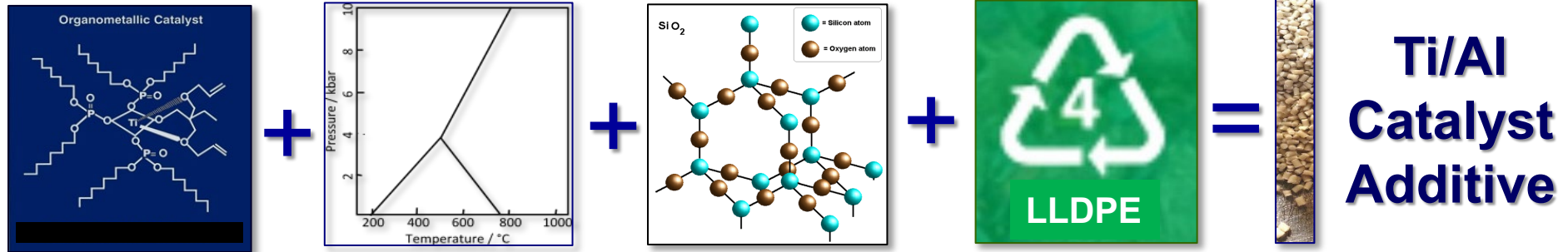
Incompatibility PP & PET & PE



There are THREE Types of Compatibilizers:

1. **Bi-Polar Thermoplastics:** Links two dissimilar polymers. Works for PIR.
2. **Maleated PP /Polymers:**
 - Couples Addition polymers.
 - Does not couple fillers.
 - Often, depolymerizes Condensation polymers.
3. **Ti/Zr Coupling/Catalyst:** Synergistic with 1. & 2. Catalyzes all polymers/Couples all inorganic & organic fillers, pigments, additives, etc.

Compatibilization of Addition & Condensation Polymers



Incompatibility PP & PET & PE

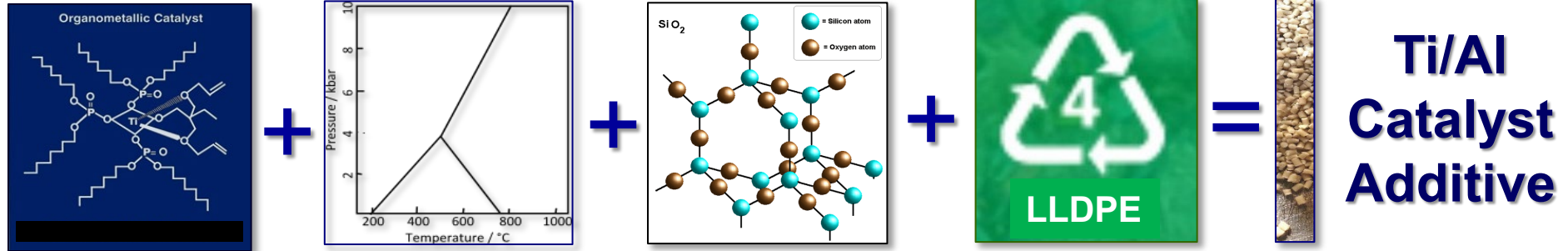


The effect of 1.5% **Ken-React® CAPS® KPR® 12/LV** on Brabender melt compounded **PP/PET/PE** Recycle Plastics @ 9% lower temperatures. Larger batches later extruded.

Materials obtained from post-industrial waste streams:

1. **LLDPE** is an Addition polymer.
2. **PP** is an Addition polymer.
3. **PET** is a Condensation polymer.

Compatibilization of Addition & Condensation Polymers



Incompatibility PP & PET & PE



The effect of 1.5% **Ken-React® CAPS® KPR® 12/LV** on Brabender melt compounded **PP/PET/PE** Recycle Plastics @ 9% lower temperatures. Larger batches later extruded.

Materials obtained from post-industrial waste streams:

1. **LLDPE** from a fractional melt film,
2. **PP** Copolymer from mixed 20-35 MFI injection molded caps,
3. **PET** from thermoformed clamshell food packaging.

Compatibilization of Addition & Condensation Polymers

Material ground into 1/4 – 1/2” flakes and melt compounded into pellets for IM using a 30:1 L/D - 20 mm single screw extruder.

