July 20 from 2 pm – 4 pm ET:

Mechanical Recycling

Improvements in mechanical recycling continue to be made for the vinyl industry. Speakers will discuss additives to bolster recycled material performance and quality, and advanced sorting technology to remove contaminants and increase the yield of recycled material.

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents, *Salvatore Monte, Kenrich Petrochemicals*

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents

Salvatore J. Monte – Kenrich Petrochemicals, Inc.

July 20, 2021 – 2:00-4:00pm

KENRICH PETROCHEMICALS, INC.

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents

Hosted VINYLTEC 2010 as President the P-NJ Section

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 DOD IMEM Program

PLASTICS Hall of Fame 2021

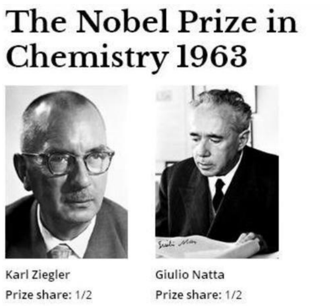
Salvatore J. Monte, President

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents

Presentation Outline – Key Points

- **Titanium/Aluminum coupling and catalysis applications are demonstrated in mechanical recycling.**
- **Ziegler, Natta & Kaminisky used Titanium and Aluminum catalysts to produce Addition Polymers – Vinyl is an Addition polymer;**
- **Titanate catalysts produce Condensation Polymers;**
- **Heteroatom Titanates couple fillers and catalyze Polymers;**
- **Mercuric Chloride and Palladium catalysts convert monomer to PVC polymer. Heteroatom Titanates REPOLYMERIZE PVC polymer.**
- **Monte uses Ti/Al in powder/pellet form to recycle PVC/Polymer compounds in the extruder melt.**

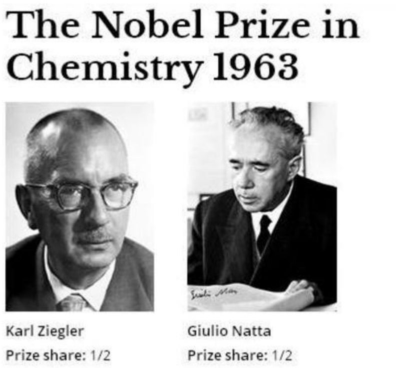
Titanium and Aluminum Additive Chemistry



- 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.

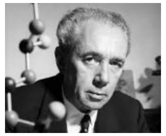
Titanium and Aluminum Additive Chemistry



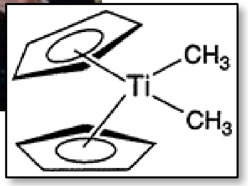
German Karl Ziegler, for his discovery of first titanium-based catalysts, and Italian Giulio Natta, for using them to prepare stereo regular polymers from propylene, were awarded the Nobel Prize in Chemistry in 1963.

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

- Ziegler showed a combination of $TiCl_4$ and $Al(C_2H_5)_2Cl$ useful for the production of polyethylene.

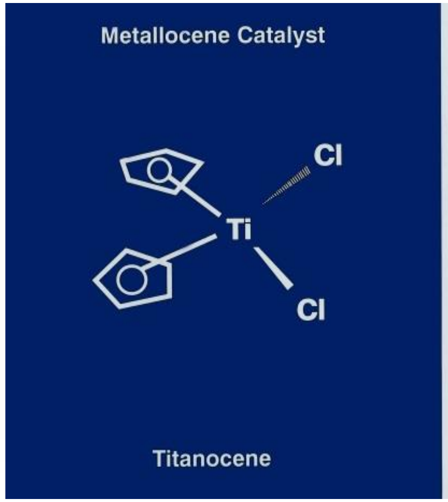


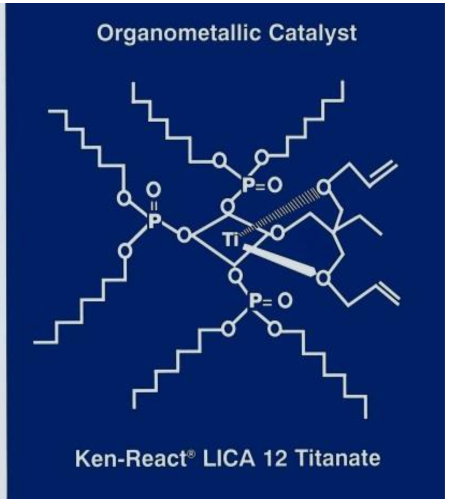
- Natta used crystalline α-$TiCl_3$ in combination with $Al(C_2H_5)_3$ to produce the first isotactic polypropylene.



- 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) −[O−Al(CH3)]n).

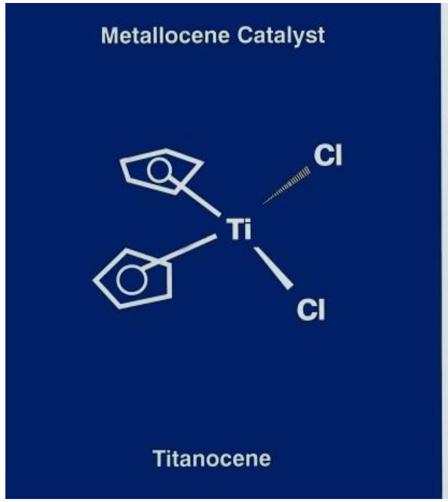
Titanium and Aluminum Additive Chemistry

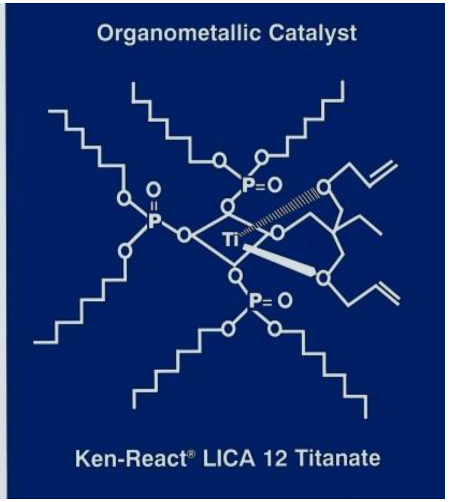




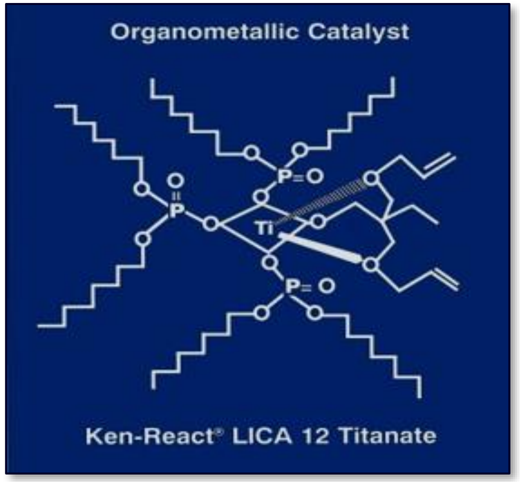
- **Monte uses Neoalkoxy Titanate in combination with Al_2SIO_5 mixed metal catalyst in Powder & Pellet forms for In Situ Macromolecular Repolymerization and Copolymerization in the melt – i.e. Polymer Compatibilization… AND … The Neoalkoxy Titanate proton coordinates with inorganic fillers and organic 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



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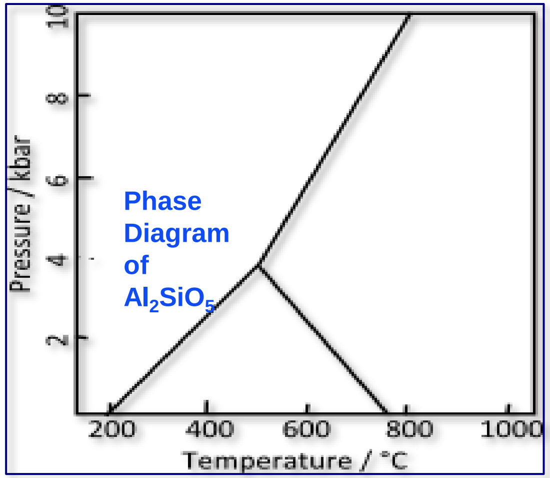
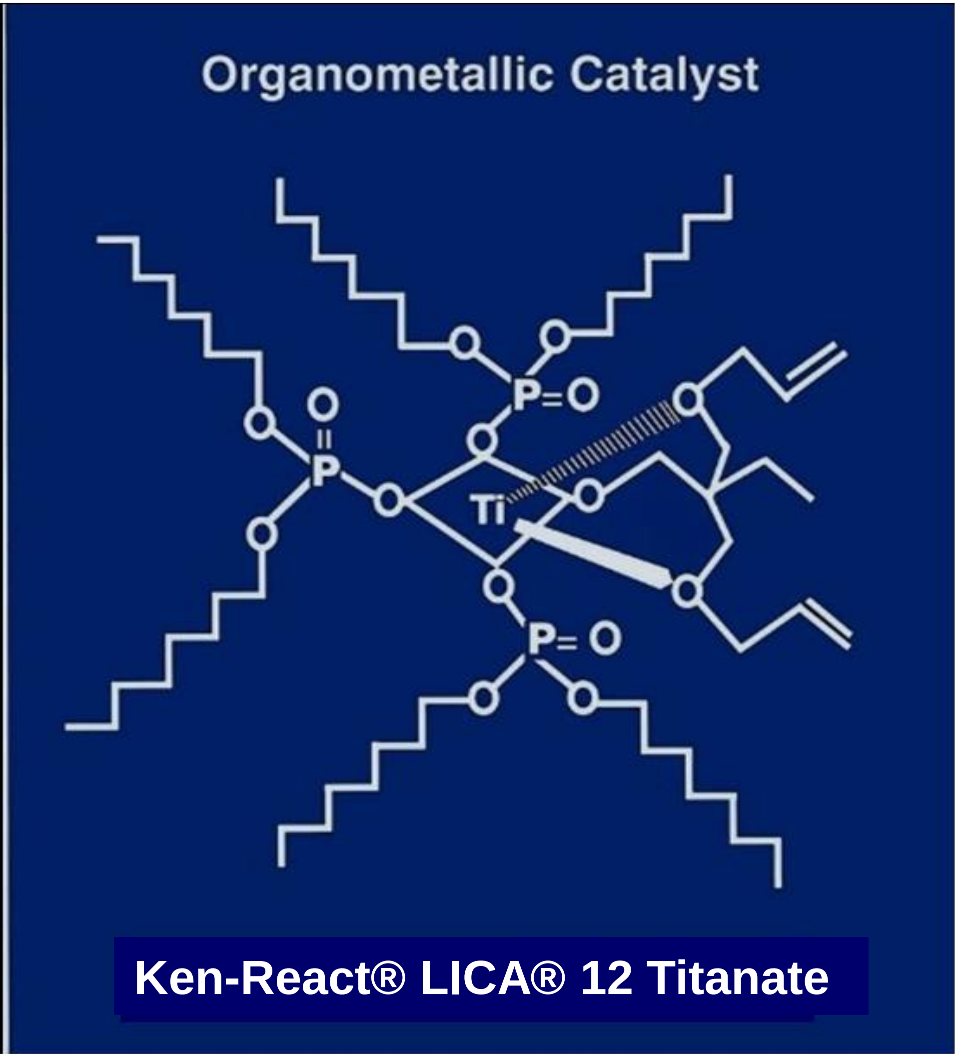


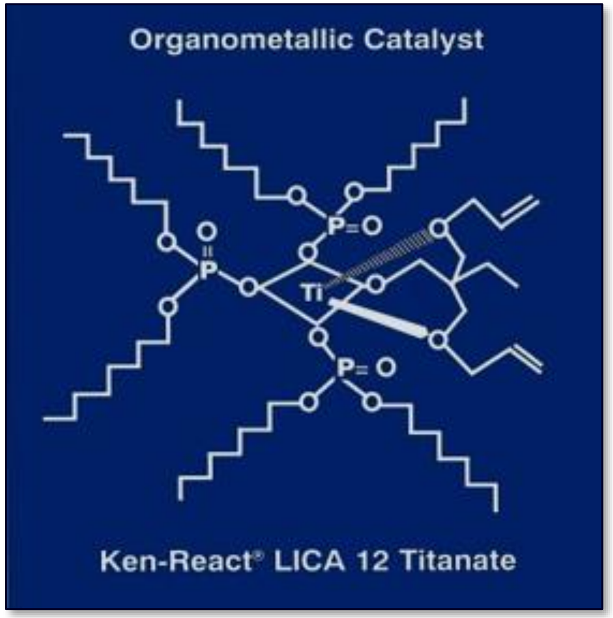
Introducing Titanium & Aluminum Additive Chemistry

This
is
The
Titanium
Catalyst
Portion



Introducing Titanium & Aluminum Additive Chemistry

This is The Titanium Catalyst Portion



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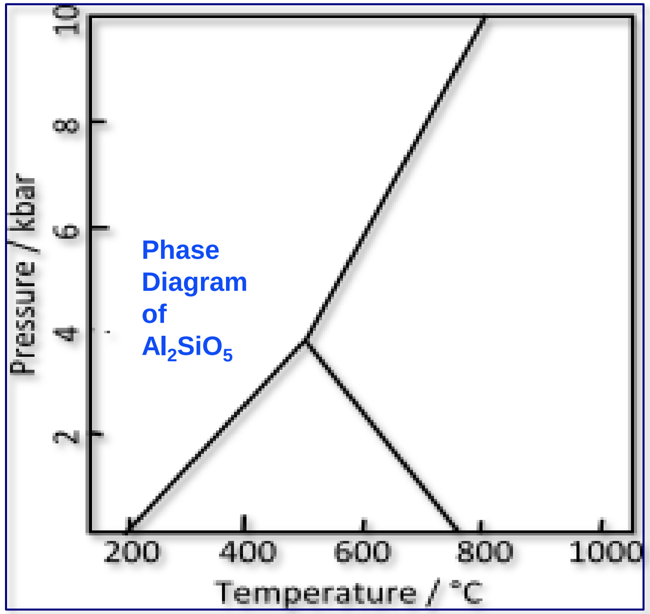
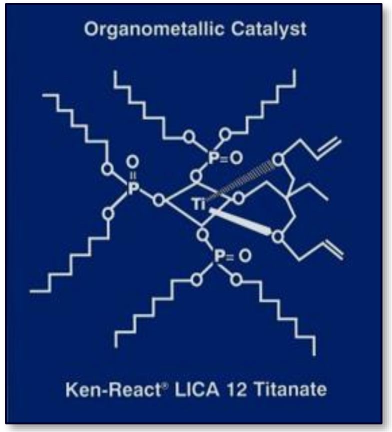


This is The Mixed Metal Catalyst Portion

Ken-React® CAPS® KPR® 12/LV



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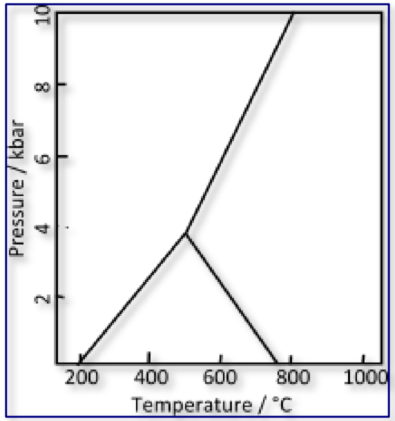

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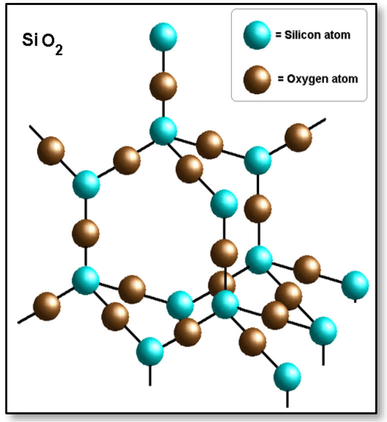

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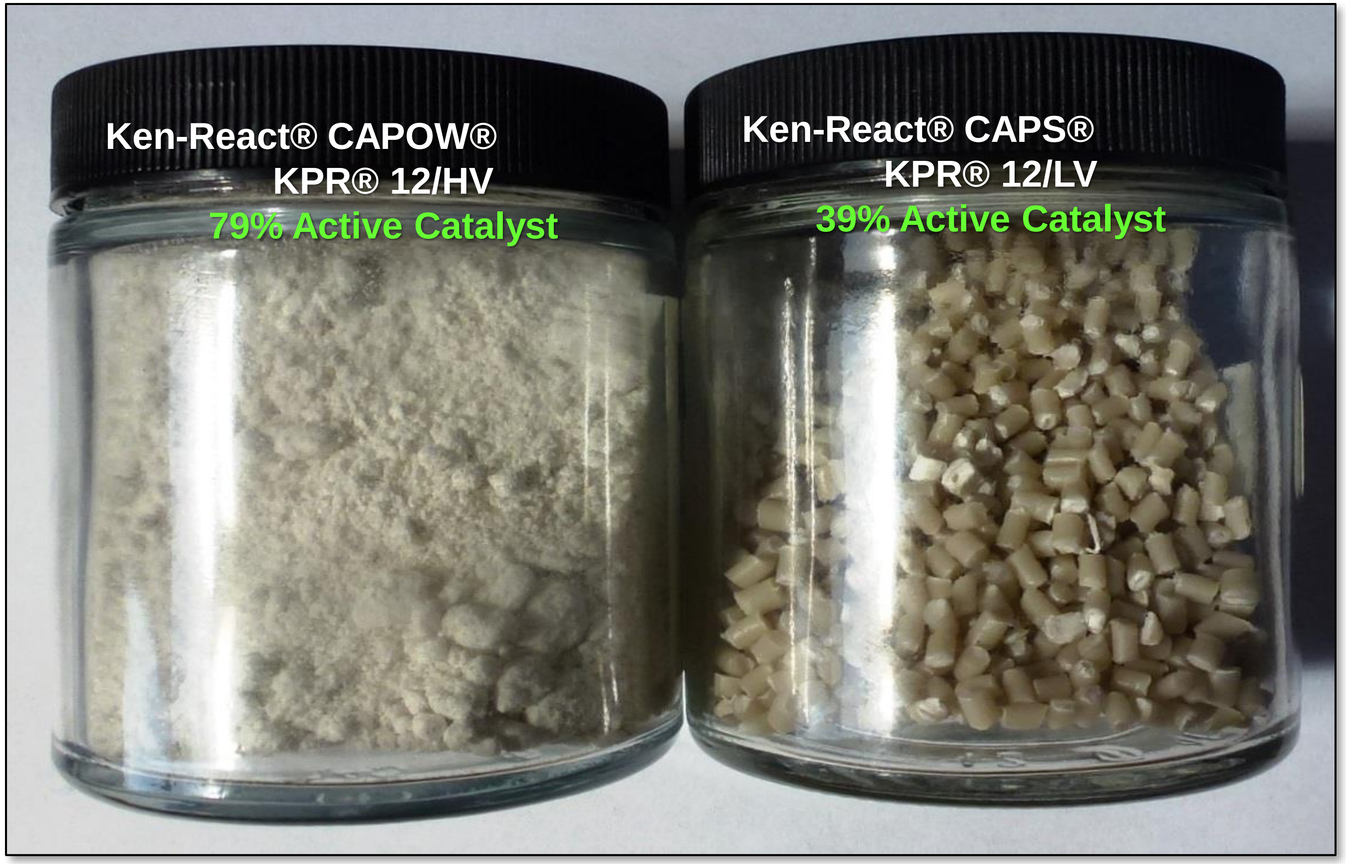
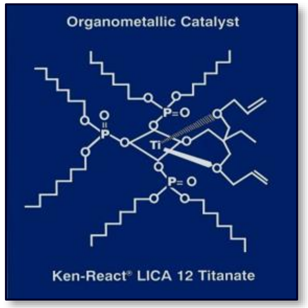
Ken-React®
CAPS®
KPR® 12/LV



Advanced Solution Chemistry



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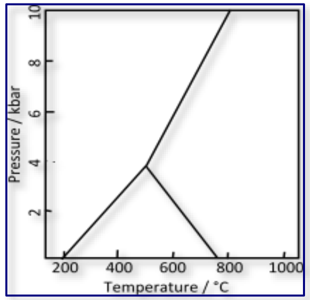

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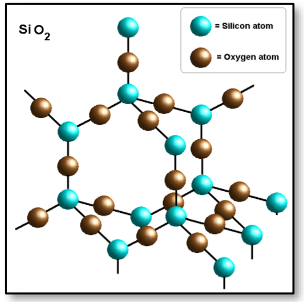

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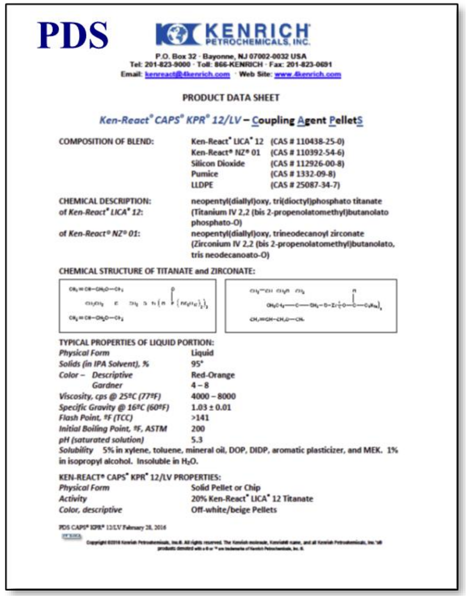
Ken-React® CAPS® KPR® 12/LV

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

03 PVC


PDS

KENRICH PETROCHEMICALS, INC.

P.O. Box 32 · Bayonne, NJ 07002-0032 USA
Tel: 201-823-9000 · Toll: 866-KENRICH · Fax: 201-823-0691
Email: kenreact@4kenrich.com · Web Site: www.4kenrich.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® NZ® 01	(CAS # 110392-54-6)
	Silicon Dioxide	(CAS # 112926-00-8)
	Pumice	(CAS # 1332-09-8)
	LLDPE	(CAS # 25087-34-7)

CHEMICAL DESCRIPTION:
of *Ken-React® LICA® 12*: neopentyl(diallyl)oxy, tri(dioctyl)phosphato titanate (Titanium IV 2,2 (bis 2-propenolatomethyl)butanolato phosphato-O)
of *Ken-React® NZ® 01*: neopentyl(diallyl)oxy, trineodecanoyl zirconate (Zirconium IV 2,2 (bis 2-propenolatomethyl)butanolato, tris neodecanoato-O)

CHEMICAL STRUCTURE OF TITANATE and ZIRCONATE:

TYPICAL PROPERTIES OF LIQUID PORTION:

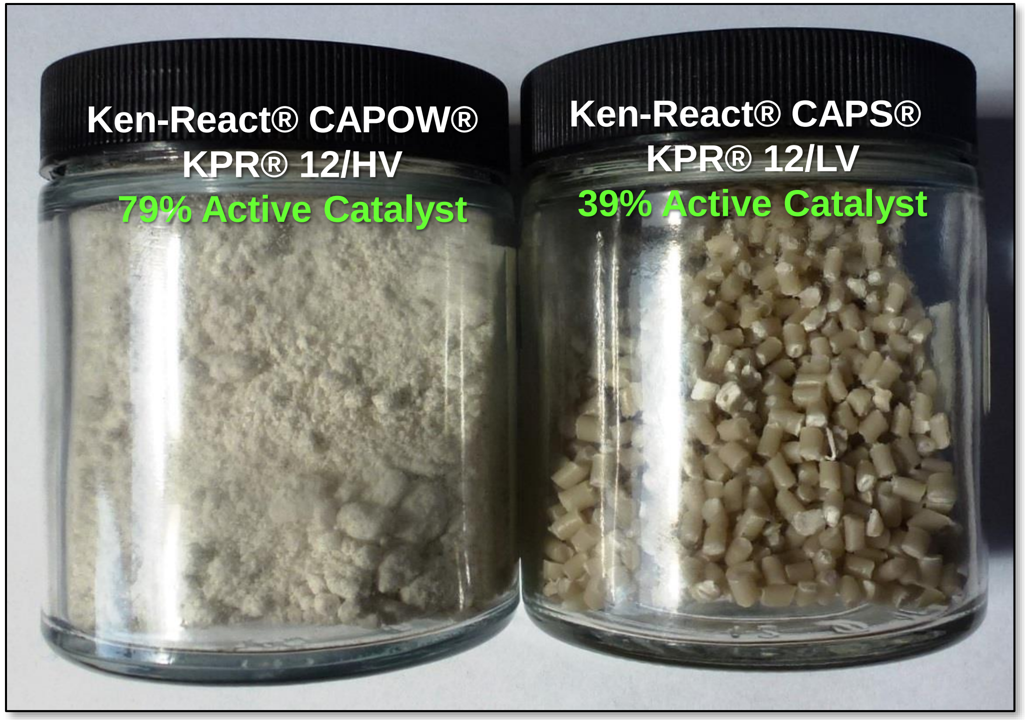
Physical Form	Liquid
Solids (in IPA Solvent), %	95*
Color – Descriptive	Red-Orange
Gardner	4 – 8
Viscosity, cps @ 25ºC (77ºF)	4000 – 8000
Specific Gravity @ 16ºC (60ºF)	1.03 ± 0.01
Flash Point, ºF (TCC)	>141
Initial Boiling Point, ºF, ASTM	200
pH (saturated solution)	5.3

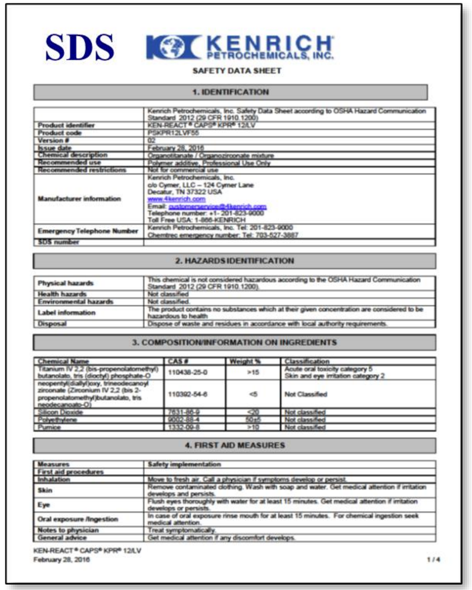
Solubility 5% in xylene, toluene, mineral oil, DOP, DIDP, aromatic plasticizer, and MEK. 1% in isopropyl alcohol. Insoluble in H_2O.