Incompatibility **PP & PET & PE**

**Polymer Specialties
International Ltd.**



175 Deerfield Road,
Newmarket, Ontario, L3Y 2L8

Cell: (905) 717-3723

E-mail: bryon.wolff@psi-cda.com

**University of Waterloo
Chemical Engineering
Department.**

The effect of 1.5% **Ken-React® CAPS® KPR® 12/LV** on Brabender melt compounded **PP/PET/PE** Recycle Plastics @ 9% lower temperatures. Larger batches later extruded.

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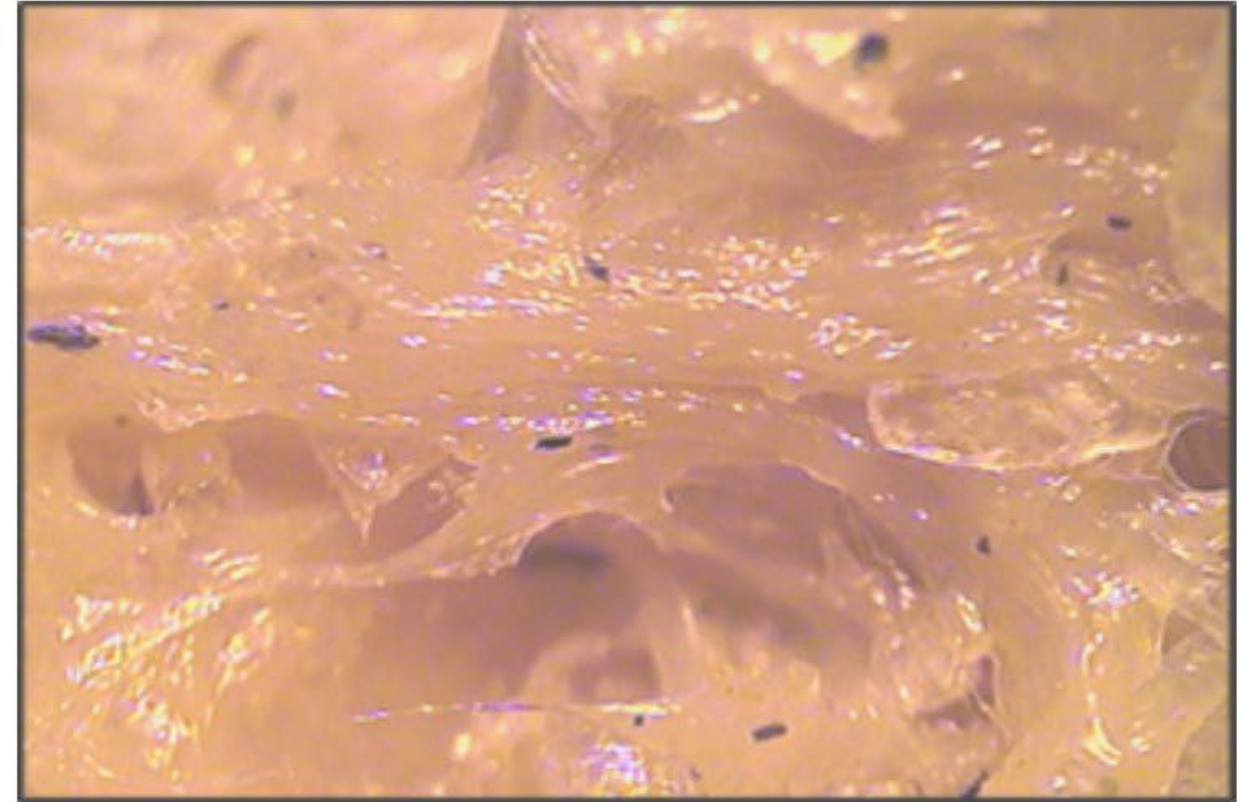
Compatibilization of Addition & Condensation Polymers