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

	Kenrich Petrochemicals, Inc. Safety Data Sheet according to OSHA Hazard Communication Standard 2012 (29 CFR 1910.1200)
Product identifier	KEN-REACT® CAPS® KPR® 12/LV
Product code	PSKPR12LVF55
Version #	02
Issue date	February 28, 2016
Chemical description	Organotitanate / Organozirconate mixture
Recommended use	Polymer additive, Professional Use Only
Recommended restrictions	Not for commercial use
Manufacturer information	Kenrich Petrochemicals, Inc. c/o Cymer, LLC – 124 Cymer Lane Decatur, TN 37322 USA www.4kenrich.com Email: customerservice@4kenrich.com Telephone number: +1- 201-823-9000 Toll Free USA: 1-866-KENRICH
Emergency Telephone Number	Kenrich Petrochemicals, Inc. Tel: 201-823-9000 Chemtrec emergency number: Tel: 703-527-3887
SDS number	

2. HAZARDS 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	The 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

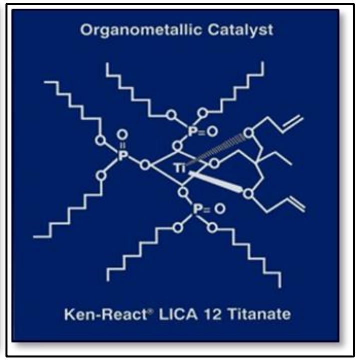
Chemical Name	CAS #	Weight %	Classification
Titanium IV 2,2 (bis-propenolatomethyl) butanolato, tris (dioctyl) phosphate-O	110438-25-0	>15	Acute oral toxicity category 5 Skin and eye irritation category 2
neopentyl(diallyl)oxy, trineodecanoyl zirconate (Zirconium IV 2,2 (bis 2-propenolatomethyl)butanolato, tris neodecanoato-O)	110392-54-6	<5	Not Classified
Silicon Dioxide	7631-86-9	<20	Not classified
Polyethylene	9002-88-4	50±5	Not classified
Pumice	1332-09-8	>10	Not classified

4. FIRST AID MEASURES

Measures	Safety implementation
First aid procedures	
Inhalation	Move to fresh air. Call a physician if symptoms develop or persist.
Skin	Remove contaminated clothing. 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 or persists.
Oral exposure /Ingestion	In case of oral exposure rinse mouth for at least 15 minutes. For chemical ingestion seek medical attention.
Notes to physician	Treat symptomatically.
General advice	Get medical attention if any discomfort develops.

KEN-REACT® CAPS® KPR® 12/LV
February 28, 2016 1 / 4

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



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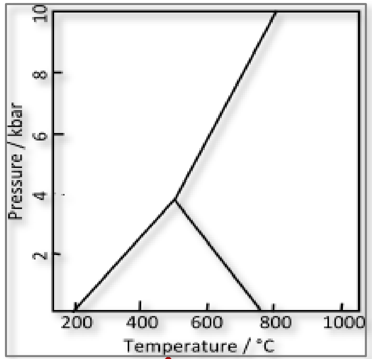

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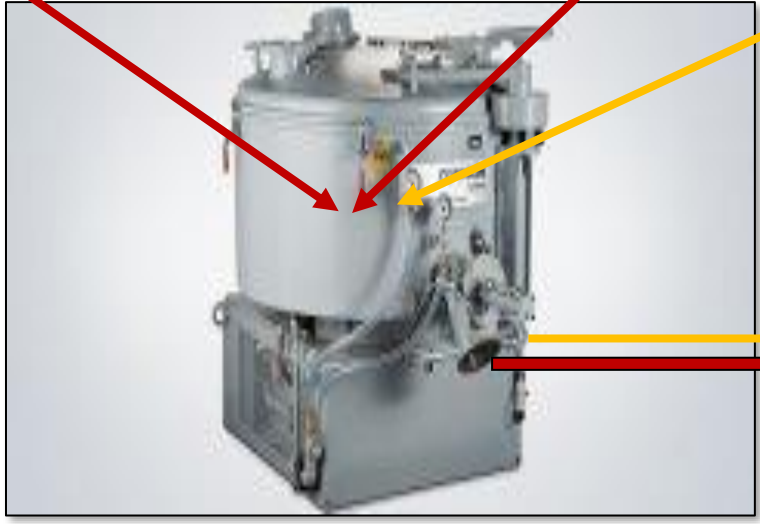
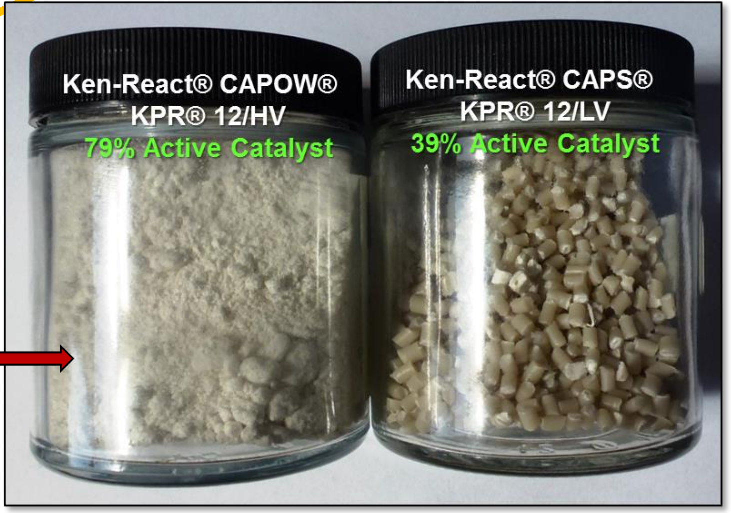
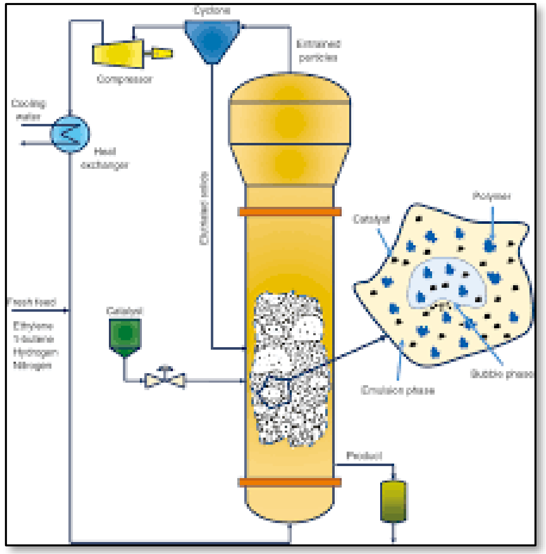
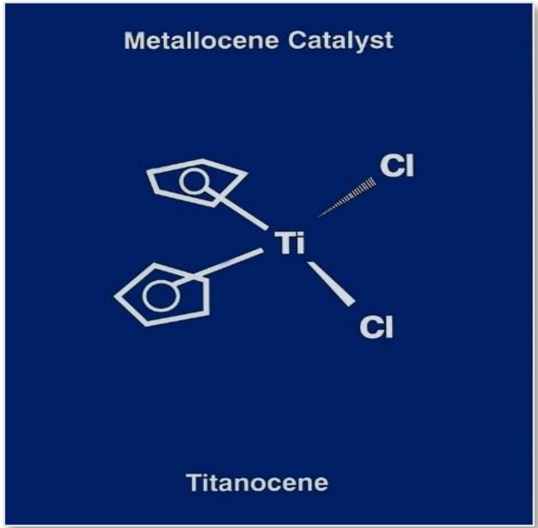




Ken-React®
CAPS®
KPR® 12/LV

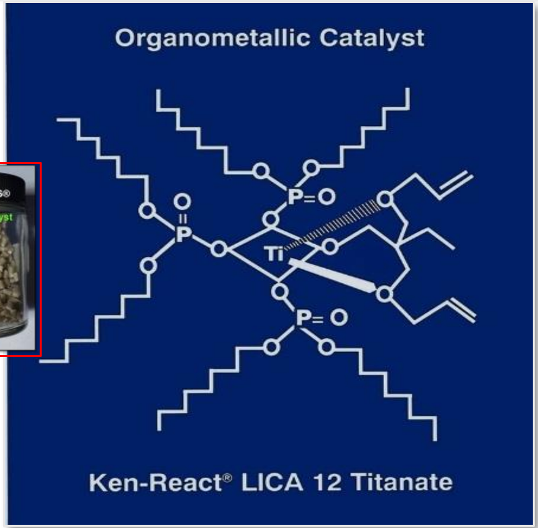
Reactor
Titanocene Polymerization – Ethylene Monomer





Titanocene:
Monomer
to
Polymer

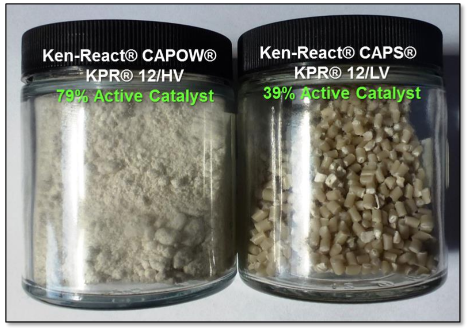
Extruder
Titanate Repolymerization – PVC & Ethylene Polymers



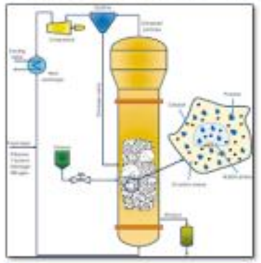
Titanate:
Recycle
to
Re-Polymer

Evolution of Subject Ti-Al Nano-Technology

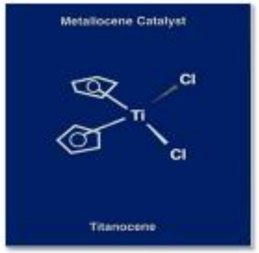
SIX FUNCTIONS



Reactor
Titanocene Polymerization – Ethylene Monomer

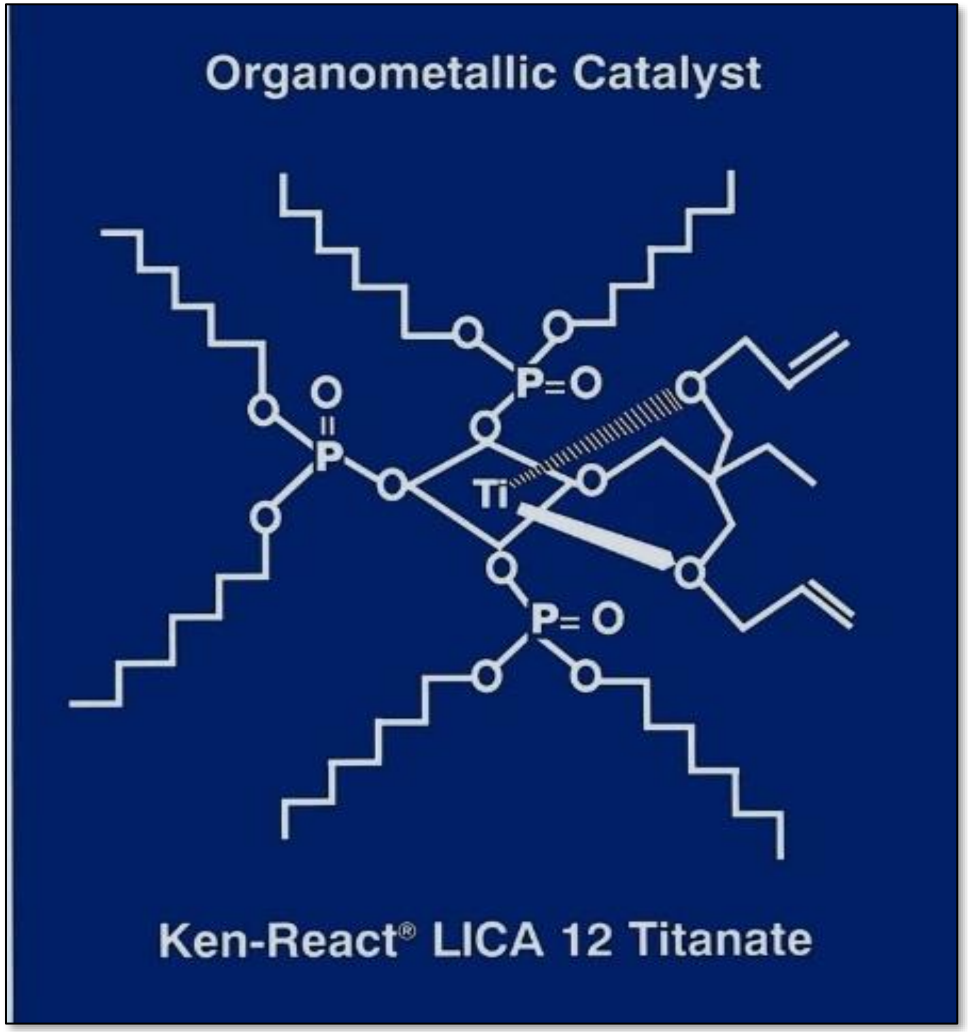


Monomer to Polymer



Extruder
Titanate Repolymerization – Ethylene Polymers

Recycle to Copolymer

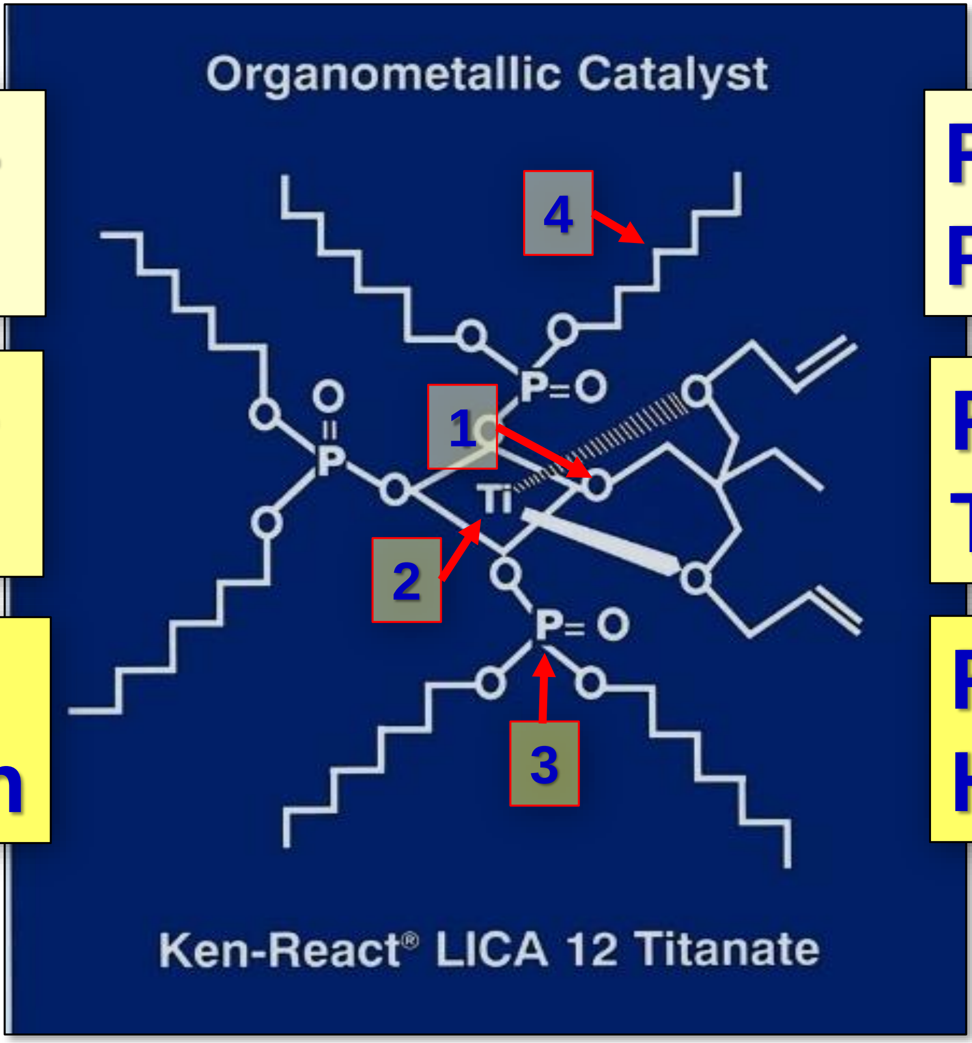


SIX FUNCTIONS

Function 1 – Coupling

Function 2 – Catalysis

Function 3 - Phosphatization

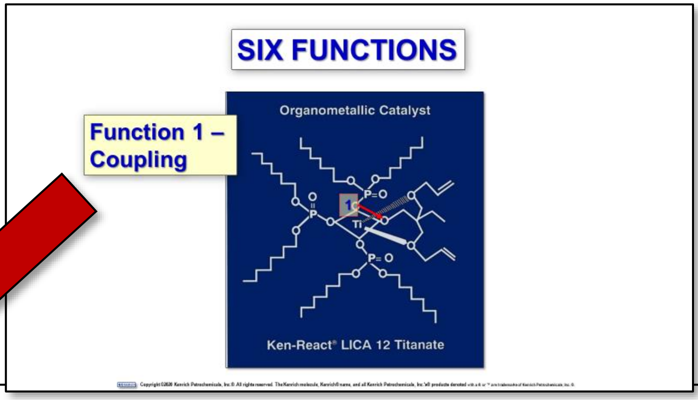


Function 4 – Polarity

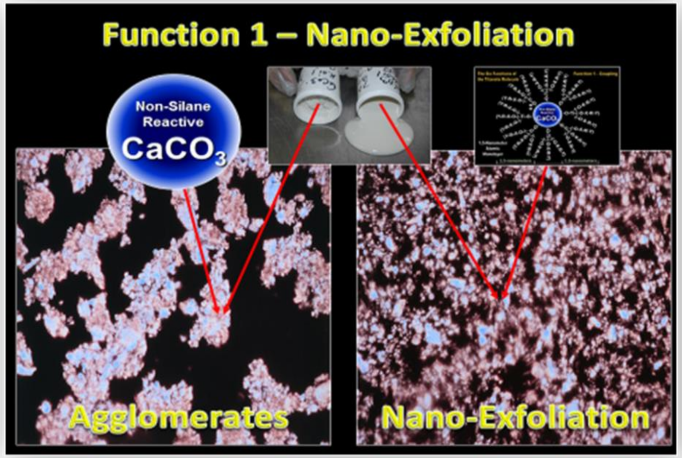
Function 5 – Thermoset

Function 6 – Hybridization

Problem Solving Takeaways From This Presentation - Coupling

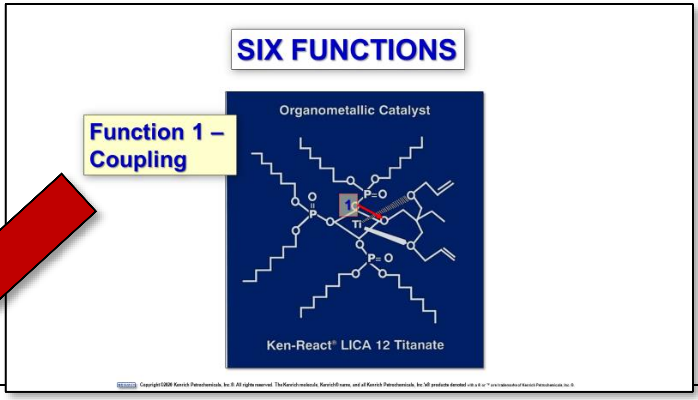


(1) Couple *in situ* via proton coordination to all fillers, pigments and organics– from CaCO3 to Carbon to AZO:



Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents

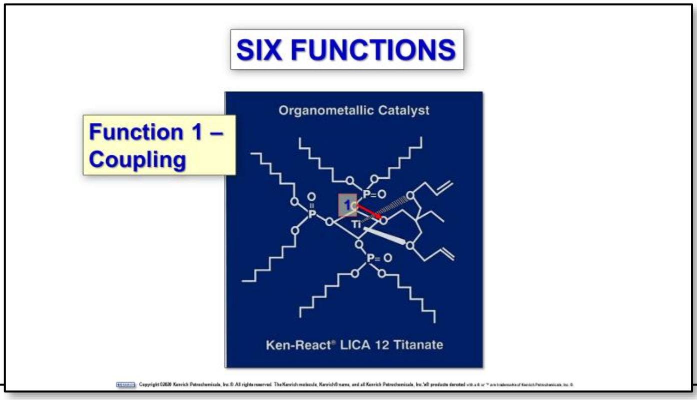
Problem Solving Takeaways From This Presentation - Coupling



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

- No hydrolysis as with Silanes – No pretreatment.
- Functionalize – Increase electron and heat transfer.
- Nano-Titanium Phosphatize for Flame Retardance.
- Use polymer melt (or plasticizer) as coupling medium.
- Filler viscosity reduction – shift in pigment/binder CPVC.

Problem Solving Takeaways From This Presentation - Coupling



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- **Nano-Titanium Phosphatize for Flame Retardance.**
- Use polymer melt (or plasticizer) as coupling medium.
- Filler viscosity reduction – shift in pigment/binder CPVC.

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

July 19, 20, 26, & 27 | 2pm - 4pm ET | Virtual

2021 Vinyl Recycling Summit

Hosted by VINYL SUSTAINABILITY COUNCIL

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents

Salvatore J. Monte – Kenrich Petrochemicals, Inc.

July 20, 2021 – 2:00-4:00pm

KENRICH PETROCHEMICALS, INC.

PROBLEM SOLVING RECYCLE IS A COMPLEX MATERIALS CHALLENGE

Insensitive Munitions & Energetic Materials (IMEM) Technology Symposium

April 7-8, 2021

Virtual Conference

NDIA National Defense Industrial Association

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

Salvatore J. Monte

sjmonte@4kenrich.com · www.4kenrich.com

KENRICH PETROCHEMICALS, INC.

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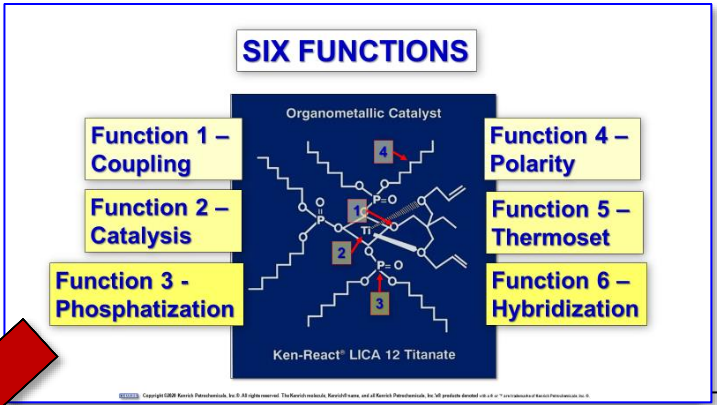
PROBLEM SOLVING INSENSITIVE MUNITIONS IS A COMPLEX MATERIALS CHALLENGE

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents



Problem Solving Takeaways From This Presentation –
Coupling – Catalysis – Phosphatization

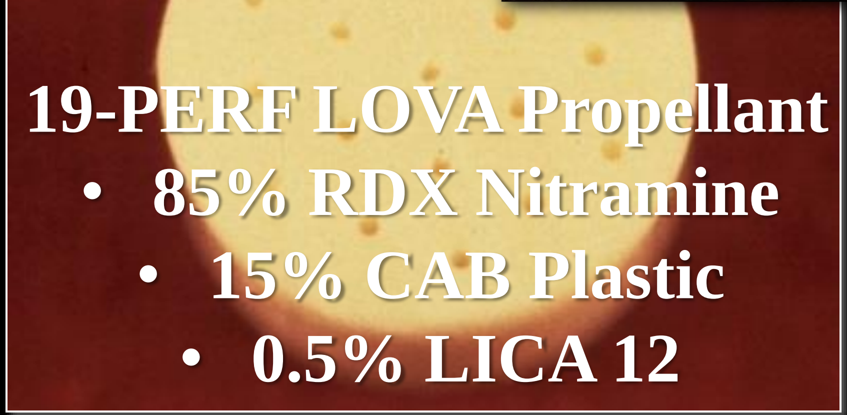
(1) Couple *in situ* via proton coordination to all fillers, pigments and organics– from CaCO3 to Carbon to AZO:

- Nano-Titanium Phosphatize for Flame Retardance.

IM Problem Solved: Unsustainable unplanned detonation of rockets and explosives causing great loss of life and valuable equipment.

I became aware of the Insensitive Munitions Program & LOVA in early 1980

Just as in RECYCLE, to solve the Unsustainable problem of unplanned detonation – I applied the lessons learned dealing with similar or same materials in PVC & polymer composites



19-PERF LOVA Propellant
- 85% RDX Nitramine
- 15% CAB Plastic
- 0.5% LICA 12

1980 – Monte theorizes:
1. We can make AZO nitramine blowing agent more explosive for PVC pool floats.
2. We can create nano-titanium intumescence on any interface for flame retardance.
3. We can improve the flow and strength of Injection Molded CAB screwdriver handles.