Brabender Plasticorder Blends of Three Recycled Polymers: PP/PET/PE



Incompatible PP/PET/PE—

No Additive



Compatibilized PP/PET/PE—

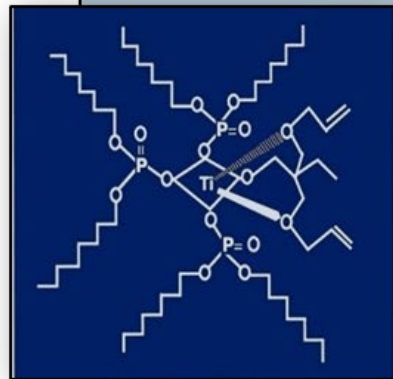
1.5%

Ti/Al Catalyst Additive

Pellets

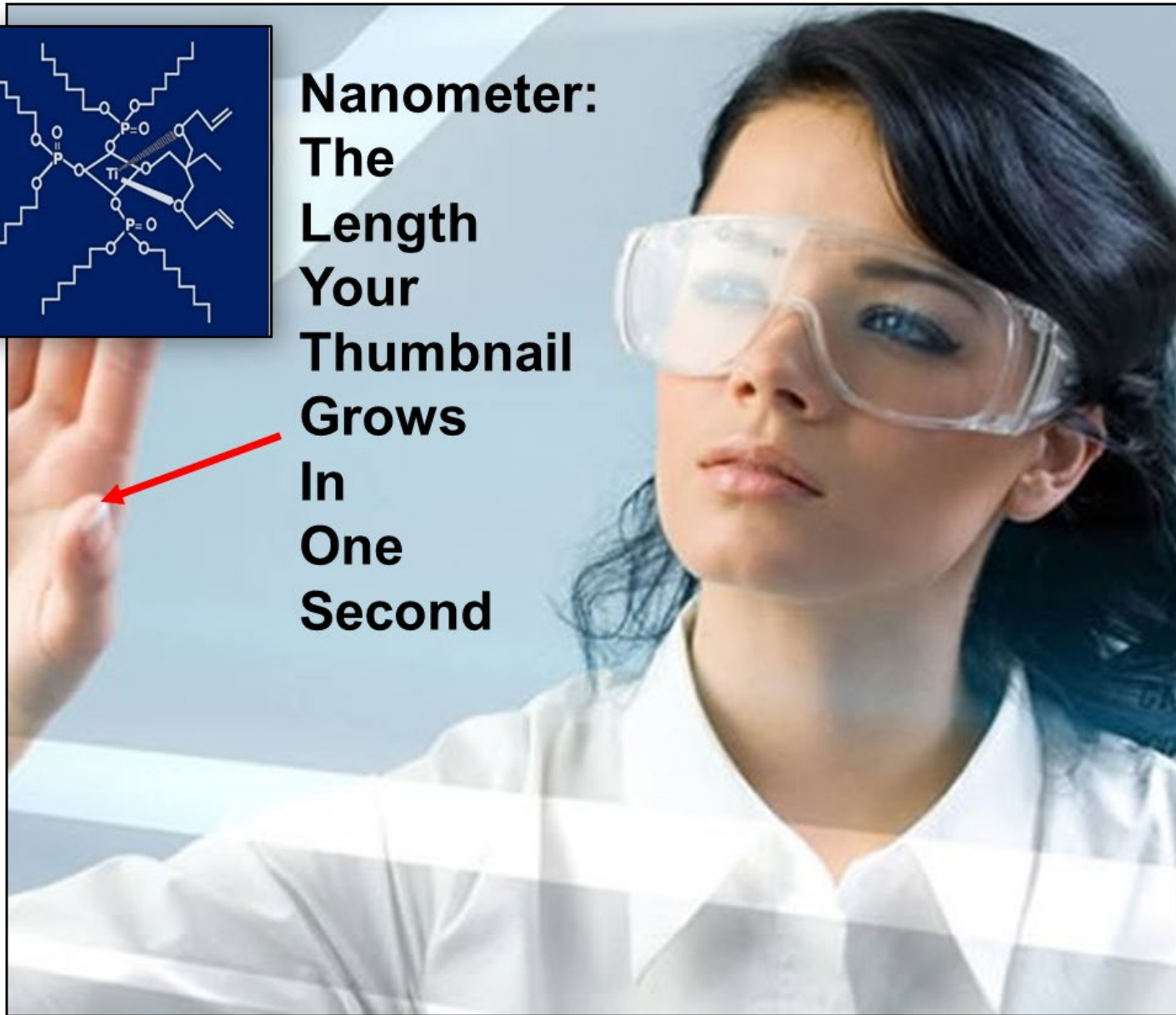
One Nanometer = 10 Carbons = c - c - c - c - c - c - c - c - c

Compatibilization of Addition/Condensation Polymers & Fillers – Lower Temps.



The PHYSICS of MIXING is critical to proper use of KPR® Titanium and Aluminum Additive Chemistry

**Nanometer:
The Length Your
Thumbnail
Grows
In
One
Second**



Compatibilization of Addition/Condensation Polymers – Lower Temps.