PLASTICS EXPERIENCE IN VINYL & I.M. CAB Screwdriver Handles

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

Classified TOP SECRET for DOD IM Program

RDX/CAB & Plastic Bound Explosives

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

(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)

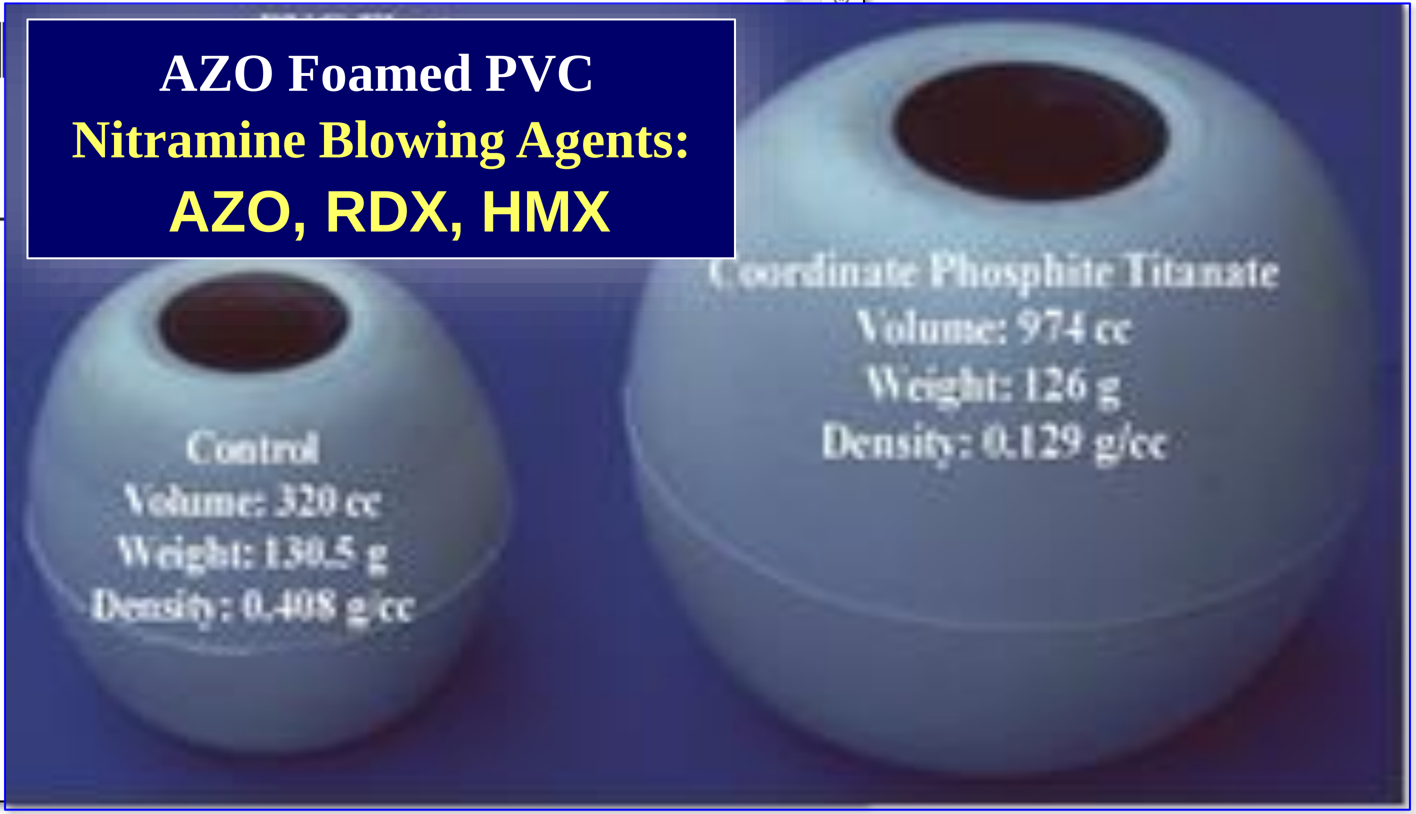
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

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

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

AZO Foamed PVC
Nitramine Blowing Agents:
AZO, RDX, HMX

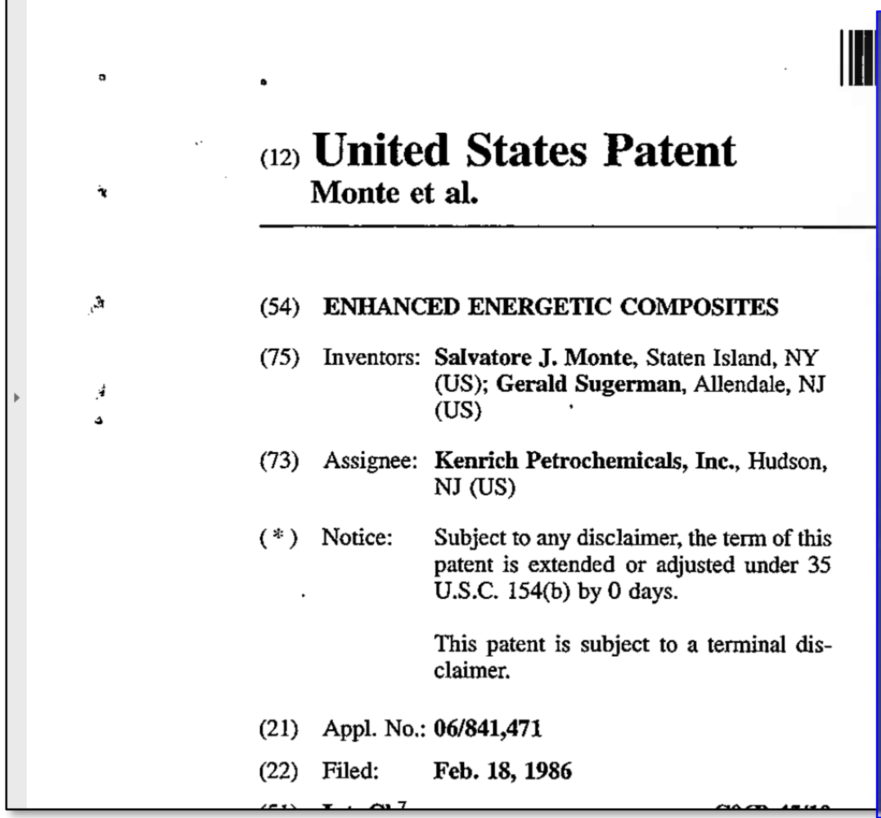


PLASTICS EXPERIENCE IN VINYL & I.M. CAB Screwdriver Handles

- Nano-Titanium Phosphatize for Flame Retardance

Classified TOP SECRET for DOD IM Program

RDX/CAB & Plastic Bound Explosives



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

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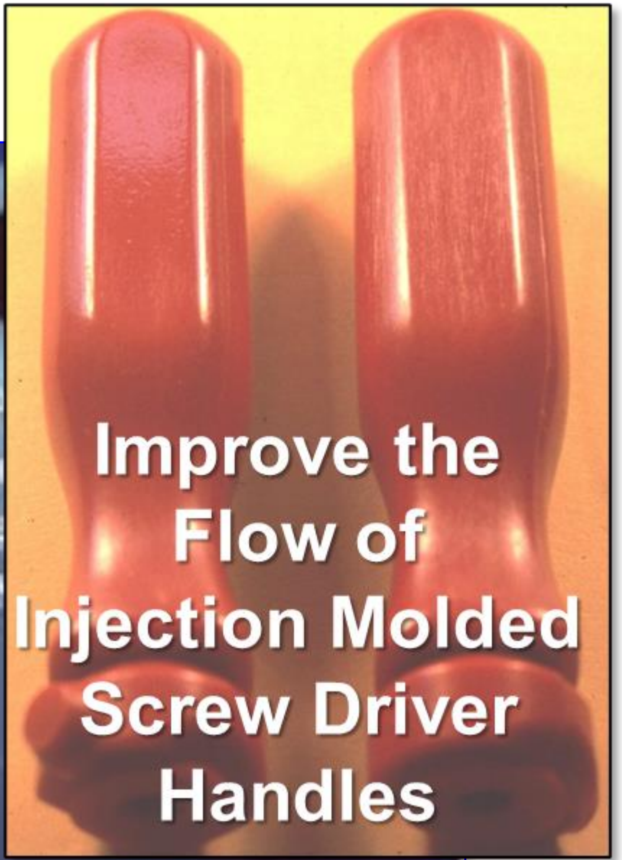

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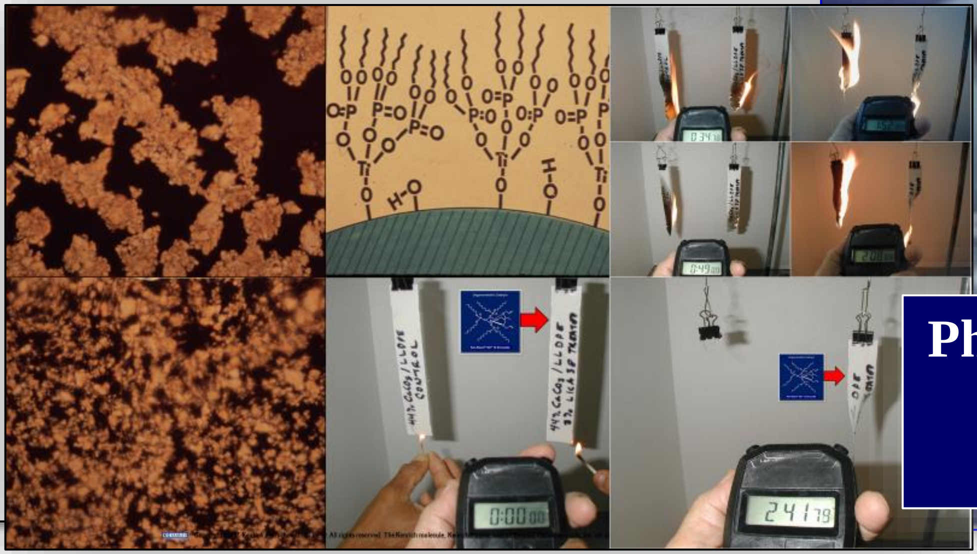

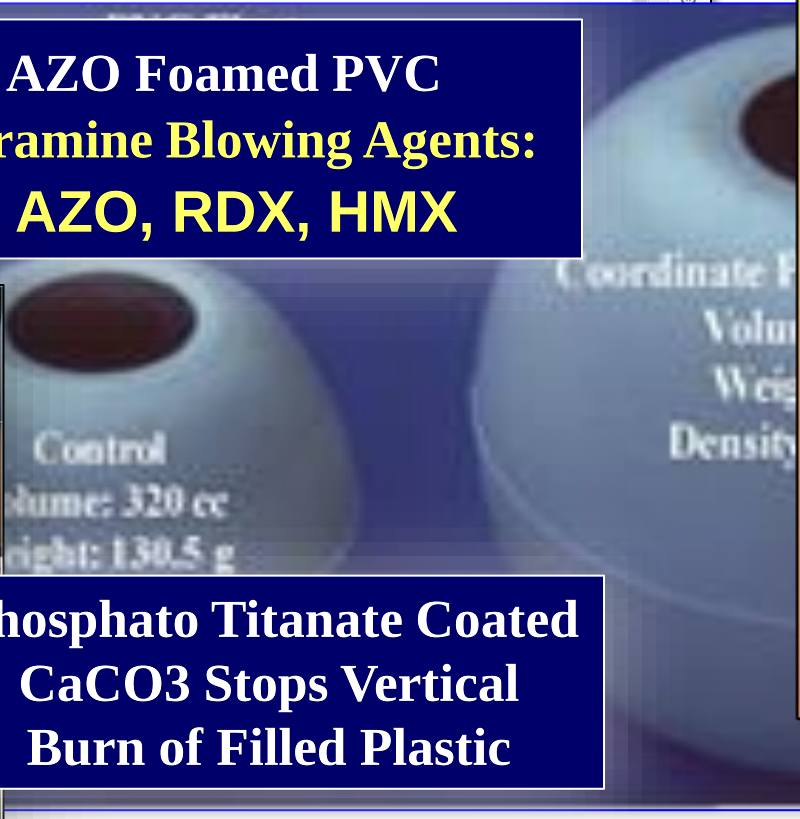

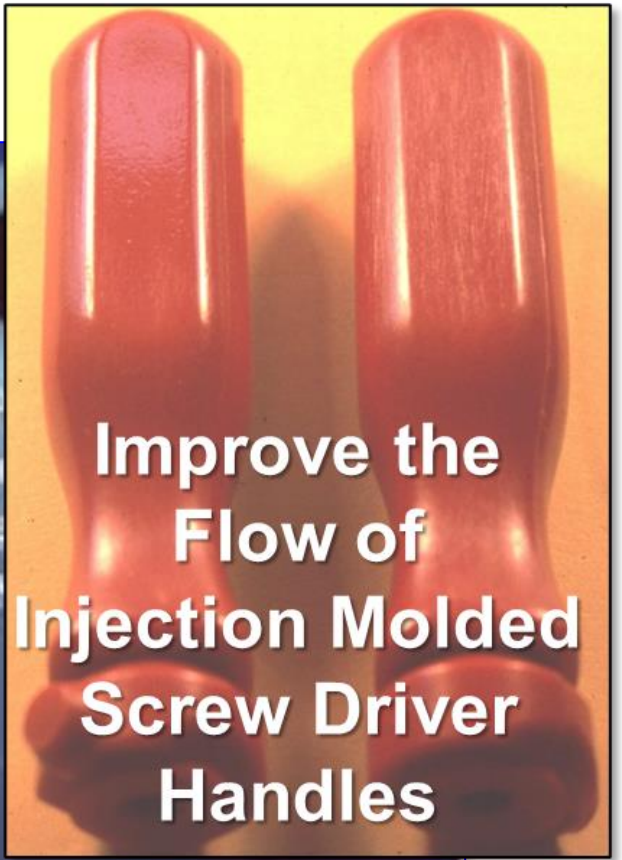

Problem Solving Takeaways – Unplanned Detonation

First ADPA Presentation – June 1, 1982

American Defense Preparedness Assoc., Joint Symposium on Compatability of Plastics/Materials with Explosives, Propellants and Pyrotechnics and Processing of Explosives, Propellants and Ingredients, June 1, 1982, Phoenix, Arizona, "*The Potential of Titanate Coupling Agents in Solid Rocket Fuel Systems*", S.J. Monte and G. Sugerman

First Picatinny Arsenal Presentation – January 10, 1983

ARRADCOM, Dover, NJ, Jan. 10, 1983

40. Center for Professional Advancement, Plastics Composites, N. Brunswick, NJ, February 25, 1983
41. Fillers and Coupling Agent Symposium, ARCO, Newton Square, PA, March 16-17, 1983
42. Naval Weapons Center, Yorktown, VA, April 20, 1983

PLASTICS EXPERIENCE IN VINYL & I.M. CAB Screwdriver Handles

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

Classified TOP SECRET for DOD IM Program

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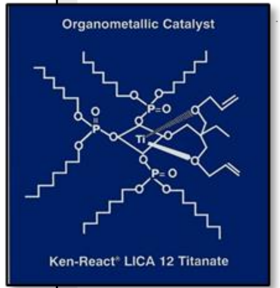


US006197135B1

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

(10) **Patent No.: US 6,197,135 B1**

(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**

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

(57) ABSTRACT

The instant invention relates to the use of certain selected neoalkoxy organo-titanates and organo-zirconates in ener-

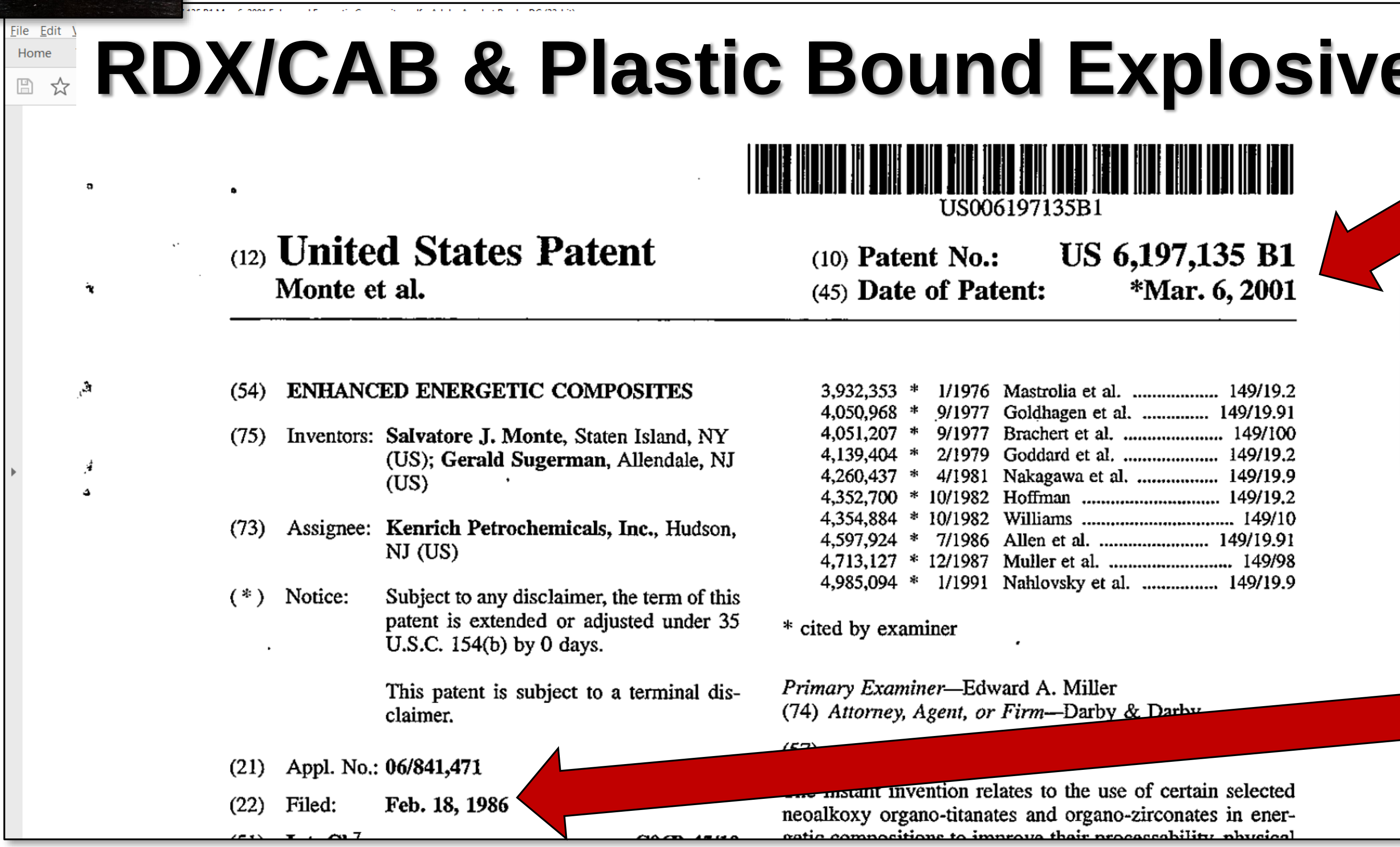
Monte et al.
US Patent 6,197,135 B1:
"ENHANCED ENERGETIC COMPOSITES"

Problem Solving Takeaways – Unplanned Detonation

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

Classified TOP SECRET for DOD IM Program

RDX/CAB & Plastic Bound Explosives



US006197135B1

(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**

3,932,353	*	1/1976	Mastrolia et al.	149/19.2
4,050,968	*	9/1977	Goldhagen et al.	149/19.91
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.	149/19.91
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

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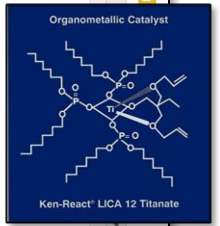


Issued Mar 6, 2001

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

Filed Feb. 18, 1986

• Nano-Titanium Phosphatize for Flame Retardance

ARMY Patent – 9-Years later Verifying Nano-Functionality

RDX/CAB & Plastic Bound Explosives

(12) United Stat
Monte et al.

(54) ENHANCED ENERG

(75) Inventors: Salvatore J (US); Gera (US)

(73) Assignee: Kenrich Pe NJ (US)

(*) Notice: Subject to patent is ex U.S.C. 154

This patent claimer.

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

(22) Filed: Feb. 18, 1986

(57) ABSTRACT

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

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

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

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

[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

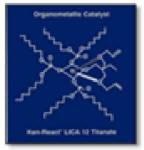
4,853,051 8/1989 Bennett et al. 149/19.4
5,240,523 8/1993 Willer 149/19.4

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

[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 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 Buterate, 1:1 bis 2,2-dinitropropyl acetate and bis 2,2-dinitropropropyl 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



Filed, Feb. 1, 1995
INSENSITIVE EXPLOSIVE COMPOSITION

Filed Feb. 18, 1986
ENHANCED ENERGETIC COMPOSITES

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

[54] **INSENSITIVE EXPLOSIVE COMPOSITION**

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

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

[21]

[22]

[63]

[51]

[52]

[58]

- **Aluminum Powder**
- **(HMX)**
- **Cellulose Acetate Butyrate**
- **Bis 2,2-dinitropropyl acetate**
- **Bis 2,2-dinitropropyl formal**
- **Tri(dioctyl Phosphato) Titanate @ 0.25 to 0.75 percent**

4,853,051	8/1989	Bennett et al.	149/19.4
5,240,523	8/1993	Willer	149/19.4

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

Issued Dec. 5, 1995

[57] **ABSTRACT**

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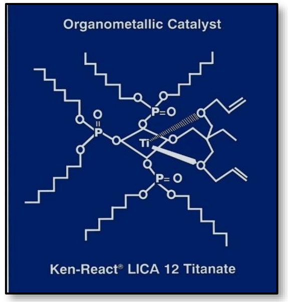
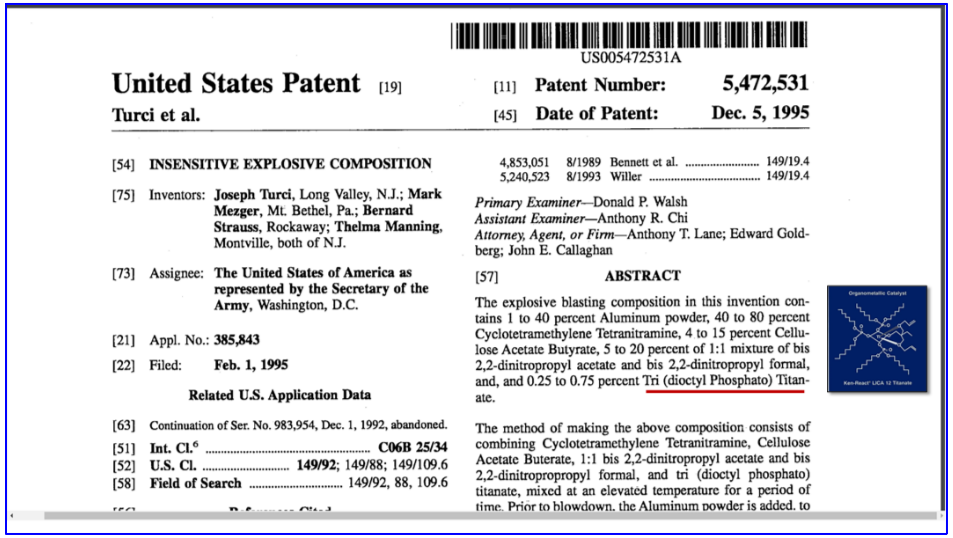


• Nano-Titanium Phosphatize for Flame Retardance

Utility



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

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

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[21] Appl. No.: 385,843

[22] Filed: Feb. 1, 1995

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[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

4,853,051 8/1989 Bennett et al. 149/19.4
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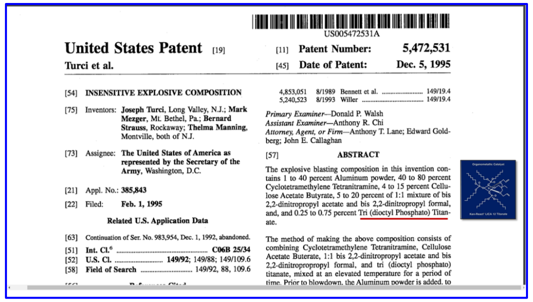
This explosive is used in the Penetration Augmented Munition as well as having potential for use on the guns for the Bradley Fighting vehicle, <u>in addition it has applications in the following programs which involve blasting munitions: Multi-purpose Individual Munition, Bunker defeat Munition, Explosive foxhole digger, Bridge Road Munition, and any mining or rock blasting application….</u>

Note 2: Our composition is the only one that is not sensitive to impact sensitivity, or sympathetic detonation.

BACKGROUND



US005472531A

United States Patent [19] Turci et al.

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

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[52] U.S. Cl. 149/92; 149/88; 149/109.6
[58] Field of Search 149/92, 88, 109.6

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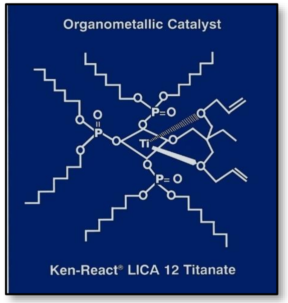


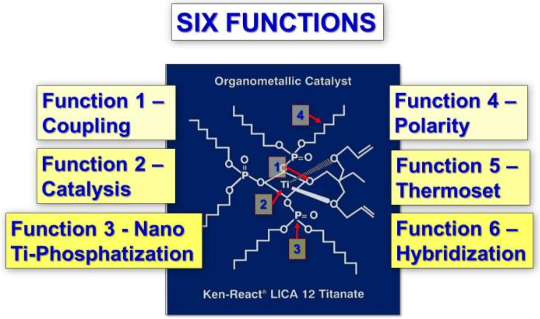
…Safety is the uppermost in the minds of the military when fielding such compositions.

…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.*

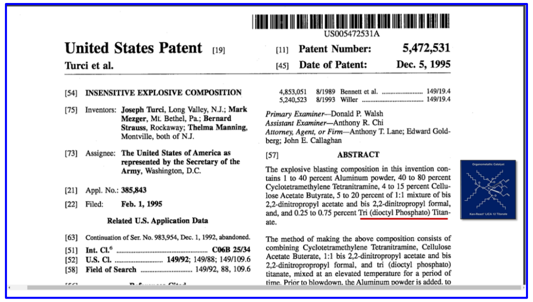
METHOD OF MAKING PREFERRED EMBODIMENT OF THE INVENTION

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.*



BACKGROUND



US005472531A

United States Patent [19] **Turci et al.**

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

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[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

4,853,051 8/1989 Bennett et al. 149/19.4
5,240,523 8/1993 Willer 149/19.4

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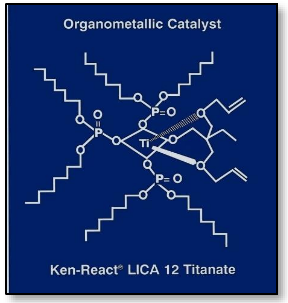


...Safety is the uppermost in the minds of the military when fielding such compositions.

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.*

METHOD OF MAKING PREFERRED EMBODIMENT OF THE INVENTION

Nano-Note: Δ 0.25 wt.% -- Optimal to Inert

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.*

• Nano-Titanium Phosphatize for Flame Retardance

Classified TOP SECRET for DOD IM Program

Al/AP/HTPB PU Solid Rocket Fuel

US005753853A

United States Patent [19] — Monte et al.

[11] Patent Number: 5,753,853

[45] Date of Patent: *May 19, 1998

[54] SOLID PROPELLANT WITH TITANATE BONDING AGENT

[75] Inventors: Salvatore J. Monte, Staten Island, N.Y.; Gerald Sugerman, Allendale, N.J.; Scott J. Dixon, Colorado Springs, Colo.

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

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,753,853.