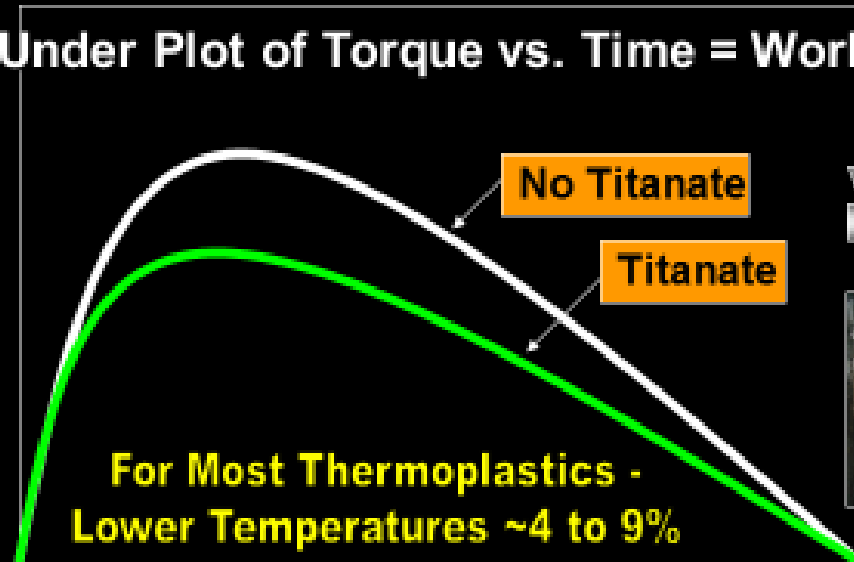
The PHYSICS of MIXING is critical to proper use of KPR[®] Titanium and Aluminum Additive Chemistry

Lower Process Temps. to Make Titanate Nanotechnology Work

Specific Energy Input = Lower Temps.; Increase rpm's; Increase Back Pressure

Area Under Plot of Torque vs. Time = Work Energy

Torque



Time



Compatibilization of Addition & Condensation Polymers

LOWERING THE PROCESS TEMPERATURE FOR REACTIVE COMPOUNDING SHEAR IS CRITICAL



From: Bryon Wolff [mailto:bryon.wolff@psi-cda.com]
To: Salvatore J. Monte sjmonte@4kenrich.com
Subject: Re: 2015 Global Plastics Summit

Good afternoon Sal
Below I've written a response to each of your questions. Should you require additional information etc. please don't hesitate to come back to me.
Best Regards

Bryon Wolff
Chief Technology Officer



University of Waterloo
Chemical Engineering Dept.

Polymer Specialties International Ltd.
175 Deerfield Road,
Newmarket, Ontario, L3Y 2L8
Cell: (905) 717-3723
E-mail: bryon.wolff@psi-cda.com



In your opinion, does the 10% drop in temperature from 320°F to 290°F indicate clearly the importance of reactive compounding shear?

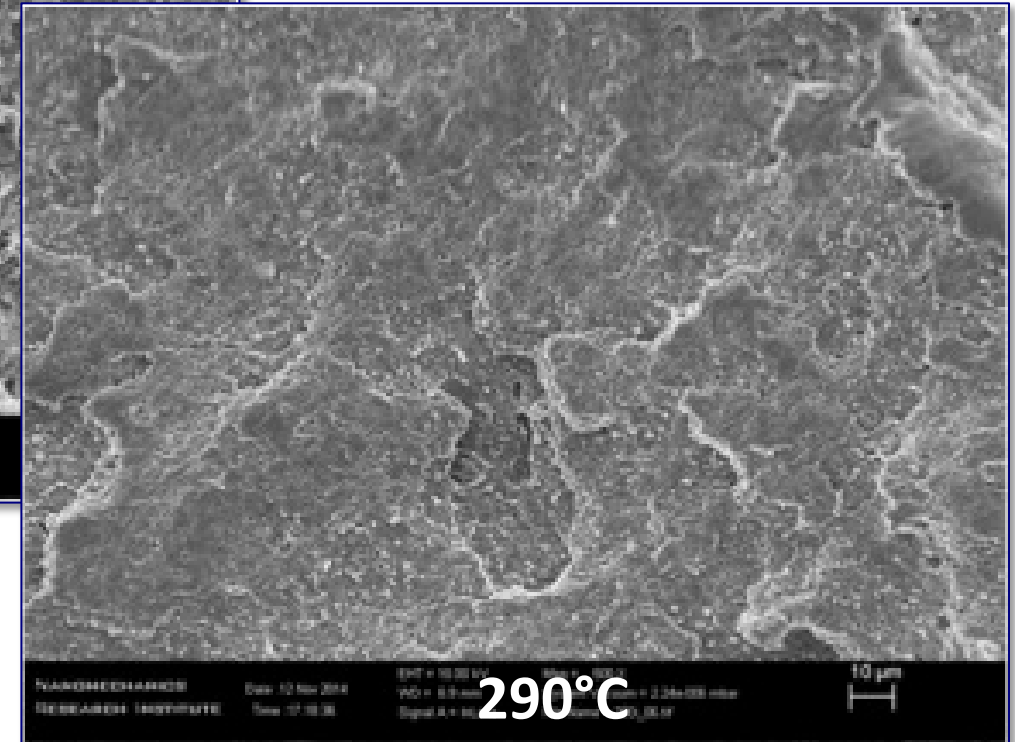
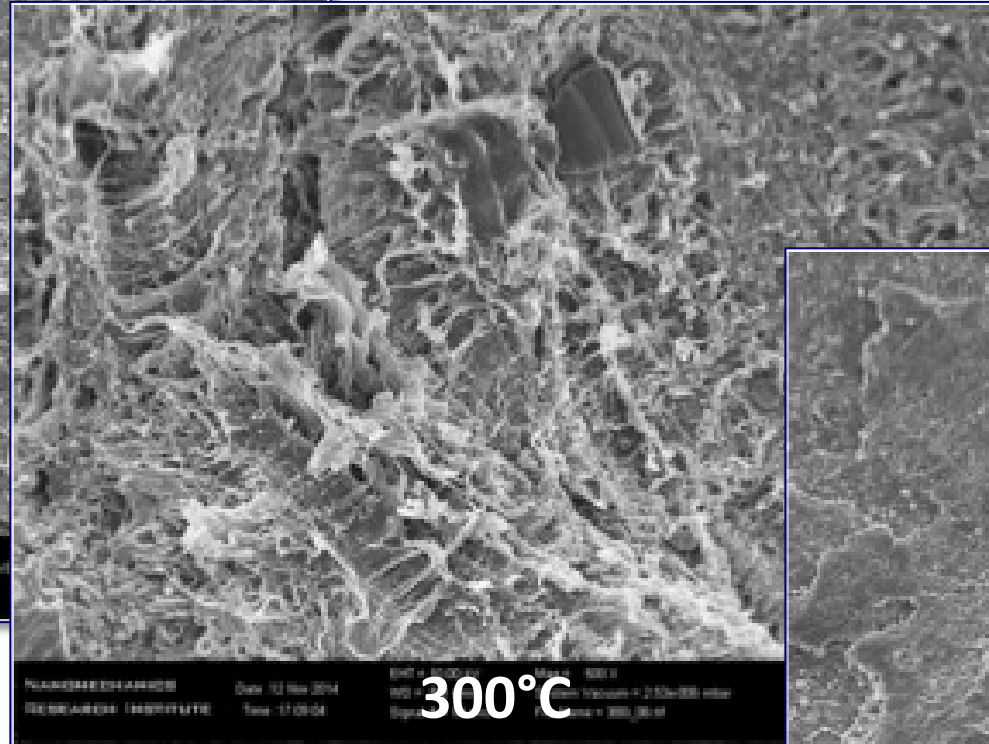
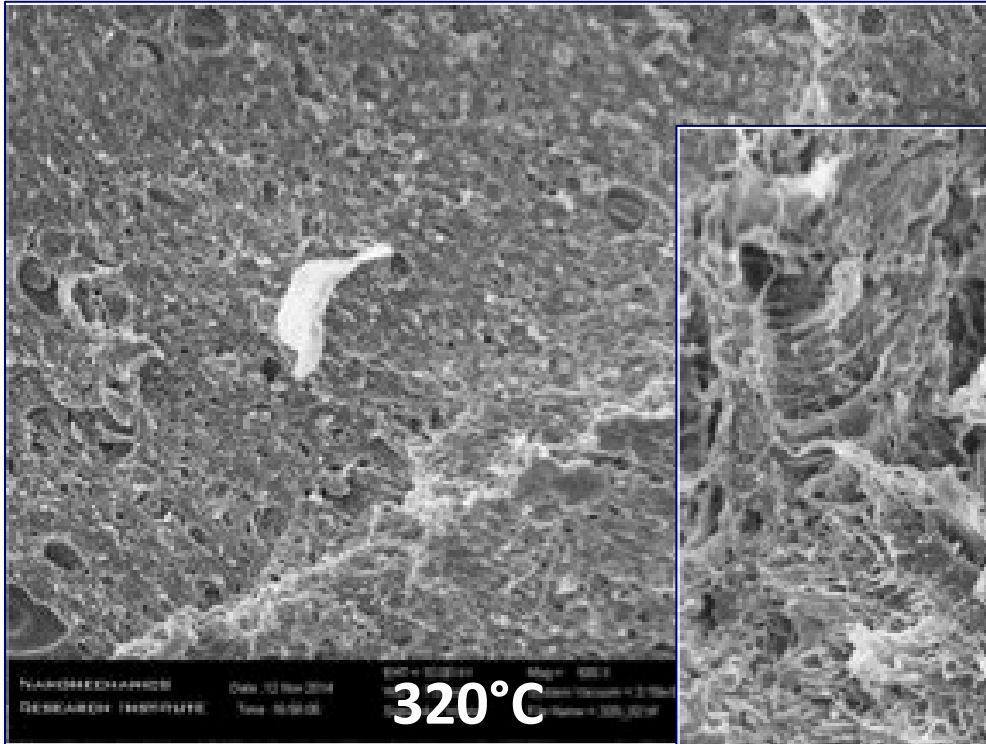
 The surface of the extrudate exiting the die became significantly smoother. Upon further analysis with SEM and Izod, it was clear that the increasing the shear dramatically improved the dispersion and physical properties of the compound.