[21] Appl. No.: 835,879

[22] Filed: Feb. 20, 1986

[51] Int. Cl.[6] C06B 45/10

[52] U.S. Cl. 149/19.2; 149/19.4; 149/19.9

[58] Field of Search 149/19.2, 19.1, 149/19.9

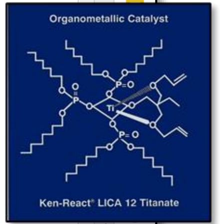
4,050,968	9/1977	Goldhagen et al.	149/19.4
4,090,893	5/1978	Cuckser et al.	149/19.9
4,122,062	10/1978	Monte et al.	524/567
4,430,131	2/1984	Tremblay	149/19.4
4,597,924	7/1986	Allen et al.	149/19.4
4,634,785	1/1987	Sugerman	556/17

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

[57] ABSTRACT

Liquid elastomer-based propellant having incorporated ... organo-titanates have positive ballistic and physical effects on the propellants, serving to reduce burn rate exponents and overall burn rates, as well as increasing the tensile strength and elasticity of the propellant. Organo-phosphate and pyro-phosphate titanates are used as the preferred organo-

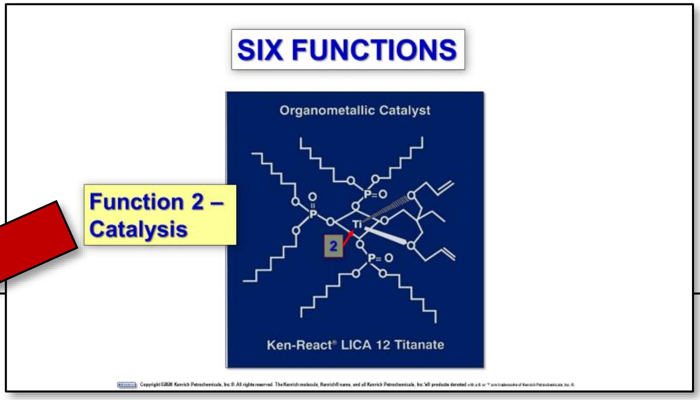
Issued May 19, 1998



Held under DoD Secrecy Orders for 12-years-3-months

Filed Feb. 20, 1986

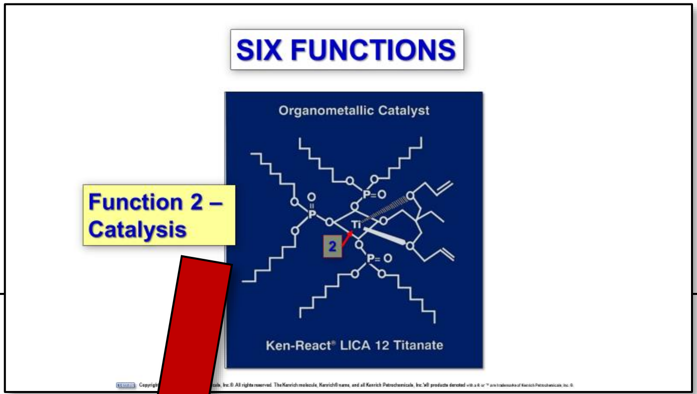
Problem Solving Takeaways From This Presentation - Catalysis



(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.
- **Repolymerization:** Regenerate regrind to virgin properties.

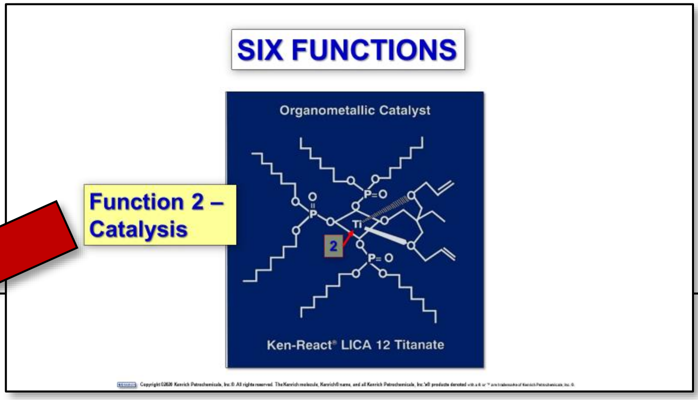
Problem Solving Takeaways From This Presentation - Catalysis



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

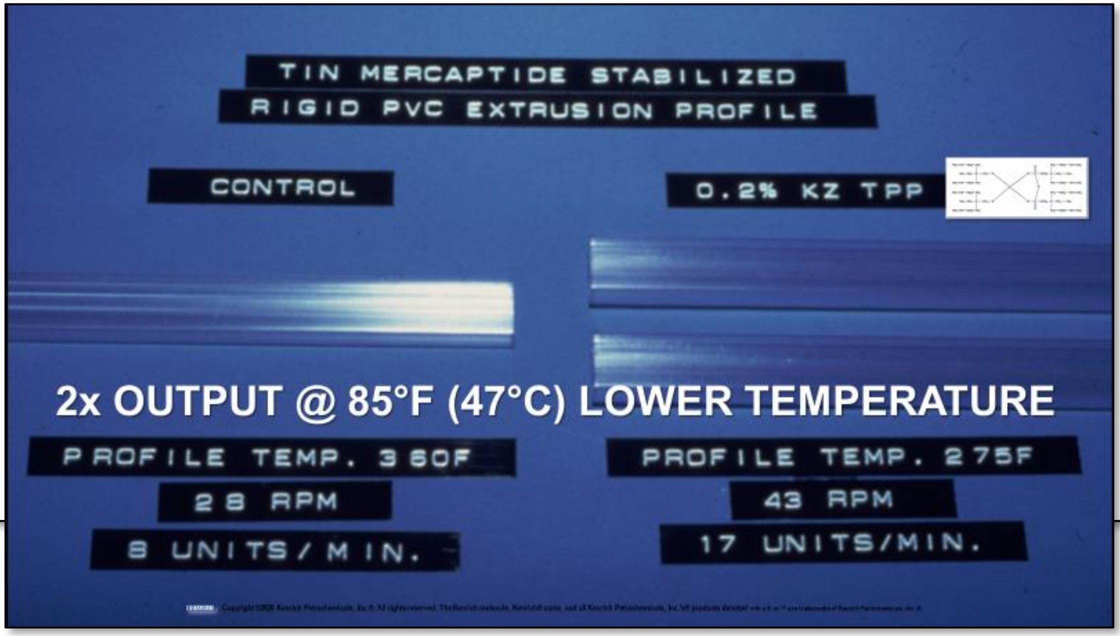
- Lower process temperatures from 10 to 40%.
- **Repolymerization:** Regenerate regrind to virgin properties.

Problem Solving Takeaways From This Presentation - Catalysis

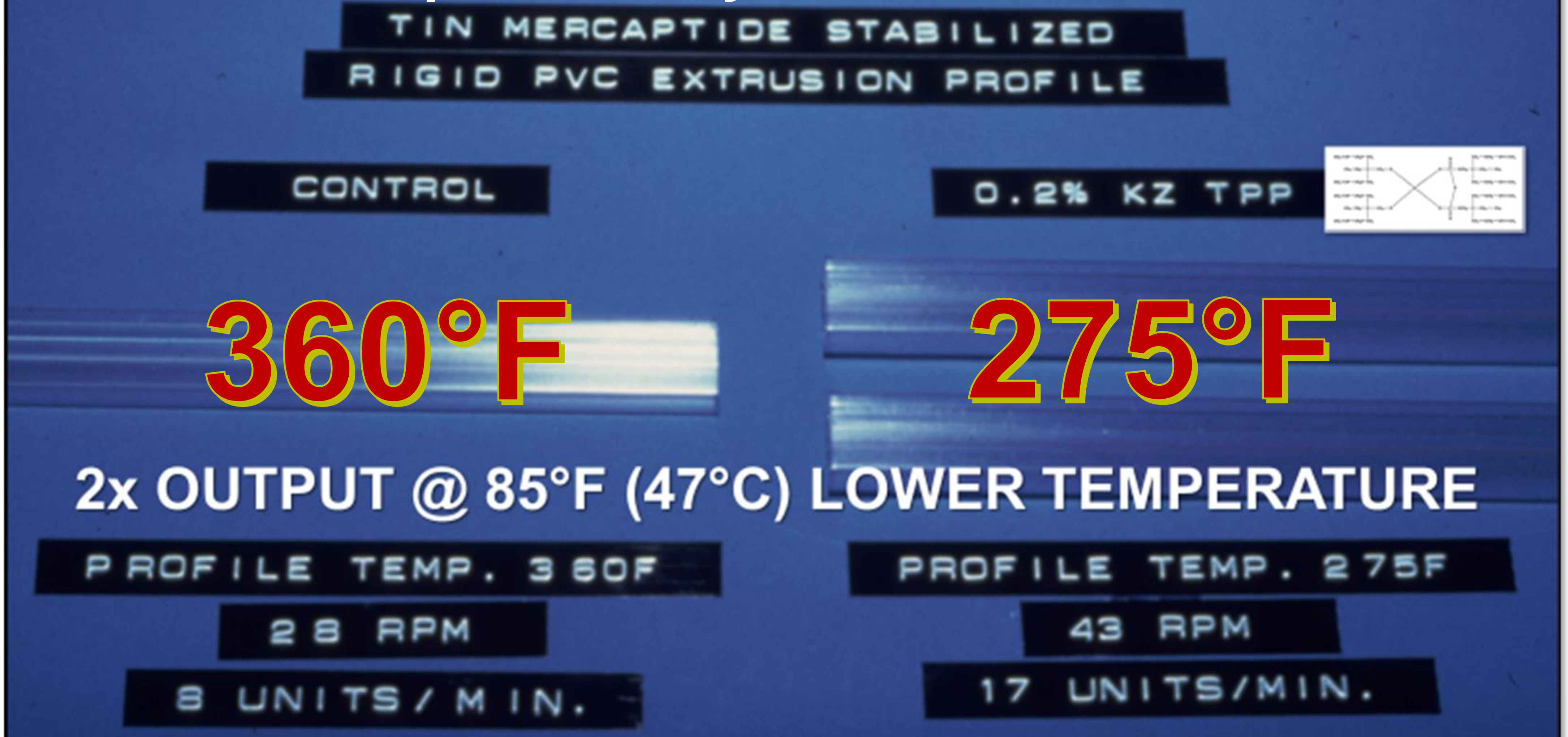


(2) Titanium, Zirconium & Aluminum Polymer Catalysis – without or with filler allows:

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



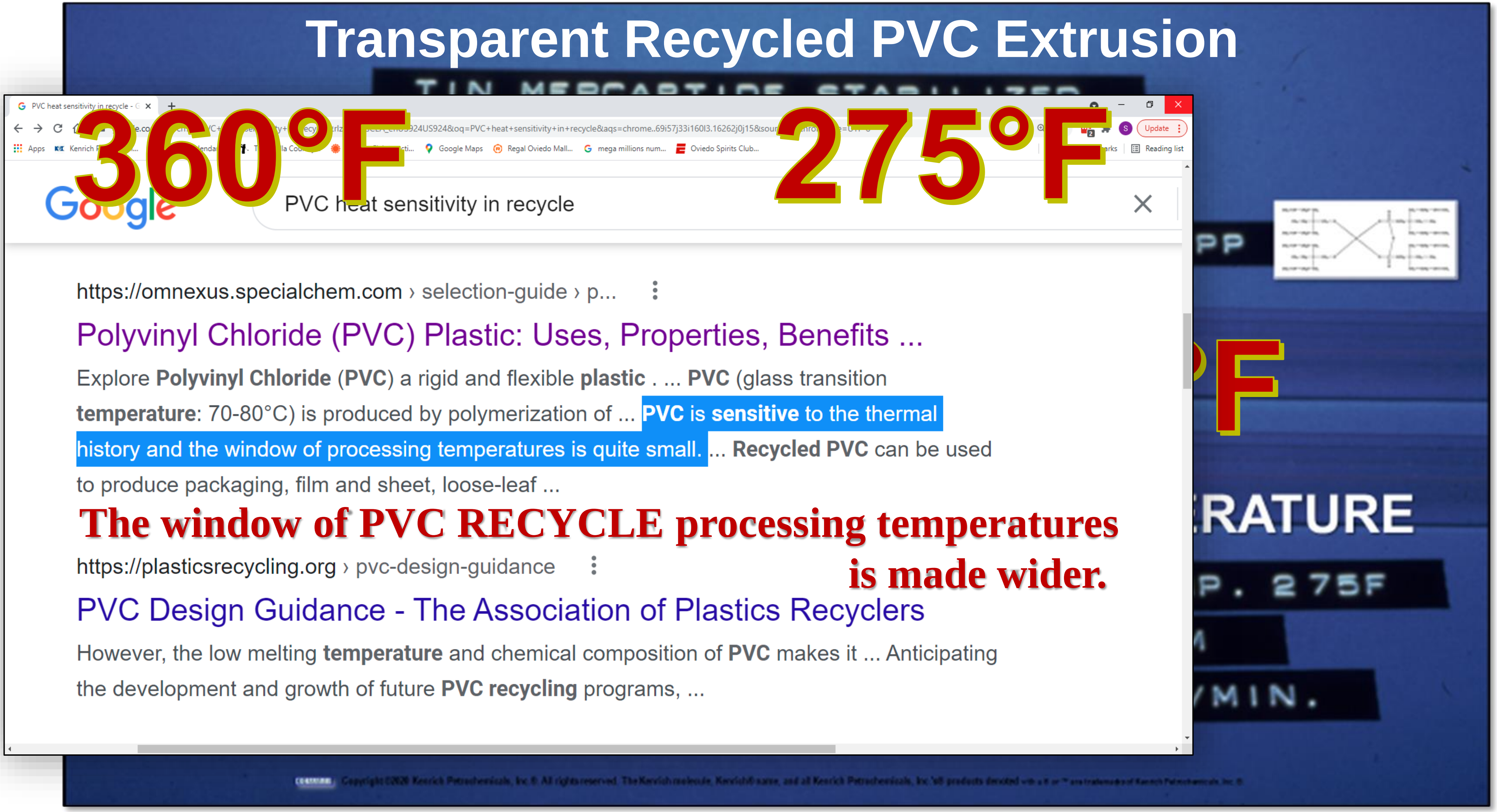
Transparent Recycled PVC Extrusion



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

2021 Vinyl Recycling Summit

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents



Titanium Catalysis

REPOLYMERIZATION

Hosted VINYLTEC 2010 as Preside

PLASTICS INDUSTRY ASSOCIATION Voting Member & Recycle Su

SPE Fellow & Honored Service Me

PPA Plastics Pioneers Association PPA Board of Governors – N

SCIENCE IP CAS Search Service 450- ACS CAS Abstracted Wo

32-US Patents Filed Worldwide

Classified TOP SECRET for DOD IM

PLASTICS Hall of Fame 2021

Salvatore J. Monte, President

KENRICH PETROCHEMICALS, INC.

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

***

6-Ti/Zr @ 4 dosages

United States Patent [19]

Sugerman et al.

[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

Related U.S. Application 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

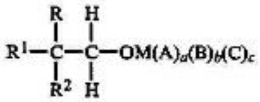
4,036,796	7/1977	Sugiyama et al.	525/437 X
4,115,371	9/1978	Bier et al.	528/286 X
4,148,989	4/1979	Tews et al.	525/437
4,452,970	6/1984	Brunelle	528/279
4,454,312	6/1984	Kuze et al.	528/279 X
4,482,700	11/1984	Kühnrich et al.	528/279

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, R^1 and R^2 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, R^2 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.

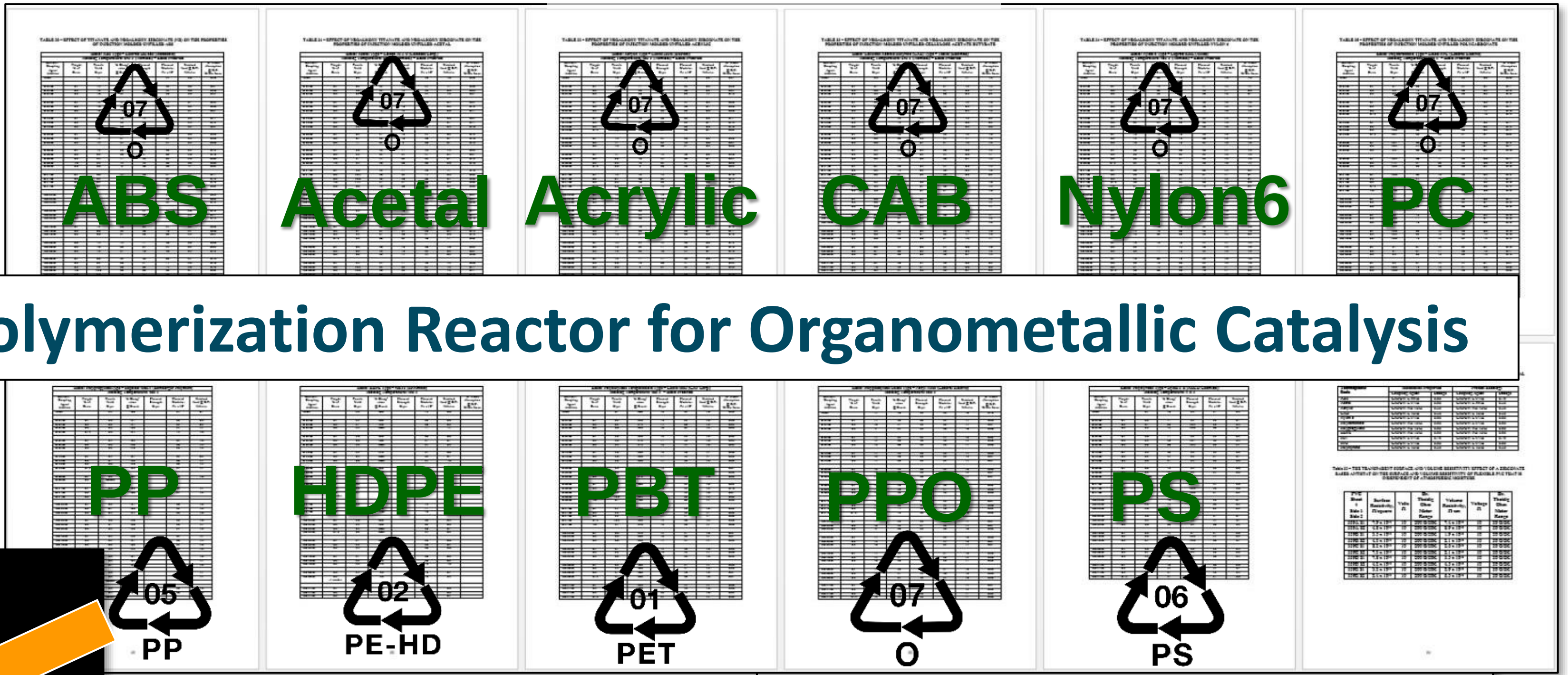
5 Claims, No Drawings

REPOLYMERIZATION
11 – Unfilled Plastics

***

6-Ti/Zr @ 4 dosages

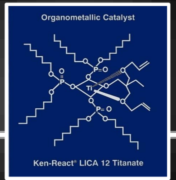
Unfilled Plastics Data



The Extruder acts as a Polymerization Reactor for Organometallic Catalysis

PP

UNFILLED PP

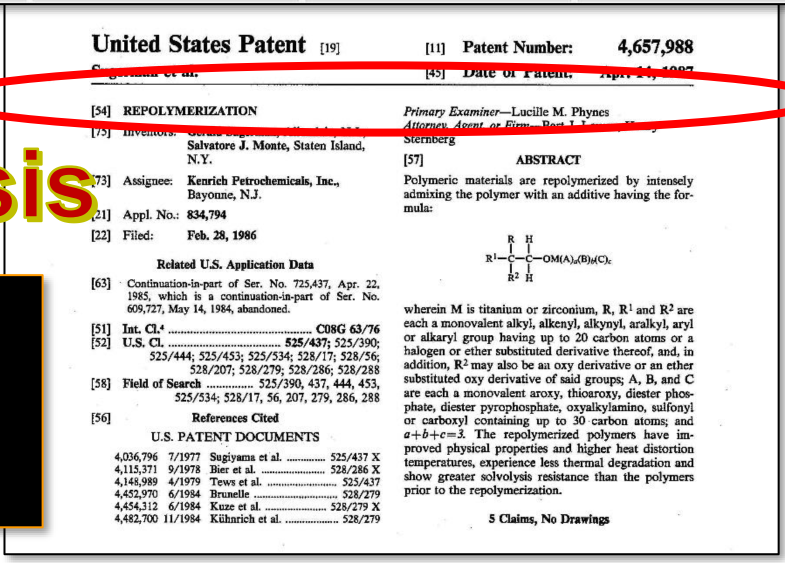


EFFECT OF NEOALKOXY TITANATE CAPOW L 12/H ON THE PROPERTIES OF INJECTION MOLDED UNFILLED PP

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]

[11] Patent Number: 4,657,988

[54] REPOLYMERIZATION

Salvatore J. Monte, Staten Island, N.Y.

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

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4,454,312	6/1984	Kuze et al.	528/279 X
4,482,700	11/1984	Kühnrich et al.	528/279

Primary Examiner—Lucille M. Phynes

Sternberg

[57] ABSTRACT

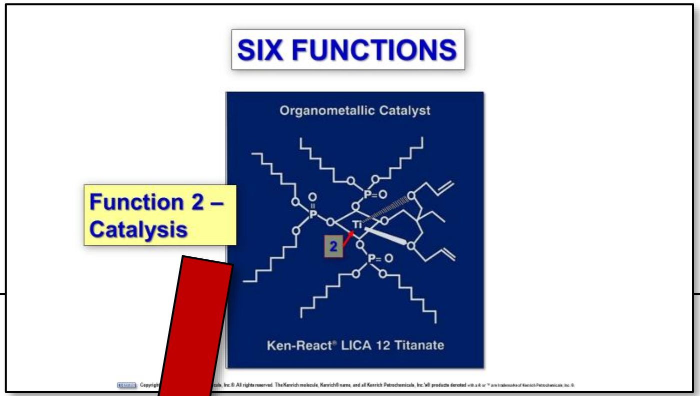
Polymeric materials are repolymerized by intensely admixing the polymer with an additive having the formula:

$$R^1-\underset{R^2}{\overset{R}{C}}-\underset{H}{\overset{H}{C}}-OM(A)_a(B)_b(C)_c$$

wherein M is titanium or zirconium, R, R^1 and R^2 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, R^2 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.

5 Claims, No Drawings

Problem Solving Takeaways From This Presentation - Catalysis

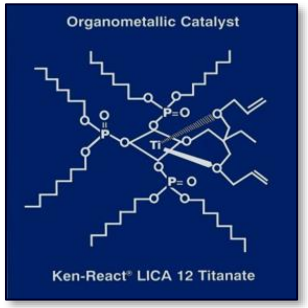


(2) Titanium, Zirconium & Aluminum Polymer Catalysis –without or with filler allows:

Polymer Mechanical Properties Are Increased.

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

Commercial Products Chemistry



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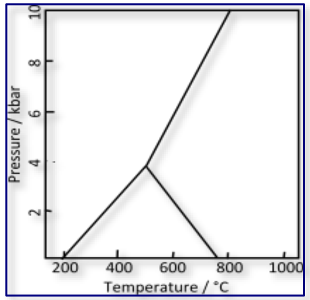

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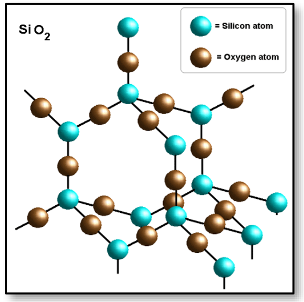

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LLDPE

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Ken-React®
CAPS®
KPR® 12/LV

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

03
PVC

Developed from a Half-Century of Nano-TITANATE Experience

1974 Modern Plastics Article

By S.J. Monte* and P.F. Bruins†

New coupling agent for filled polyethylene

Ken-React TTS[1], a triisostearic isopropyl titanate ester, is a very effective coupling agent for calcium carbonate filler in PE. The compounder can take 100 lb. of HDPE and fill it with 157 lb. of $CaCO_3$ filler and obtain properties essentially equivalent to 100% unfilled HDPE. These properties are obtained at significantly reduced energy consumption and are unobtainable without coagent treatment with TTS.

A technical feature
Gordon M. Kline, technical editor

Until recently, energy and fillers were two of the lesser considered items in polymeric compounding. Today, however, the compounder must consider every available resource to achieve end properties efficiently. Therefore, research on the extension and reinforcement of polyolefinic thermoplastics and rubber by means of the filler route has intensified in an effort to offset rising prices and low availability of polymers.

The incorporation of a mineral filler in a polyolefinic thermoplastic usually results in an increase in tensile modulus and a decrease in impact strength. When filler loadings exceed 20 parts per hundred of polymer, the elongation and impact strength are severely affected and the compounder's genius is challenged.

A number of theories have been postulated to explain filler strain phenomena occurring in the macromolecular state using conventional filler compounding techniques: 1) The imparted strain to the composite occurs in the polymer phase independent of the filler phase (1).[2] 2) The imparted strain to the composite occurs equally in the polymeric matrix and filler phase; if the tensile strength of the filler phase is greater than that of the polymer phase, the strength of the composite will increase as the filler loading in the composite increases (2). 3) The imparted strain to the composite is transferred from the polymer matrix to the filler phase as well as from filler to filler particle. At loadings in excess of 20% filler, the mean distance between filler particles is of the same order of magnitude as the dimensions of a filler particle. The poor physical properties result only from stress failure at a weak interface between the polymer matrix and the filler phase (3).

The research scientist's goal, therefore, is to eliminate or minimize the distinct "phasing" that occurs between the inorganic filler and the organic polymer. This has led to new technology that has been successful in chemically bonding the filler phase to the polymer matrix in cured systems. Witness the success of silane-modified silicas and clays in improving the properties of peroxide-cured systems (vinyl silane A-172) (4) and sulfur-cured systems (mercapto silane A-189) (5). These coagents overcome the intrinsic incompatibility of inorganic fillers in organic media by attaching organofunctional substituents to the filler surface and to the organic backbone via an interfacial reaction illustrated in Fig. 1.

The inorganic material, when treated with coagents, is converted to a mineral filler with organic appendages that results in the following filler property changes: 1) organophilic and hydrophobic rather than organophobic and hydrophilic; 2) improved compatibility and dispersion; 3) ability of the filler organic appendage to enter into the crosslink mechanism in thermoset polymerics; 4) availability of the filler organic appendages to mix with the organic matrix and provide a molecular chain for the transfer of stress energy from the polymer matrix to the filler phase without bond rupture in thermoplastic polymerics.

The effect on fillers treated with unsaturated organofunctional silane coagents in cured systems is well documented (6-10). Although the silane-modified fillers have made significant breakthroughs on improving the tensile strength, modulus, and heat-deflection temperatures of reinforced thermoplastics, fillers still adversely affected the processibility, impact strength, elongation, and modulus of the polymeric compound in applications such as coatings, fibers, and blown film. What is needed to overcome these filler limitations is a coagent molecule designed specifi-

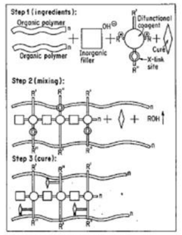

Fig. 1: Coupling in cured systems with polyfunctional coagents.

*Executive vice president, Kenrich Petrochemicals Inc.
†Professor, Chemical Engineering, Polytechnic Institute of New York.
1–Trademark, Kenrich Petrochemicals Inc.
2–Numbers in parentheses designate references at end of article.

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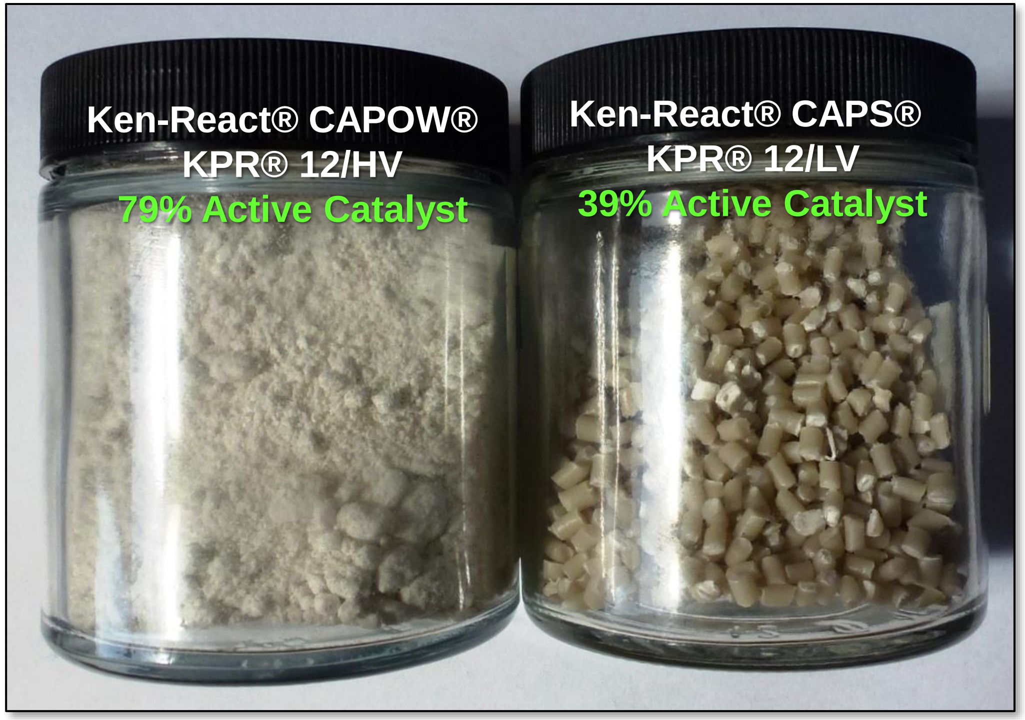
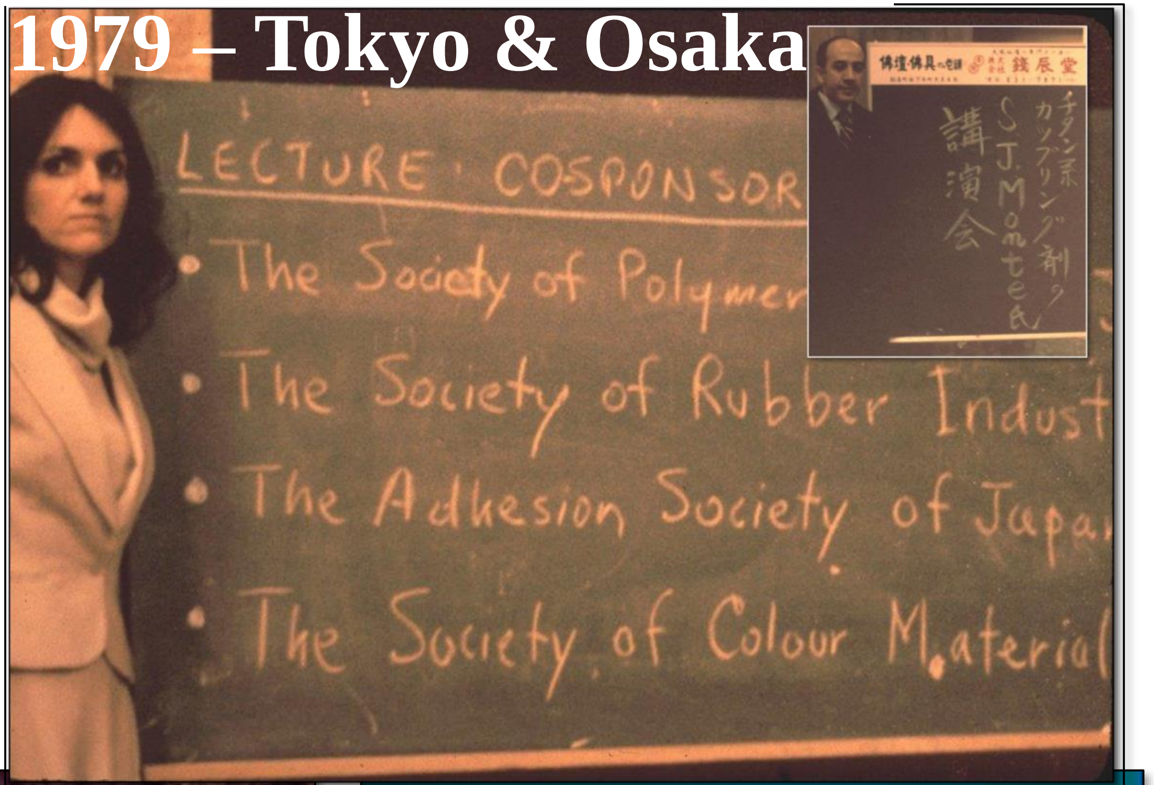
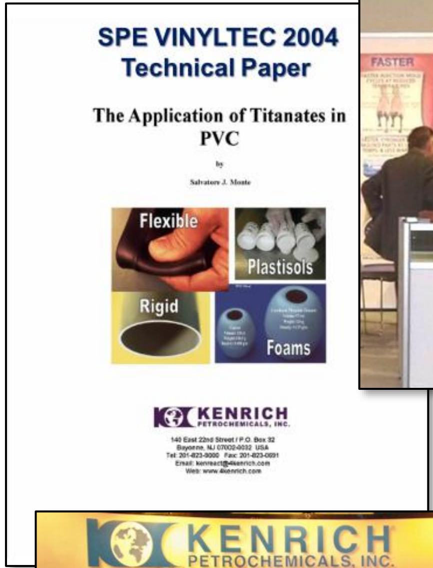


My Mission Statement for the last 46-years is "…To teach the more efficient use of raw materials through the use of titanates and zirconates."



Trade Shows, TableTops & Conference Papers


SPE VINYLTEC 2004
Technical Paper

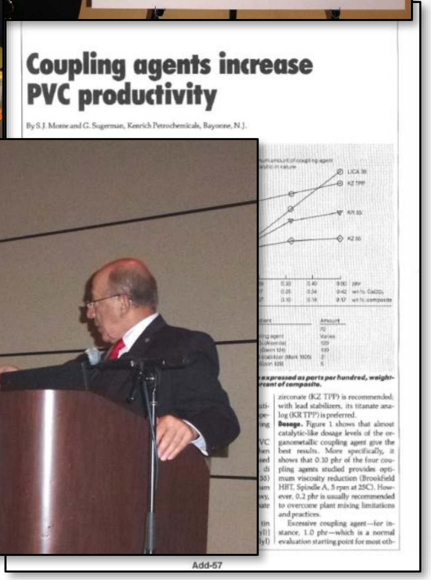
The Application of Titanates in PVC

by

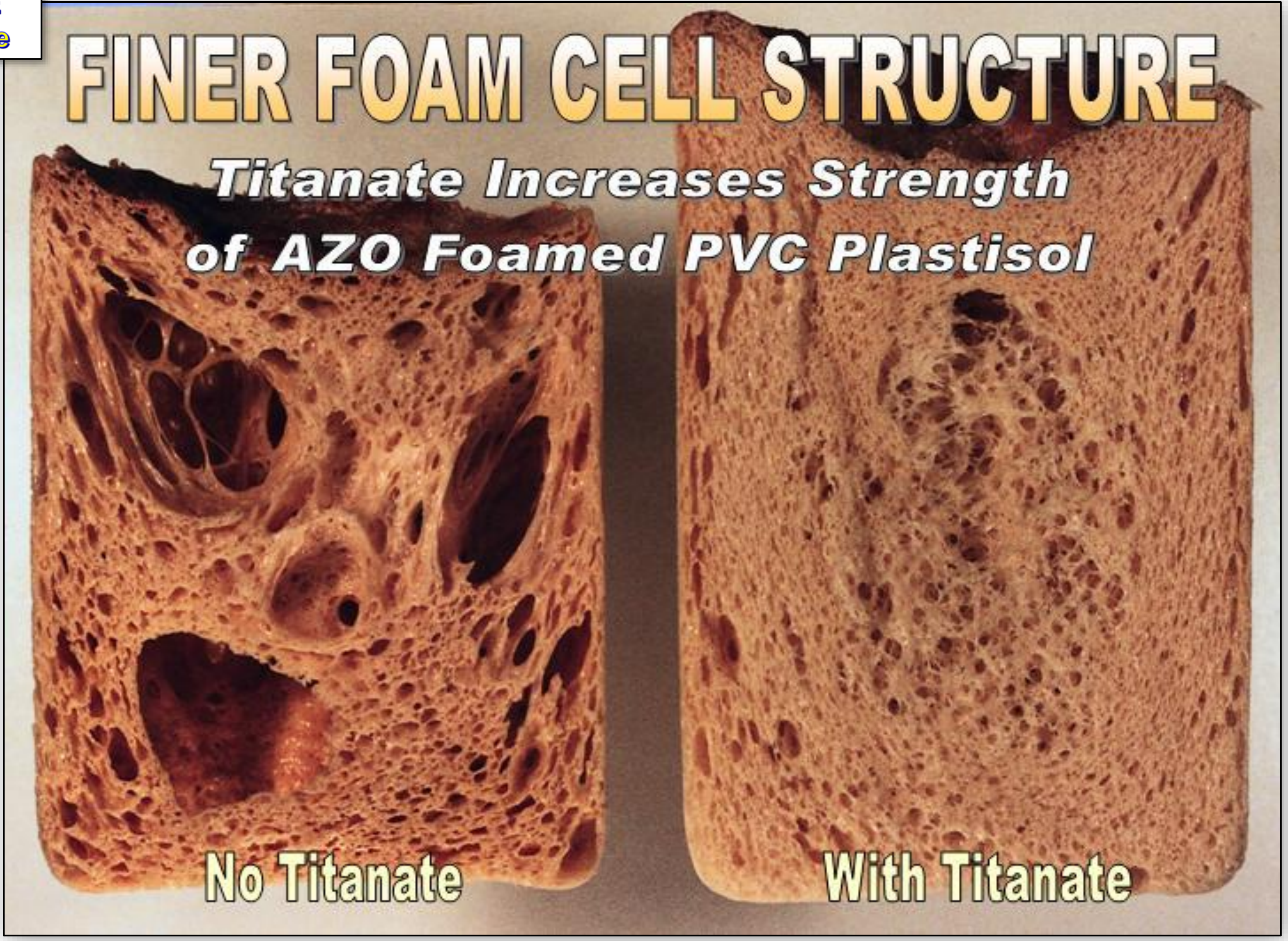
Salvatore J. Monte

KENRICH PETROCHEMICALS, INC.

Developed from a Half-Century of Nano-TiTANATE Experience


Coupling agents increase PVC productivity

By S.J. Monte and G. Sugerman, Kenrich Petrochemicals, Bayonne, N.J.



VINYLTEC® 2004 Paper – Over 450 Published Works

Developed from a Half-Century of Nano-TITANATE Experience

64-pages: 43-Tables, 46-Figures, & 48-References capturing 3-decades of PVC developments & applications

SPE VINYLTEC 2004
Technical Paper

The Application of Titanates in PVC

by

Salvatore J. Monte

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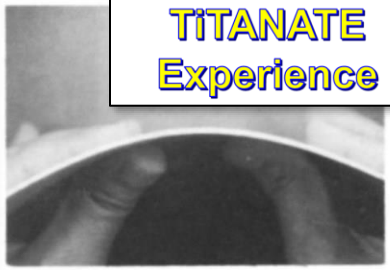
Web: www.4kenrich.com



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

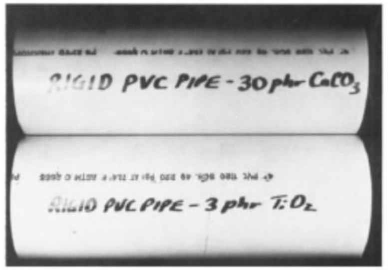


Figure 44 – Compares equivalent impact strength 3 phr $CaCO_3$ (marked as TiO_2) filled pipe titanate to a pipe containing 30 phr $CaCO_3$ (2.5 micron), 0.5% KR 38S.

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.

64

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

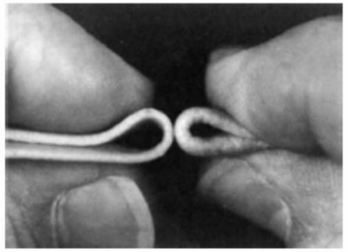
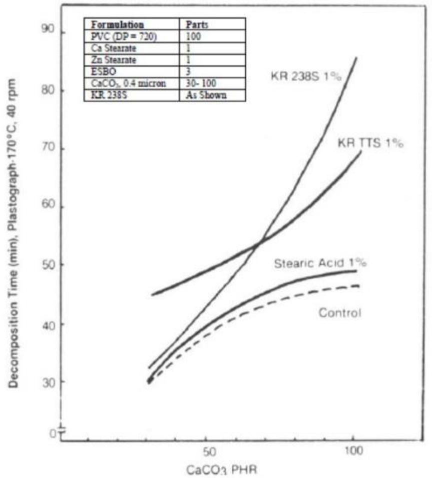


Figure 33 – Both azodicarbonamide foamed PVC plastisol luggage covering samples represent a successful reduction in the PVC:$CaCO_3$ ratio from 8:1 to 2:1(increase in $CaCO_3$ from 12.5 to 33.3%) while maintaining excellent film strength using KR 138S. The sample on the left exhibited a reduction in "hand" or feel e 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.

59

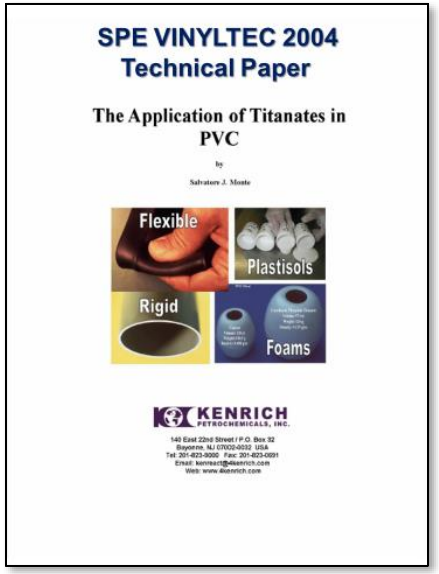


Formulation	Parts
PVC (DP = 720)	100
Ca Stearate	1
Zn Stearate	1
ESBO	3
$CaCO_3$, 0.4 micron	30- 100
KR 238S	As Shown

Figure 41 – Increased heat stabilizing effect of titanate treated $CaCO_3$ in filled rigid PVC.

Figure 42 – 60 phr 5μ $CaCO_3$, 1% KR 38S pretreated filled rigid PVC injection molded yoke.

63



SPE VINYLTEC 2004
Technical Paper

The Application of Titanates in PVC

by

Salvatore J. Monte

Flexible
Plastisols
Rigid
Foams

KENRICH PETROCHEMICALS, INC.

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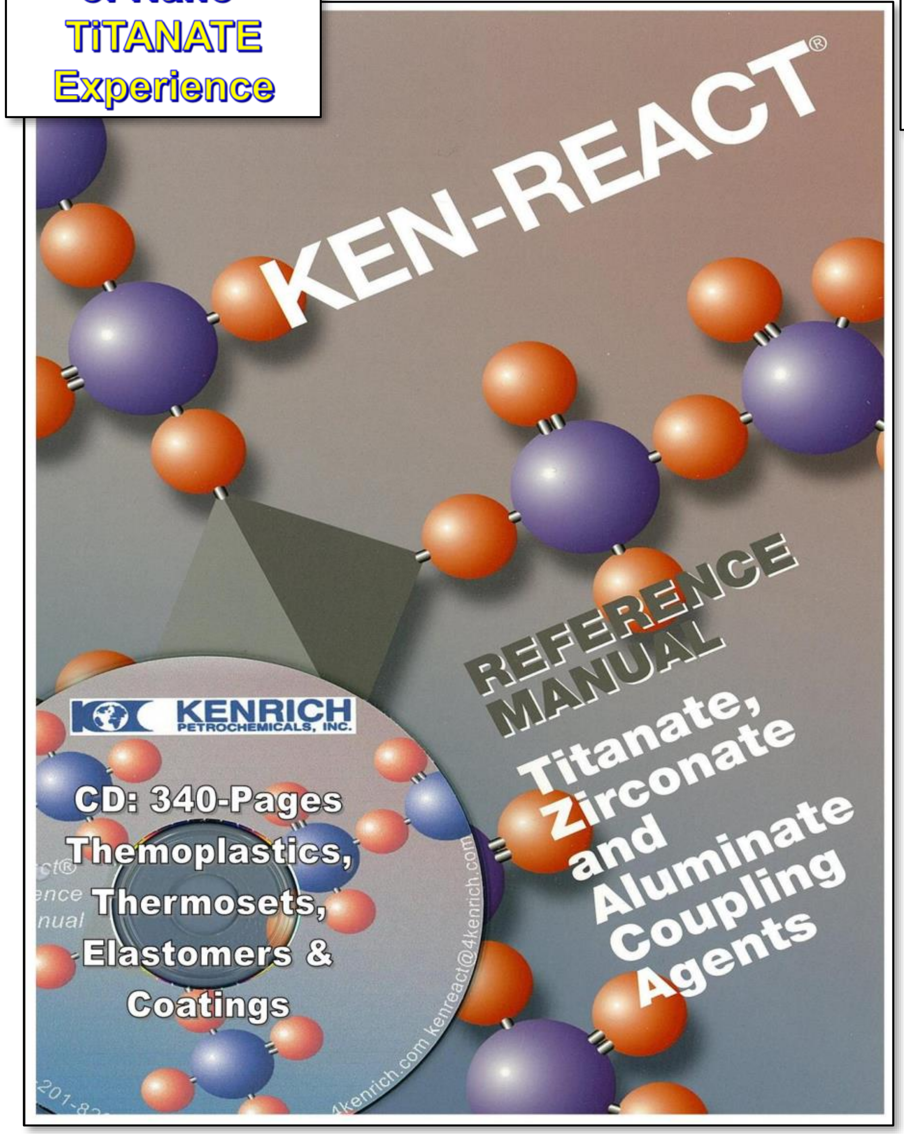
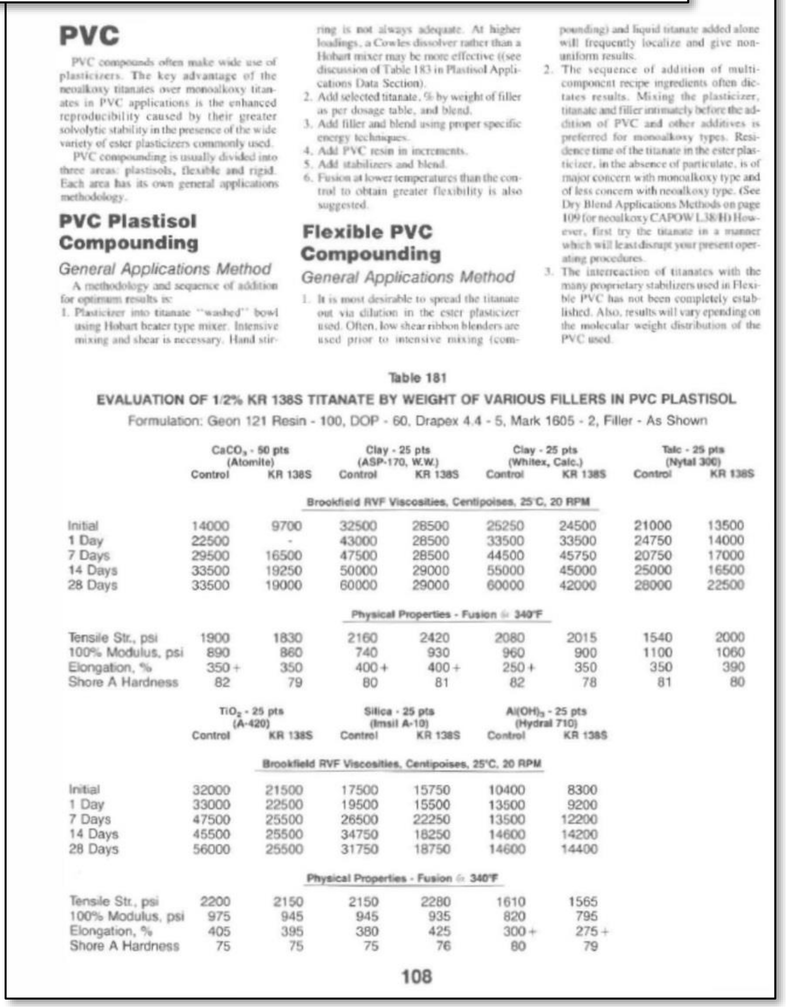
Developed from a Half-Century of Nano-TiTANATE Experience

340-Page Reference Manual



PVC Chapter – Reference Manual – Pages 108-120 Printed in 1985



PVC

PVC compounds often make wide use of plasticizers. The key advantage of the neoalkoxy titanates over monoalkoxy titanates in PVC applications is the enhanced reproducibility caused by their greater solvolytic stability in the presence of the wide variety of ester plasticizers commonly used.

PVC compounding is usually divided into three areas: plastisols, flexible and rigid. Each area has its own general applications methodology.

PVC Plastisol Compounding

General Applications Method

A methodology and sequence of addition for optimum results is:

1. Plasticizer into titanate "washed" bowl using Hobart beater type mixer. Intensive mixing and shear is necessary. Hand stirring is not always adequate. At higher loadings, a Cowles dissolver rather than a Hobart mixer may be more effective ((see discussion of Table 183 in Plastisol Applications Data Section).
2. Add selected titanate, % by weight of filler as per dosage table, and blend.
3. Add filler and blend using proper specific energy techniques.
4. Add PVC resin in increments.
5. Add stabilizers and blend.
6. Fusion at lower temperatures than the control to obtain greater flexibility is also suggested.

Flexible PVC Compounding

General Applications Method

1. It is most desirable to spread the titanate out via dilution in the ester plasticizer used. Often, low shear ribbon blenders are used prior to intensive mixing (compounding) and liquid titanate added alone will frequently localize and give non-uniform results.
2. The sequence of addition of multi-component recipe ingredients often dictates results. Mixing the plasticizer, titanate and filler intimately before the addition of PVC and other additives is preferred for monoalkoxy types. Residence time of the titanate in the ester plasticizer, in the absence of particulate, is of major concern with monoalkoxy type and of less concern with neoalkoxy type. (See Dry Blend Applications Methods on page 109 for neoalkoxy CAPOW L38/H) However, first try the titanate in a manner which will least disrupt your present operating procedures.
3. The intereaction of titanates with the many proprietary stabilizers used in Flexible PVC has not been completely established. Also, results will vary epending on the molecular weight distribution of the PVC used.

Table 181

EVALUATION OF 1/2% KR 138S TITANATE BY WEIGHT OF VARIOUS FILLERS IN PVC PLASTISOL

Formulation: Geon 121 Resin - 100, DOP - 60, Drapex 4.4 - 5, Mark 1605 - 2, Filler - As Shown

	$CaCO_3$ - 50 pts (Atomite)		Clay - 25 pts (ASP-170, W.W.)		Clay - 25 pts (Whitex, Calc.)		Talc - 25 pts (Nytal 300)	
	Control	KR 138S	Control	KR 138S	Control	KR 138S	Control	KR 138S
Brookfield RVF Viscosities, Centipoises, 25°C, 20 RPM								
Initial	14000	9700	32500	28500	25250	24500	21000	13500
1 Day	22500	-	43000	28500	33500	33500	24750	14000
7 Days	29500	16500	47500	28500	44500	45750	20750	17000
14 Days	33500	19250	50000	29000	55000	45000	25000	16500
28 Days	33500	19000	60000	29000	60000	42000	28000	22500
Physical Properties - Fusion @ 340°F								
Tensile Str., psi	1900	1830	2160	2420	2080	2015	1540	2000
100% Modulus, psi	890	860	740	930	960	900	1100	1060
Elongation, %	350 +	350	400 +	400 +	250 +	350	350	390
Shore A Hardness	82	79	80	81	82	78	81	80

	TiO_2 - 25 pts (A-420)		Silica - 25 pts (Imsil A-10)		$Al(OH)_3$ - 25 pts (Hydral 710)	
	Control	KR 138S	Control	KR 138S	Control	KR 138S
Brookfield RVF Viscosities, Centipoises, 25°C, 20 RPM						
Initial	32000	21500	17500	15750	10400	8300
1 Day	33000	22500	19500	15500	13500	9200
7 Days	47500	25500	26500	22250	13500	12200
14 Days	45500	25500	34750	18250	14600	14200
28 Days	56000	25500	31750	18750	14600	14400
Physical Properties - Fusion @ 340°F						
Tensile Str., psi	2200	2150	2150	2280	1610	1565
100% Modulus, psi	975	945	945	935	820	795
Elongation, %	405	395	380	425	300 +	275 +
Shore A Hardness	75	75	75	76	80	79

108

PVC Chapter – Addendum to 340-Page Reference Manual

SPE VINYLTEC 2004
Technical Paper

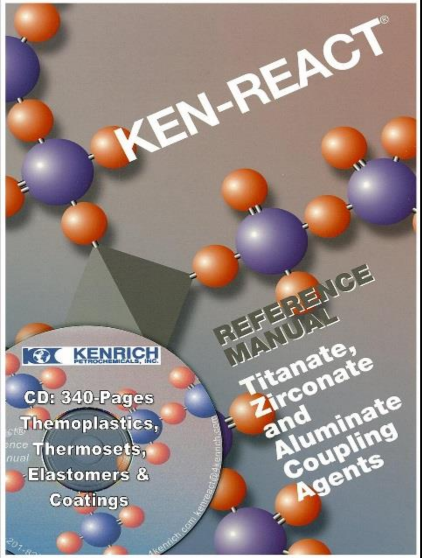
The Application of Titanates in PVC

by

Salvatore J. Monte

KENRICH PETROCHEMICALS, INC.
140 East 22nd Street / P.O. Box 32
Bayonne, NJ 07002-0032 USA

Developed from a Half-Century of Nano-TITANATE Experience



PVC Chapter – Reference Manual Addendum – Pages Add-57 to Add-63 Printed in 1993

Coupling agents increase PVC productivity

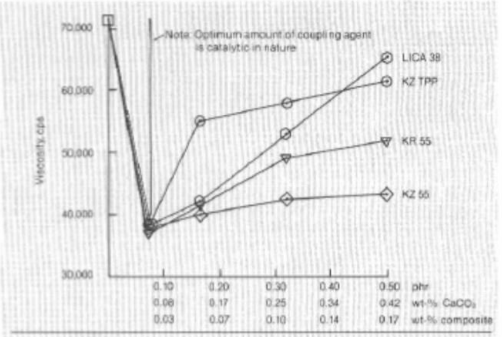
By S.J. Monte and G. Sugerman, Kenrich Petrochemicals, Bayonne, N.J.