Compatibilization of Addition & Condensation Polymers

**LOWERING THE PROCESS TEMPERATURE FOR
REACTIVE COMPOUNDING SHEAR IS CRITICAL**

SEM

Injection Molded



Materials obtained from post-industrial waste streams:

1. LLDPE from a fractional melt film,
2. PP Copolymer from mixed 20-35 MFI injection molded caps,
3. PET from thermoformed clamshell food packaging.

CONCLUSION

We have shown In Situ Macromolecule Titanate/Al Coupling & Catalysis is a significant strategic approach to reach Advanced Mechanical Recycling sustainability goals.

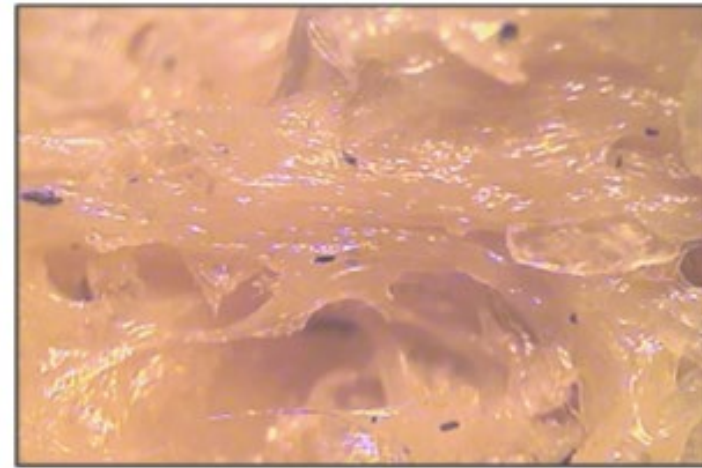
Compatibilization of Addition & Condensation Polymers

Brabender Plasticorder Blends of Three Recycled Polymers: PP/PET/PE



Incompatible PP/PET/PE—

No Additive



Compatibilized PP/PET/PE—

1.5% Ti/Al Catalyst Additive Pellets

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Extrusion 2022

PT A Plastics Technology Event

December 6-8, 2022

Omni Charlotte Hotel | Charlotte, North Carolina

The Extruder as a Reactor for Advanced Mechanical Recycling Using 1.5-Nanometer Titanates and Zirconates

Salvatore J. Monte

President | Kenrich Petrochemicals, Inc.

201-823-9000 | sjmonte@4kenrich.com | www.4kenrich.com



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<https://4kenrich.com/technical-information/>

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The Extruder as a Reactor for Advanced
Mechanical Recycling Using 1.5 Meter Diameter

Thank you

sjmonte@4kenrich.com

www.4kenrich.com

<https://4kenrich.com/technical-information/>

Time

End

www.4kenrich.com