Properly used, neoalkoxy titanate and zirconate coupling agents can bring major benefits in productivity for filled or unfilled, rigid or flexible PVC injection-molded, extruded, or foamed products. Data show that more product can be produced in less time, with fewer rejects and lower material/energy costs.

The use of neoalkoxy titanate and zirconate coupling agents in increasing flow and mechanical properties of unfilled thermoplastics has been demonstrated previously.[1] More recently, laboratory and plant trials have confirmed their efficacy in unfilled and filled, rigid and flexible PVC compounds.

Test results have indicated that some understanding of organometallic chemistry is necessary for proper application of these coupling agents. A knowledge of their specificity and sensitivity to such parameters as the heat stabilizer used in the compound, the coupling-agent dosage level, the sequence of addition of the compound ingredients, the effects of machinery surfaces, the quality of distributive mixing, dispersion characteristics, and filler level helps to optimize their benefits.

Proper understanding of these factors can lead to increased productivity, in terms of producing more PVC product in less time, with fewer rejects and lower raw-material and energy costs.



Plastisol formulation:

Sequence	Ingredient	Amount
1 - Mix	DOP	70
2 - Mix	Coupling agent	Varies
3 - Mix	$CaCO_3$ (Atomite)	120
4 - Mix	PVC (Geon 124)	100
5 - Mix	BaCd stabilizer (Mark 1605)	2
6 - Mix	EPO (Epon 828)	5

Figure 1. Coupling-agent dosage expressed as parts per hundred, weight-percent of $CaCO_3$, and weight-percent of composite.

PROPER USE

When organometallic chemistry is utilized in PVC compounds, it is specific and sensitive to the following parameters.

Stabilizer type. In plasticized PVC (plastisols and flexible vinyls), when tin and lead stabilizers are used tetra(2,2 diallyloxymethyl) butyl, di (ditridecyl) phosphito titanate (KR 55) is preferred; with barium/cadmium stabilizers, neopentyl (diallyl) oxy, tri(dioctyl) pyrophosphato titanate (LICA 38) works best.

In rigid PVC, with mercapto tin stabilizers, cyclo[dienepentyl(diallyl)] pyrophosphato dineopentyl(diallyl) zirconate (KZ TPP) is recommended; with lead stabilizers, its titanate analog (KR TPP) is preferred.

Dosage. Figure 1 shows that almost catalytic-like dosage levels of the organometallic coupling agent give the best results. More specifically, it shows that 0.10 phr of the four coupling agents studied provides optimum viscosity reduction (Brookfield HBT, Spindle A, 5 rpm at 25C). However, 0.2 phr is usually recommended to overcome plant mixing limitations and practices.

Excessive coupling agent—for instance, 1.0 phr—which is a normal evaluation starting point for most oth-

PVC Plastisol Compounding

General Applications Method

A methodology and sequence of addition for optimum results is:

1. Plasticizer into titanate "washed" bowl using Hobart beater type mixer. Intensive mixing and shear is necessary. Hand stir-

Flexible PVC Compounding

General Applications Method

1. It is most desirable to spread the titanate out via dilution in the ester plasticizer used. Often, low shear ribbon blenders are used prior to intensive mixing (compounding) and liquid titanate added alone will frequently localize and give non-uniform results.
2. The sequence of addition of multi-component recipe ingredients often dictates results. Mixing the plasticizer, titanate and filler intimately before the addition of PVC and other additives is preferred for monoalkoxy types. Residence time of the titanate in the ester plasticizer, in the absence of particulate, is of major concern with monoalkoxy type and of less concern with neoalkoxy type. (See Dry Blend Applications Methods on page 109 for neoalkoxy CAPOW L38/H) However, first try the titanate in a manner which will least disrupt your present operating procedures.
3. The interreaction of titanates with the many proprietary stabilizers used in Flexible PVC has not been completely established. Also, results will vary epending on the molecular weight distribution of the PVC used.

Table 181

EVALUATION OF 1/2% KR 138S TITANATE BY WEIGHT OF VARIOUS FILLERS IN PVC PLASTISOL

Formulation: Geon 121 Resin - 100, DOP - 60, Drapex 4.4 - 5, Mark 1605 - 2, Filler - As Shown

	$CaCO_3$ - 50 pts (Atomite)		Clay - 25 pts (ASP-170, W.W.)		Clay - 25 pts (Whitex, Calc.)		Talc - 25 pts (Nytal 300)	
	Control	KR 138S	Control	KR 138S	Control	KR 138S	Control	KR 138S
Brookfield RVF Viscosities, Centipoises, 25°C, 20 RPM								
Initial	14000	9700	32500	28500	25250	24500	21000	13500
1 Day	22500	-	43000	28500	33500	33500	24750	14000
7 Days	29500	16500	47500	28500	44500	45750	20750	17000
14 Days	33500	19250	50000	29000	55000	45000	25000	16500
28 Days	33500	19000	60000	29000	60000	42000	28000	22500
Physical Properties - Fusion @ 340°F								
Tensile Str., psi	1900	1830	2160	2420	2080	2015	1540	2000
100% Modulus, psi	890	860	740	930	960	900	1100	1060
Elongation, %	350 +	350	400 +	400 +	250 +	350	350	390
Shore A Hardness	82	79	80	81	82	78	81	80

	TiO_2 - 25 pts (A-420)		Silica - 25 pts (Imsil A-10)		$Al(OH)_3$ - 25 pts (Hydral 710)	
	Control	KR 138S	Control	KR 138S	Control	KR 138S
Brookfield RVF Viscosities, Centipoises, 25°C, 20 RPM						
Initial	32000	21500	17500	15750	10400	8300
1 Day	33000	22500	19500	15500	13500	9200
7 Days	47500	25500	26500	22250	13500	12200
14 Days	45500	25500	34750	18250	14600	14200
28 Days	56000	25500	31750	18750	14600	14400
Physical Properties - Fusion @ 340°F						
Tensile Str., psi	2200	2150	2150	2280	1610	1565
100% Modulus, psi	975	945	945	935	820	795
Elongation, %	405	395	380	425	300 +	275 +
Shore A Hardness	75	75	75	76	80	79

28th Annual Compounders Conference

FLEXIBLE VINYL
PRODUCTS DIVISION

July 9-11, 2017

PLASTICS
INDUSTRY ASSOCIATION

Brown Palace Hotel July 9-11, 2017.

Developed from a Half-Century of Nano-TiTANATE Experience

… & Conference Papers

Is China Cleaning Our R&D Clocks in PVC Compatibilization and Nanotechnology While We Combat Prop 65 and Regs

Monday – July 10, 2017 – 3:15pm-4:00pm

Salvatore J. Monte

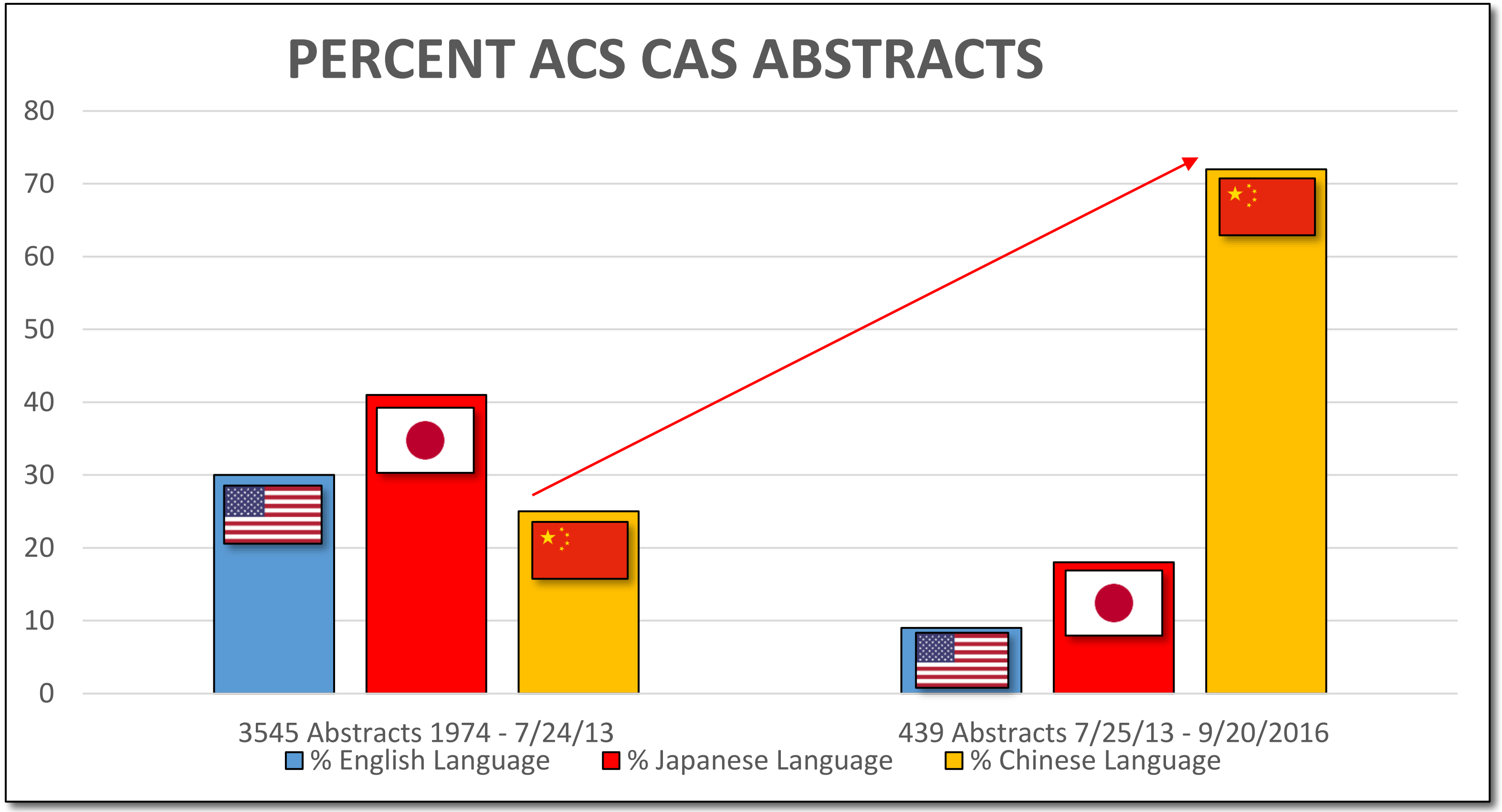
www.4kenrich.com sjmonte@4kenrich.com

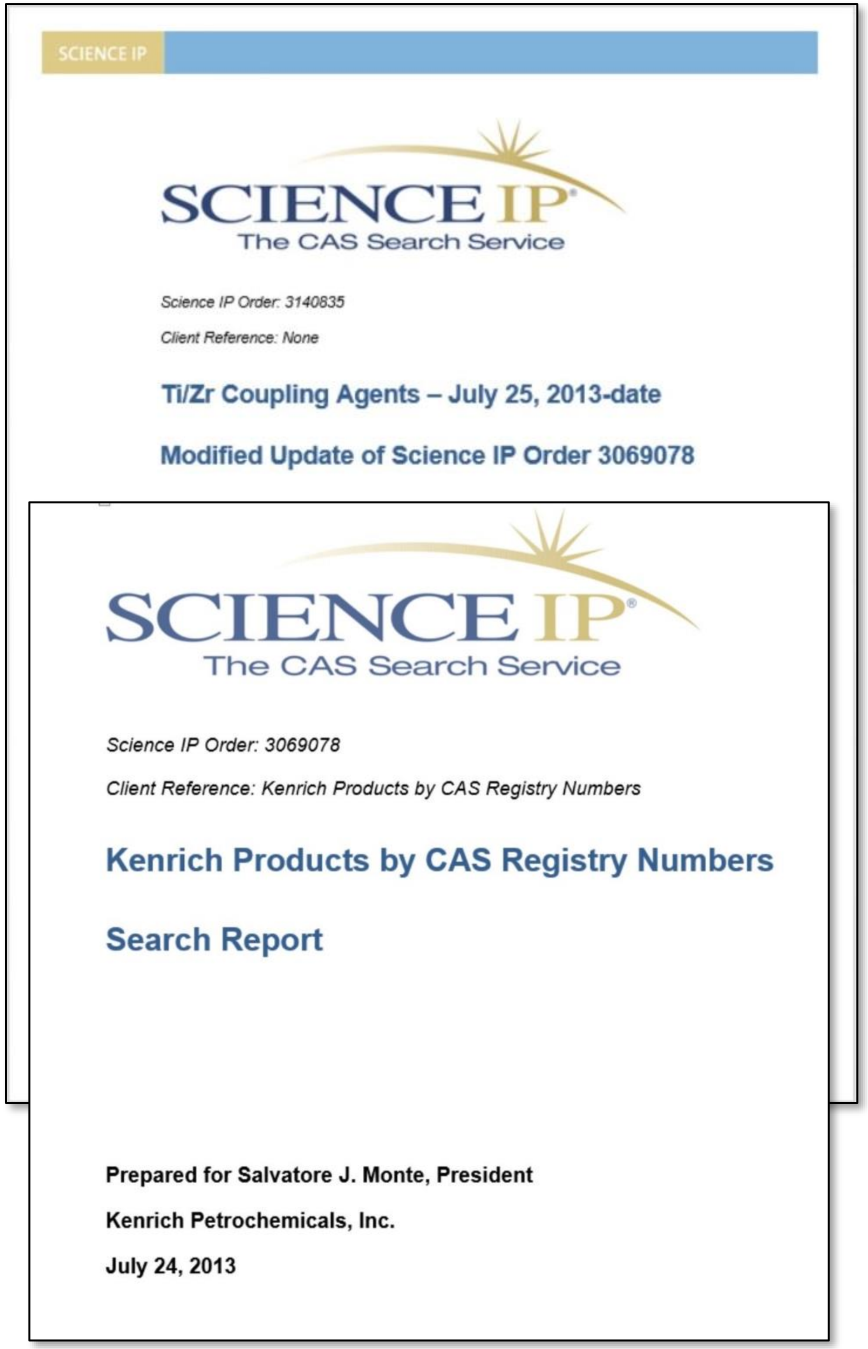
KENRICH®
PETROCHEMICALS, INC.

Abstracts Based on Subject Titanates & Zirconates

Up to 2013 – China = 25% of Abstracts
2013--2016 – China = 72% of Abstracts
2015--2020 – China = 85% of Abstracts

Developed from a Half-Century of Nano-TiTANATE Experience




SCIENCE IP

SCIENCE IP
The CAS Search Service

Science IP Order: 3140835

Client Reference: None

Ti/Zr Coupling Agents – July 25, 2013-date

Modified Update of Science IP Order 3069078

SCIENCE IP
The CAS Search Service

Science IP Order: 3069078

Client Reference: Kenrich Products by CAS Registry Numbers

Kenrich Products by CAS Registry Numbers

Search Report

Prepared for Salvatore J. Monte, President

Kenrich Petrochemicals, Inc.

July 24, 2013

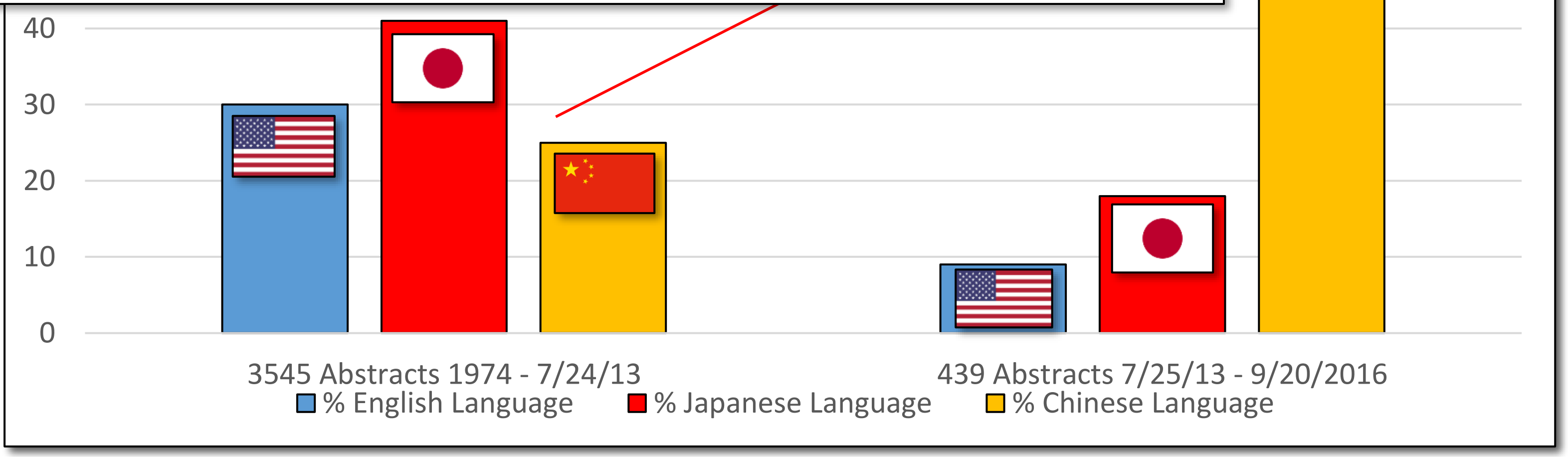
Abstracts Based on Subject Titanates & Zirconates In PVC/Polymer Blends – Regenerated PVC

```
L19  ANSWER 321 OF 3545  HCA  COPYRIGHT 2013 ACS on STN
AN   157:736344  HCA Full-text <<LOGINID::20130724>>
TI   New colored plastic steel profile manufactured from regenerated polyvinyl chloride
IN   Yuan, Xiaoju
PA   Shucheng Antai Plastic Product Co., Ltd., Peop. Rep. China
SO   Faming Zhuanli Shenqing, 7pp.
     CODEN: CNXXEV
DT   Patent
LA   Chinese
FAN.CNT 1
     PATENT NO.        KIND   DATE       APPLICATION NO.        DATE
     ---------------   ----   --------   --------------------   --------
PI   CN 102786751       A     20121121   CN 2012-10287240       20120813
PRAI CN 2012-10287240         20120813
```

AB This invention relates to prepn. of regenerated polyvinyl chloride plastic material. **The plastic comprises regenerated PVC 100-120**, modified nano Ca carbonate 25-30, Ca-Zn stabilizer 1-2, stearic acid 1-2, dioctyl ester 0.5-1, plasticizer (epoxyfatty acid Me ester) 0.5-1, chlorinated PE 2-4, ABS high-glue powder 2-5, PE wax 0.1-0.5, paraffin wax 0.5-0.7, acrylate impact modifier ACR 2-5, MBS 2-5, iron oxide red 2-5, carbon black 0.01-0.04 and pigment 0.1-0.2 part. The modified nano Ca carbonate is prepared by burning Ca carbonate at 600-700□C for 4-5h, grinding into nanopowders, adding bis(diethylhexyl diphosphato)ethylene titanate and propanediol polysebacate, drying and breaking into powders. The manufacture process comprises weighing regenerated PVC and modified nano Ca carbonate, mixing and drying at 80-90□C, adding Ca-Zn stabilizer, stearic acid, plasticizer, chlorinated PE, ABS high glue powder, PE wax, paraffin wax, acrylate impact modifier ACR, iron oxide red, C black and pigment, mixing at 130-150□C, melting, blending and granulating the obtained mixture at 155-190□C to give granules for plastic steel profile, extrusion molding the granules to give plastic steel profile, cooling, setting, cutting and packing. **The invention makes full use of waste plastic steel profile or unqualified plastic steel profile, which saves a large amount of raw materials, reduces white pollutants and protects environment, and the product has common characteristics of profiles, smooth surface, high hardness, etc.**

```
IT   65467-75-6
     RL: MOA (Modifier or additive use); USES (Uses)
        (new colored plastic steel profile manufactured from regenerated polyvinyl
        chloride)
```

Developed from a Half-Century of Nano-TITANATE Experience



SCIENCE IP

SCIENCE IP The CAS Search Service

Science IP Order: 3140835

Client Reference: None

Ti/Zr Coupling Agents – July 25, 2013-date

Modified Update of Science IP Order 3069078

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Client Reference: Kenrich Products by CAS Registry Numbers

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Search Report

Prepared for Salvatore J. Monte, President

Kenrich Petrochemicals, Inc.

July 24, 2013

L19 ANSWER 321 OF 3545 HCA COPYRIGHT 2013 ACS on STN
AN 157:736344 HCA Full-text <<LOGINID::20130724>>

SCIENCE IP The CAS Search Service

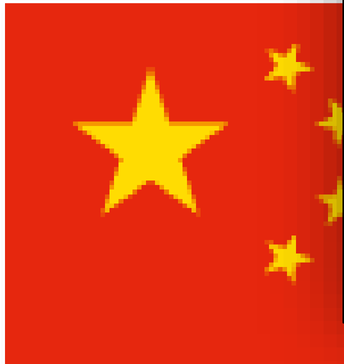
TI New colored plastic steel profile manufactured from regenerated polyvinyl chloride

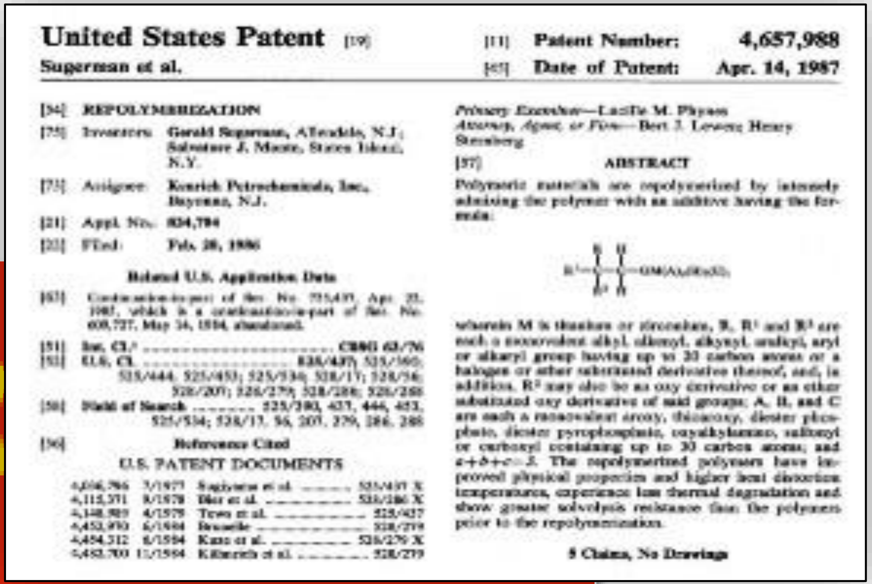
PA Shucheng Antai Plastic Product Co., Ltd., Peop. Rep. China

REPOLYMERIZATION:
Improve the mechanical properties of 11-Unfilled Polymers #1 to #7

AB The plastic comprises regenerated

- **PVC 100-120,**
- **titanate modified nano Ca carbonate 25-30,**
- Ca-Zn stabilizer 1-2,
- stearic acid 1-2,
- dioctyl ester 0.5-1,
- plasticizer (epoxyfatty acid Me ester) 0.5-1,
- chlorinated PE 2-4,
- **ABS high-glue powder 2-5,**
- PE wax 0.1-0.5,
- paraffin wax 0.5-0.7,
- acrylate impact modifier ACR 2-5,
- MBS 2-5,
- iron oxide red 2-5,
- carbon black 0.01-0.04,
- pigment 0.1-0.2 part.




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

[54] REPOLYMERIZATION

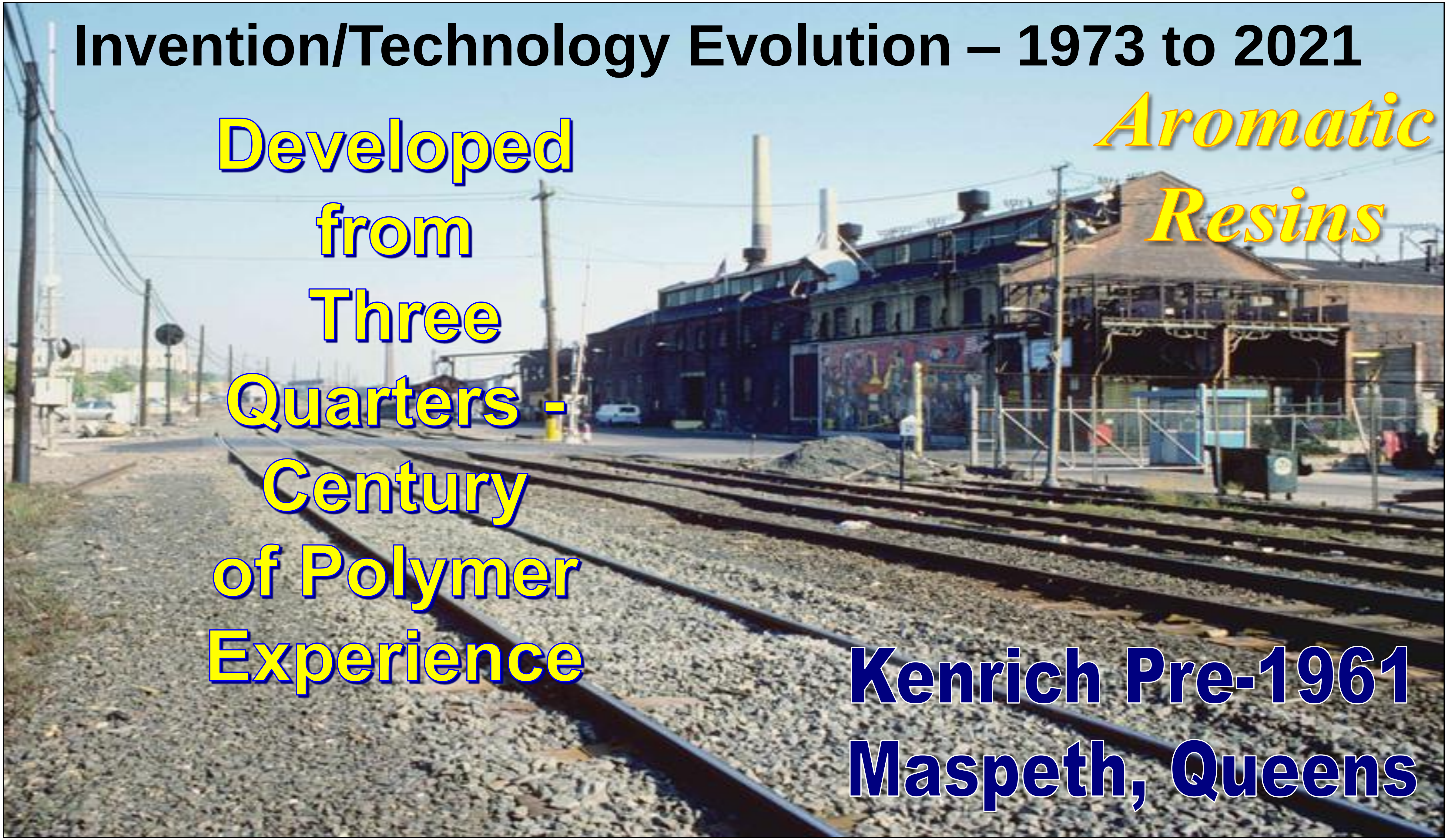
Related U.S. Application Data

References Cited
U.S. PATENT DOCUMENTS

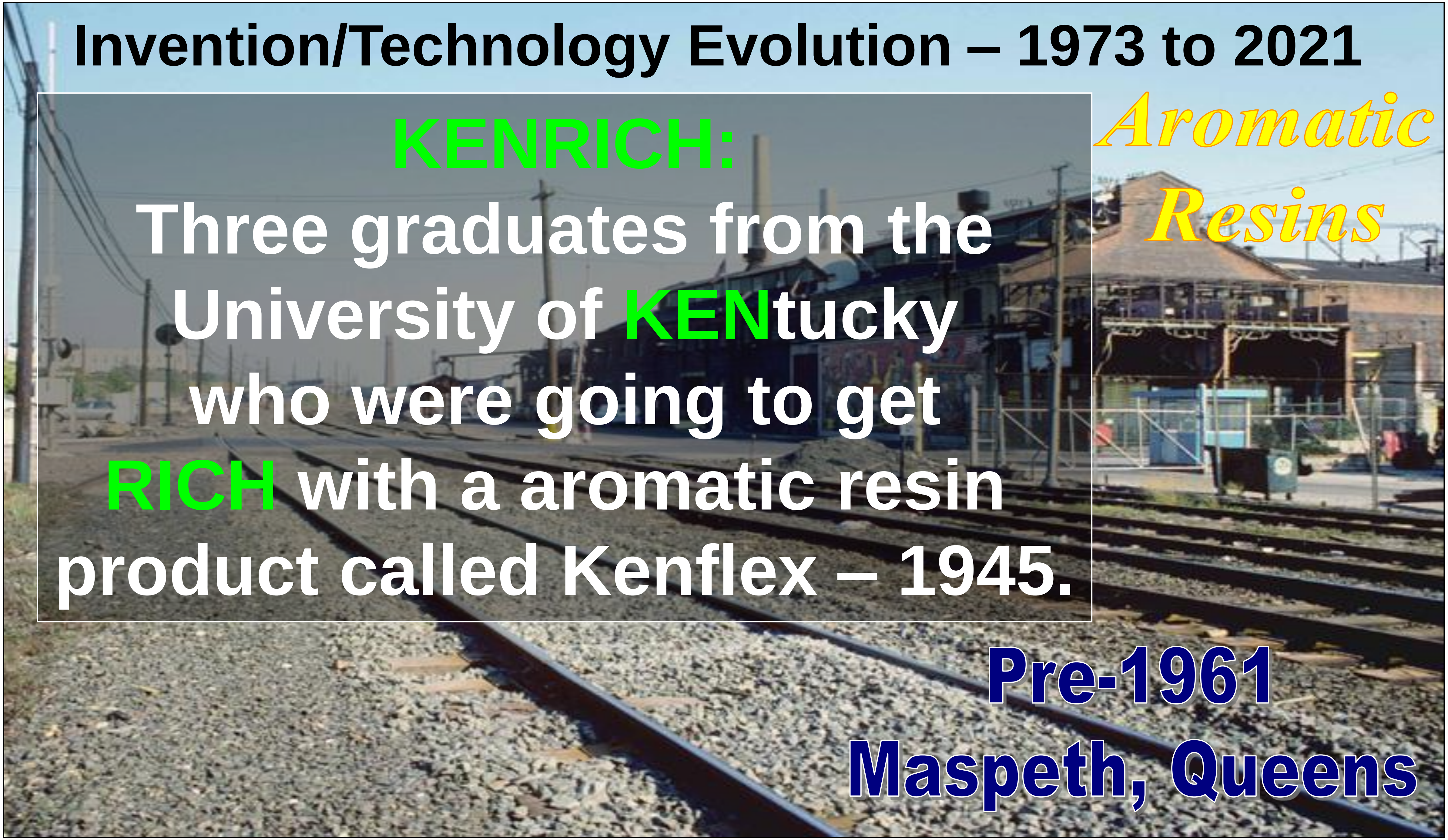
[57] ABSTRACT

5 Claims, No Drawings

Apr. 14, 1987 – Monte Patent named “REPOLYMERIZATION”


Invention/Technology Evolution – 1973 to 2021
Aromatic Resins
Developed from Three Quarters - Century of Polymer Experience
Kenrich Pre-1961
Maspeth, Queens

Invention/Technology Evolution – 1973 to 2021



KENRICH:

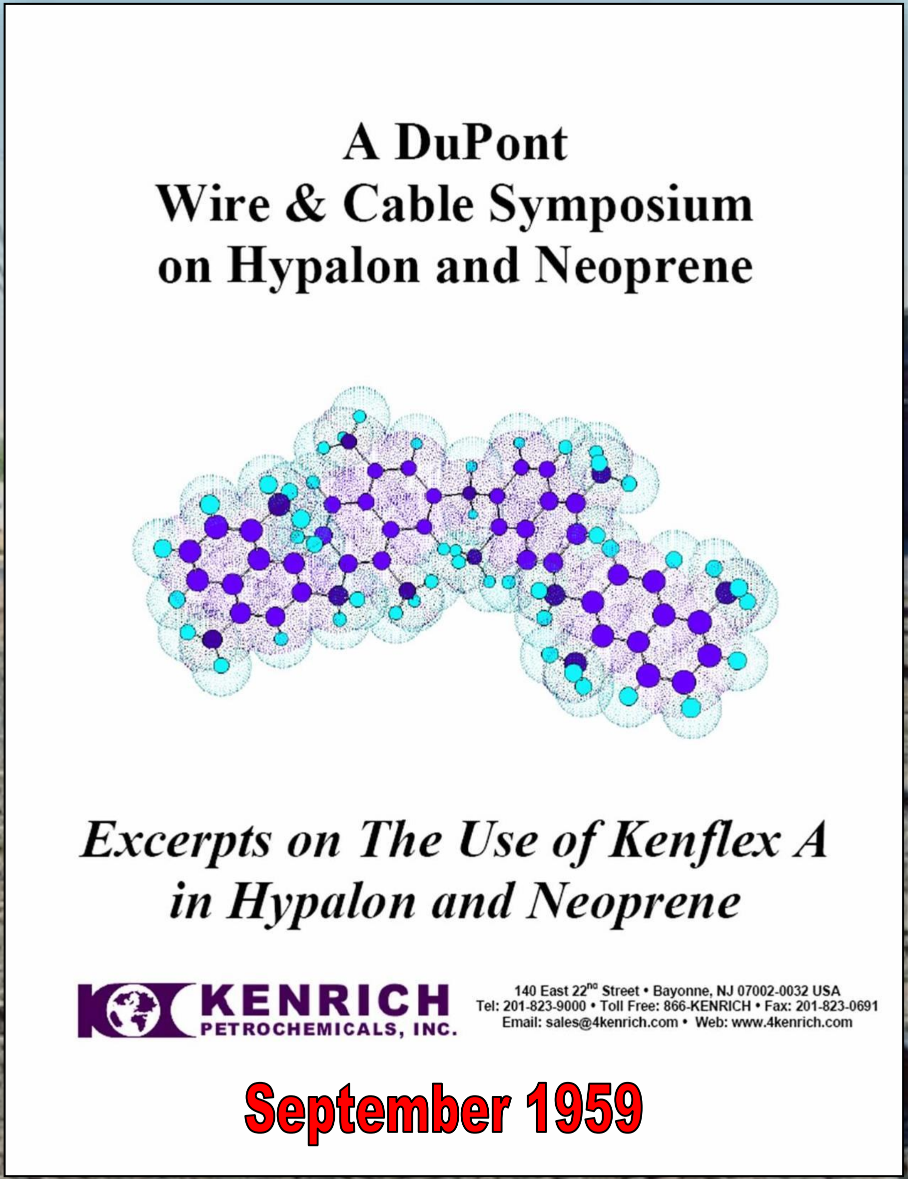
Three graduates from the University of KENtucky who were going to get RICH with a aromatic resin product called Kenflex – 1945.

Aromatic Resins

Pre-1961

Maspeth, Queens

Invention/Technology Evolution – 1973 to 2021


A DuPont
Wire & Cable Symposium
on Hypalon and Neoprene

Excerpts on The Use of Kenflex A
in Hypalon and Neoprene

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140 East 22nd Street • Bayonne, NJ 07002-0032 USA
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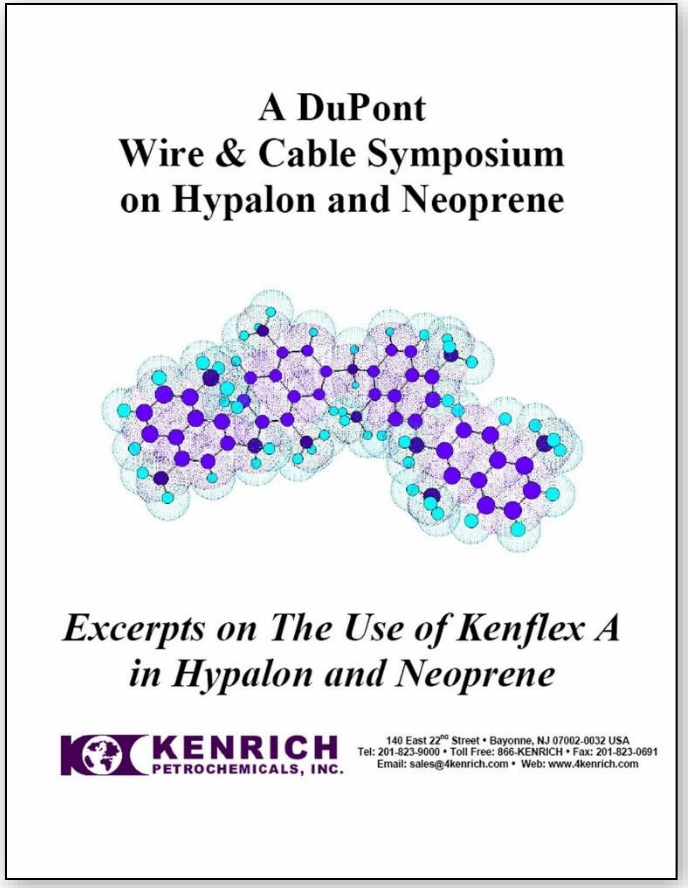
Email: sales@4kenrich.com • Web: www.4kenrich.com

September 1959

Invention/Technology Evolution – 1973 to 2021



A DuPont
Wire & Cable Symposium
on Hypalon and Neoprene

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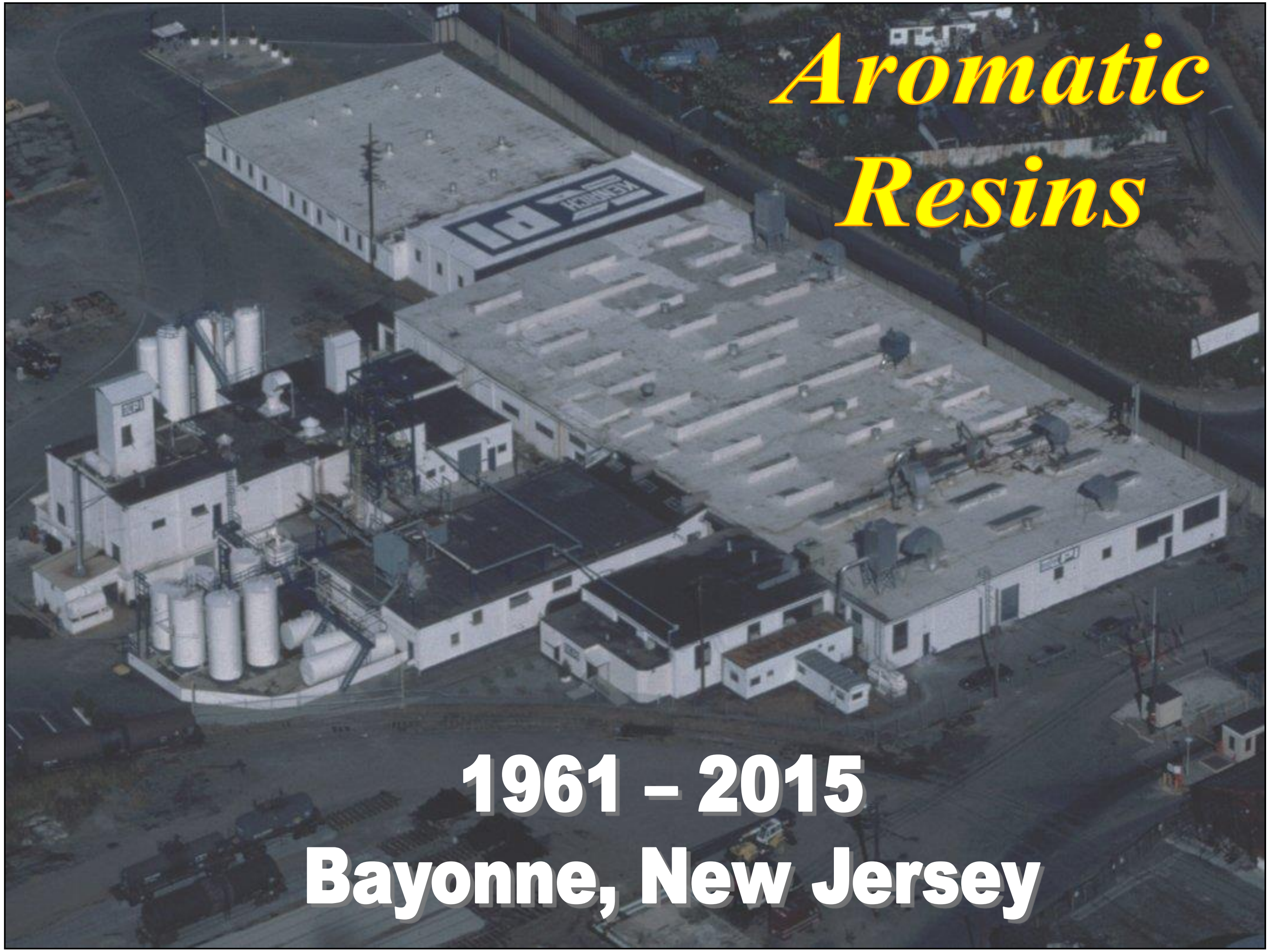

1961 to 2015
Products made in Bayonne, NJ

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

Invention/Technology Evolution – 1973 to 2020

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KENMIX® Litharge
KENLASTIC® Litharge

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* Reg. U.S. Pat. & Tm. off. (DuPont)

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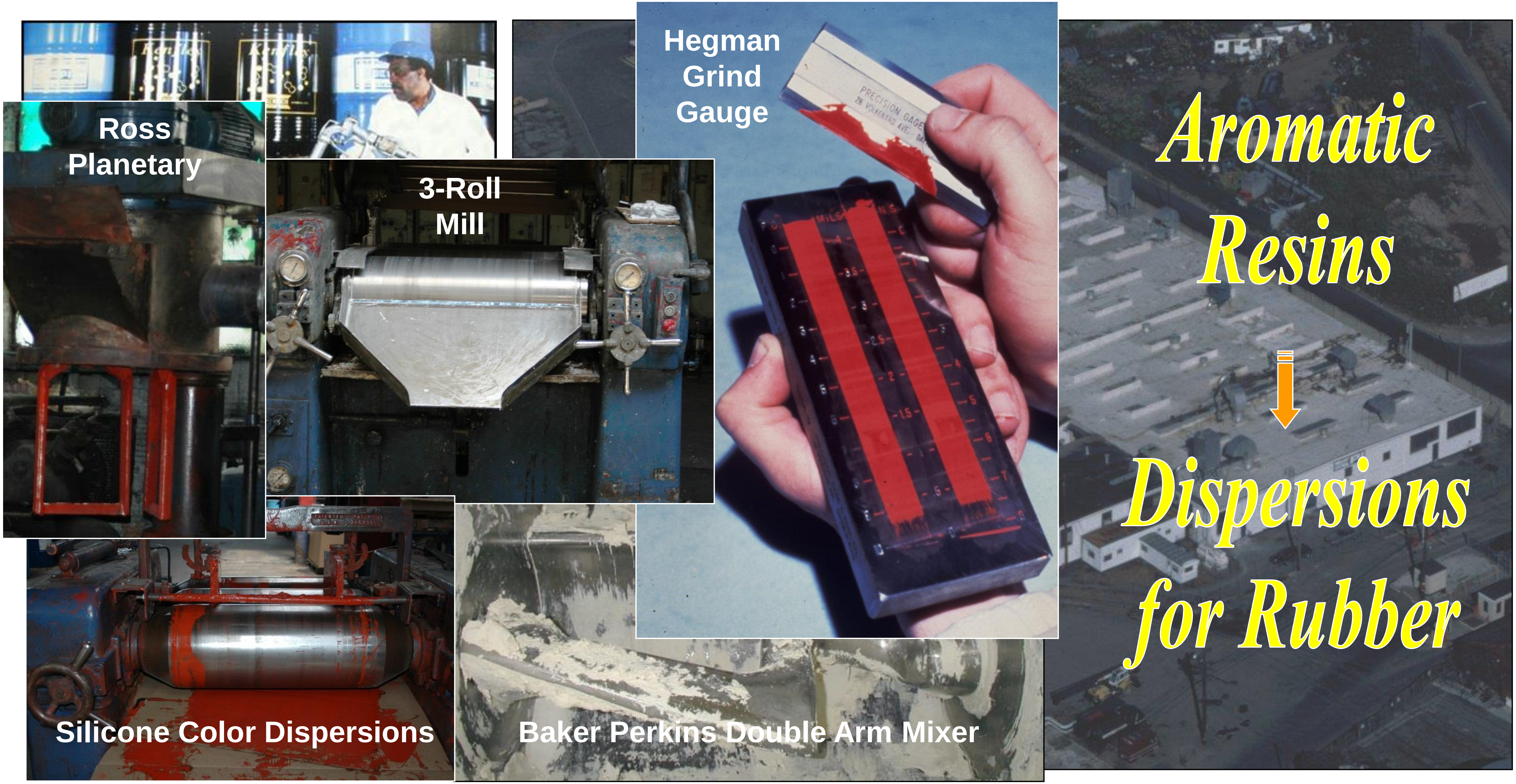
Fax (201) 823-0691 ☐ Telex 12-5023

Invention/Technology Evolution – 1973 to 2020



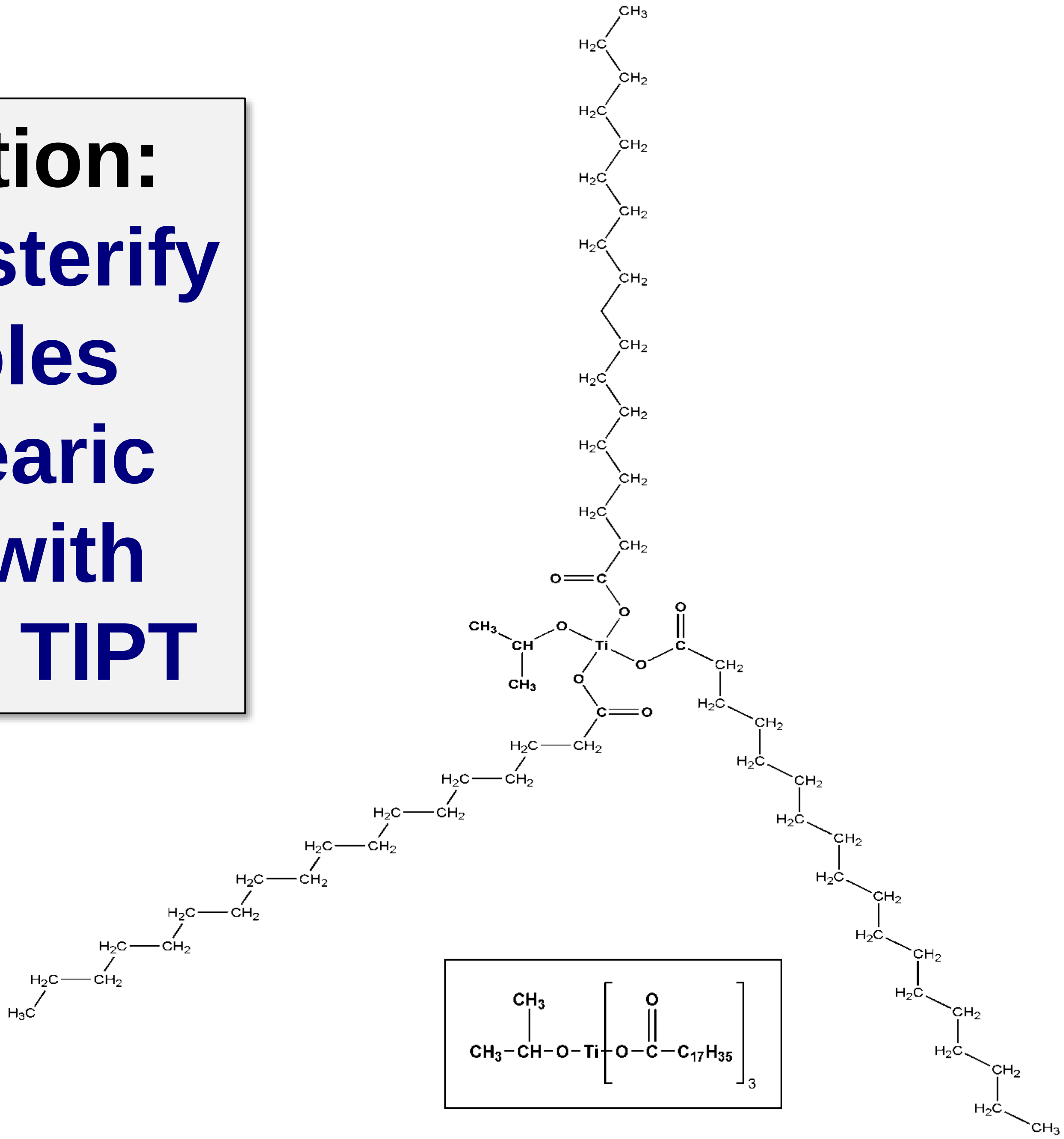
Invention/Technology Evolution – 1973 to 2020

Invention/Technology Evolution – 1973 to 2020

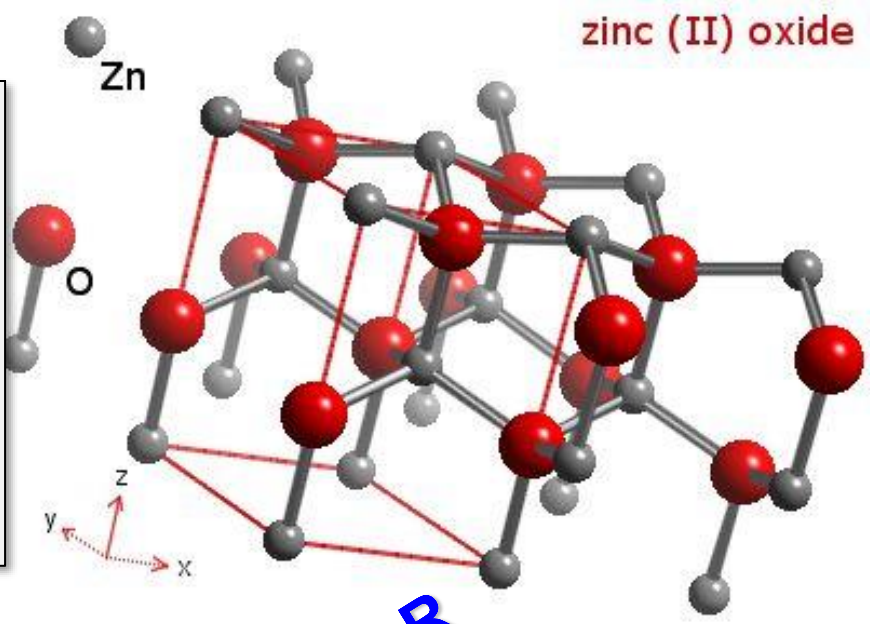

85% ZnO in Napthenic Oil/Wax

Invention:

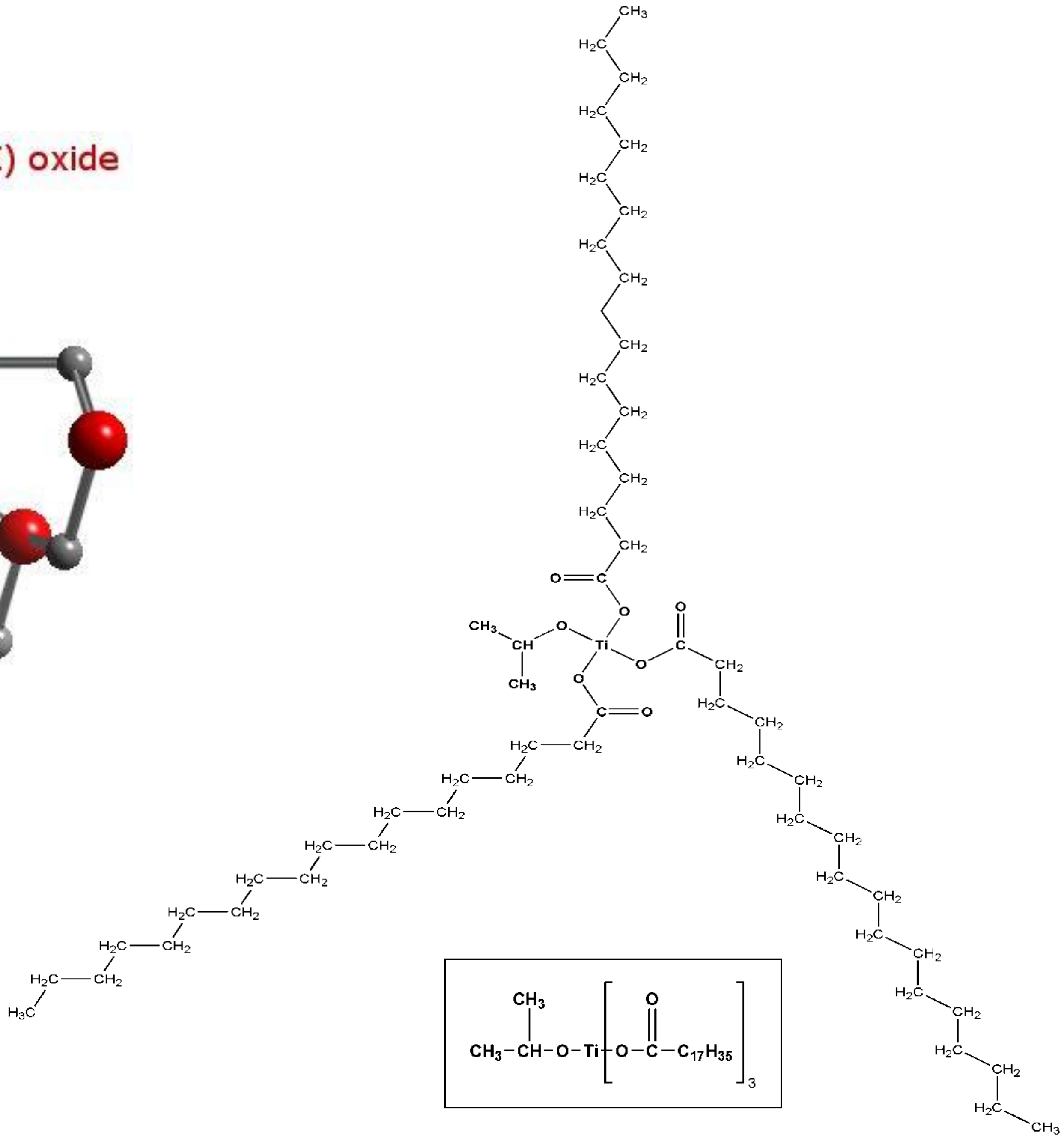
Transesterify 3-moles Isostearic Acid with 1-mole TIPT



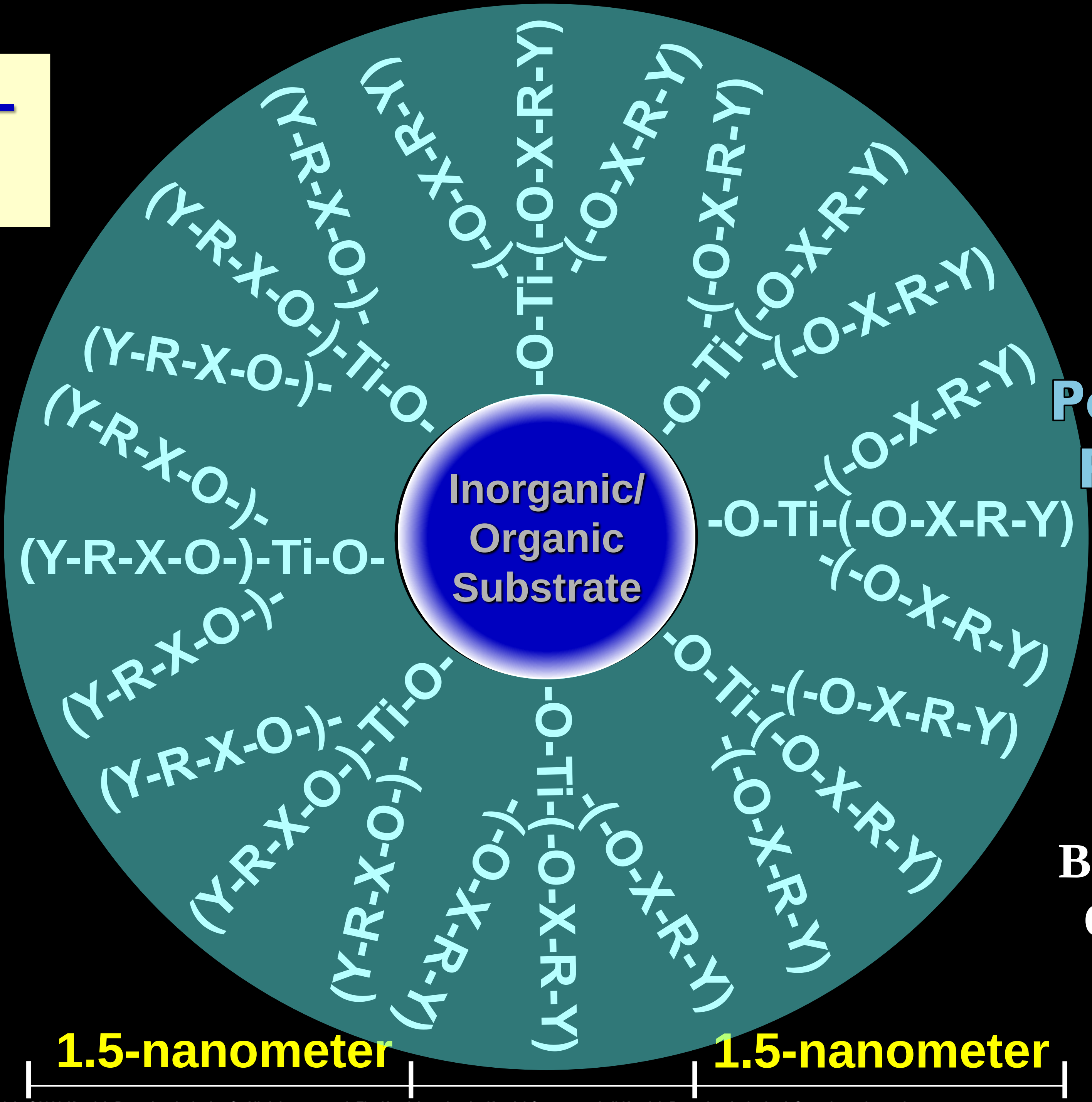
Invention:
Transesterify 3-moles Isostearic Acid with 1-mole TIPT



(Y-R-X-O-)-
(Y-R-X-O-)-Ti-O-R
(Y-R-X-O-)-



Function 1 – Coupling

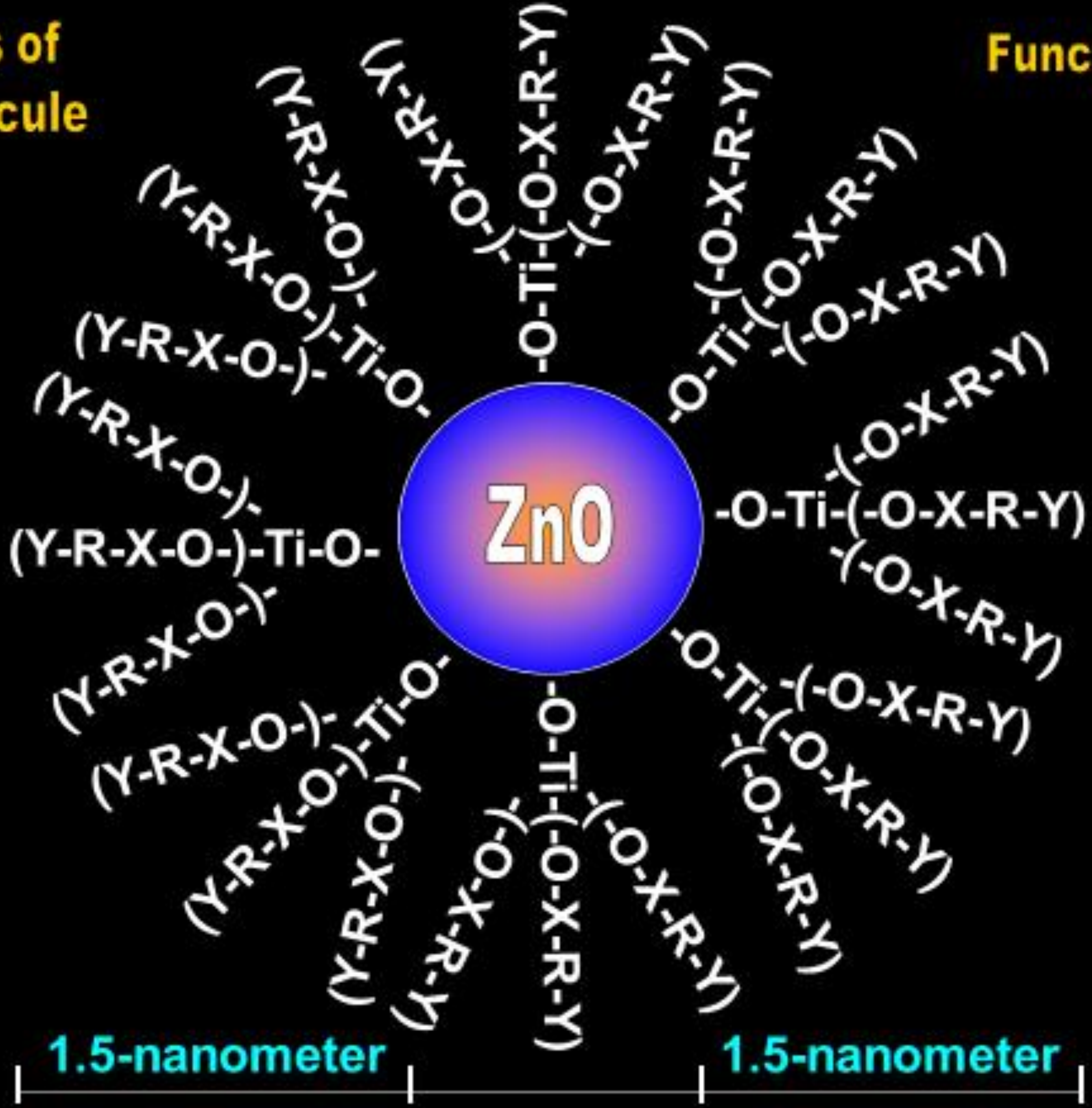


Polymer Phase

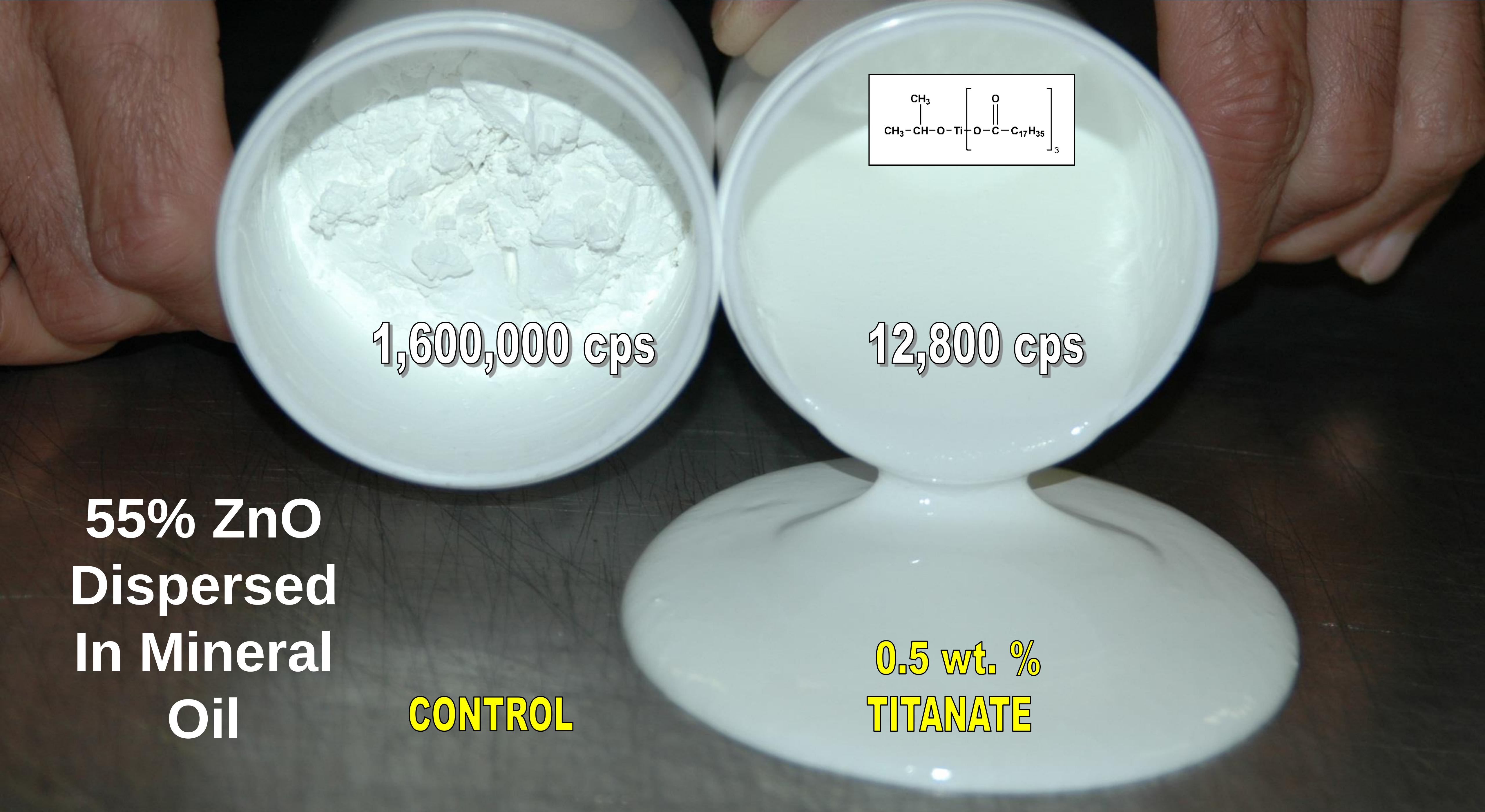
Recycled PVC Compounds Contain A Mixed Bag of Inorganic & Organic Additives

The Six Functions of the Titanate Molecule

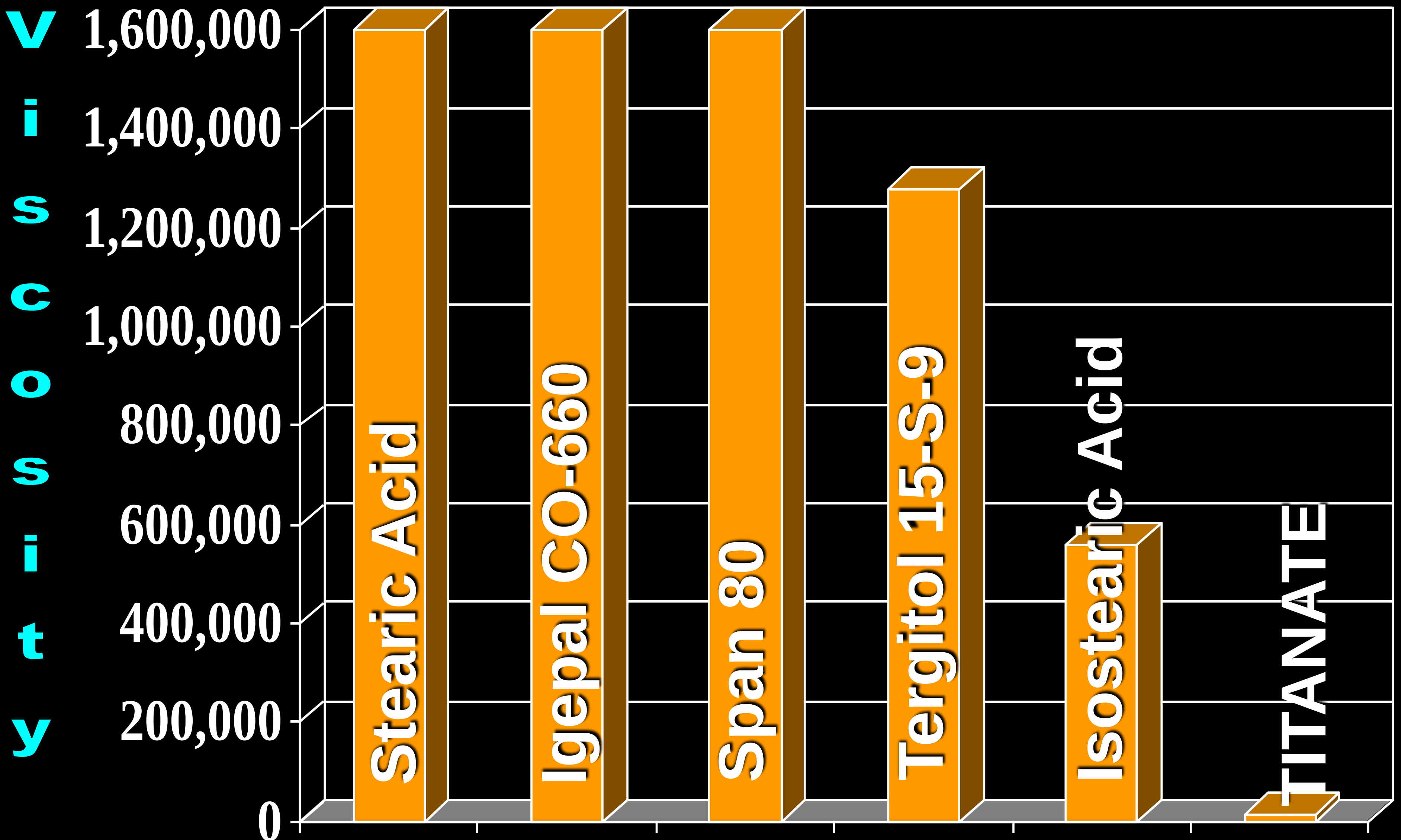
Function 1 - Coupling



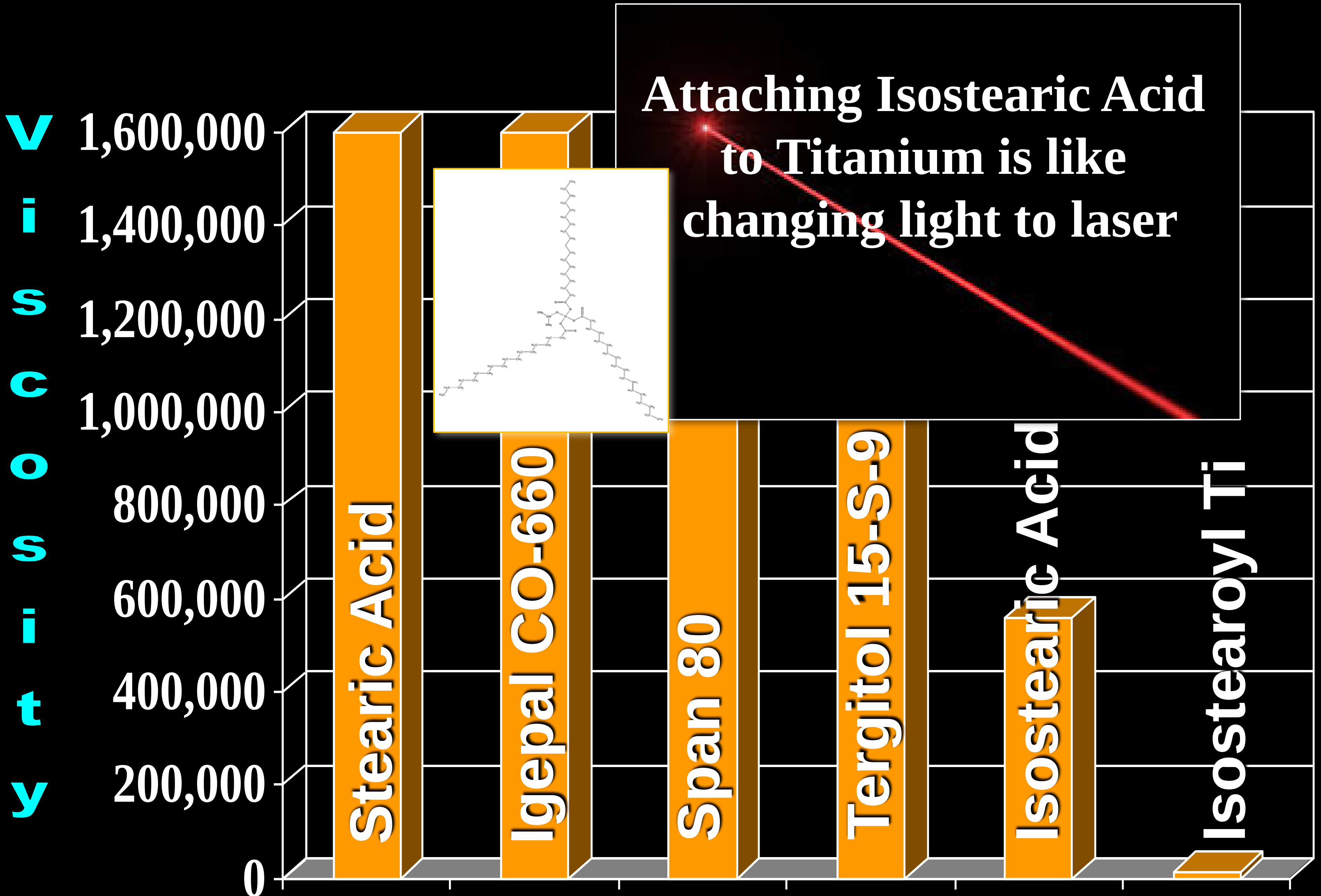
1.5-Nanometer
Atomic
Monolayer


CH3
O
CH3–CH–O–Ti–O–C–C17H35
3
1,600,000 cps
12,800 cps
55% ZnO
Dispersed
In Mineral
Oil
CONTROL
0.5 wt. %
TITANATE

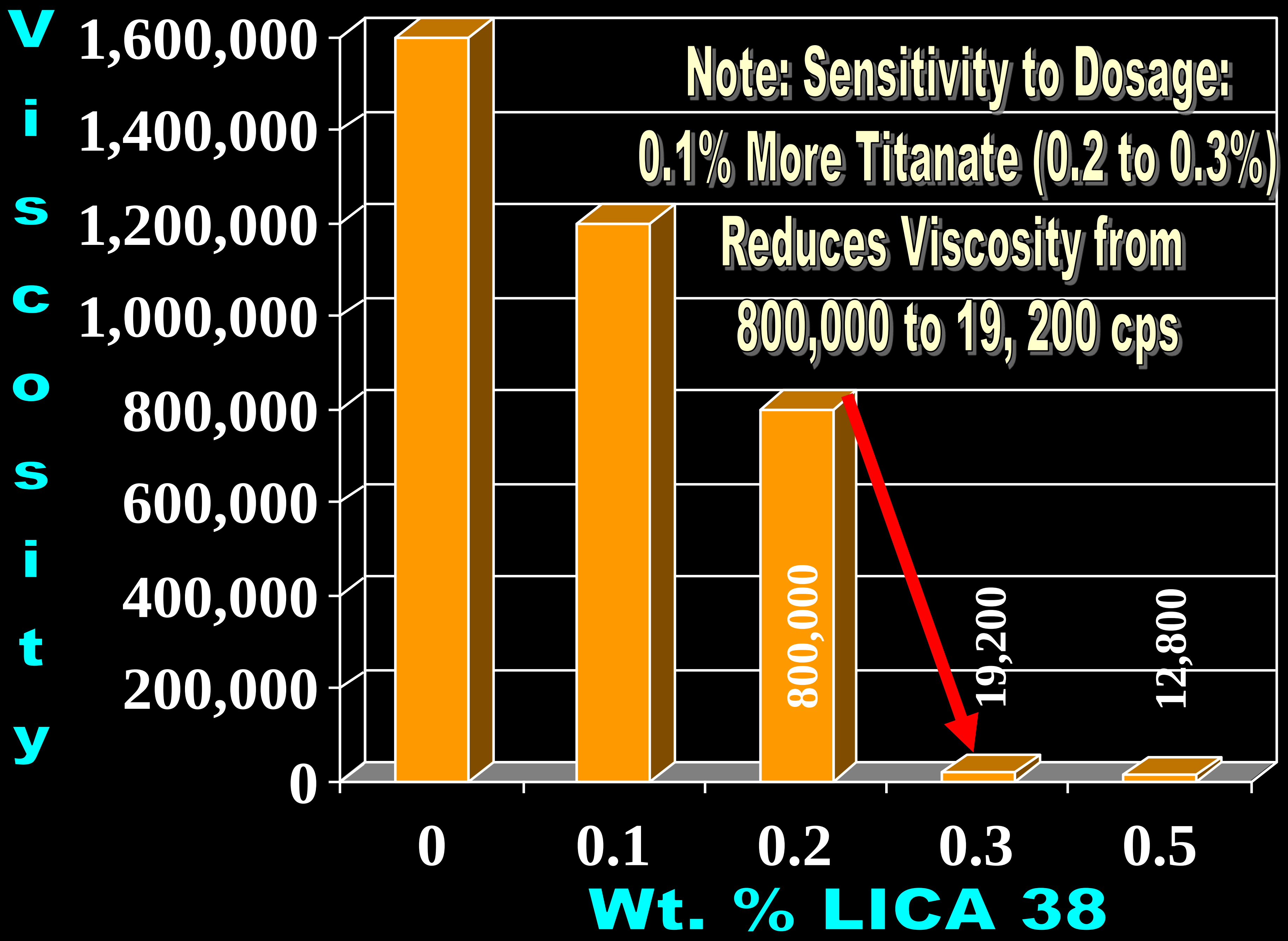
55% ZnO Dispersed In Mineral Oil



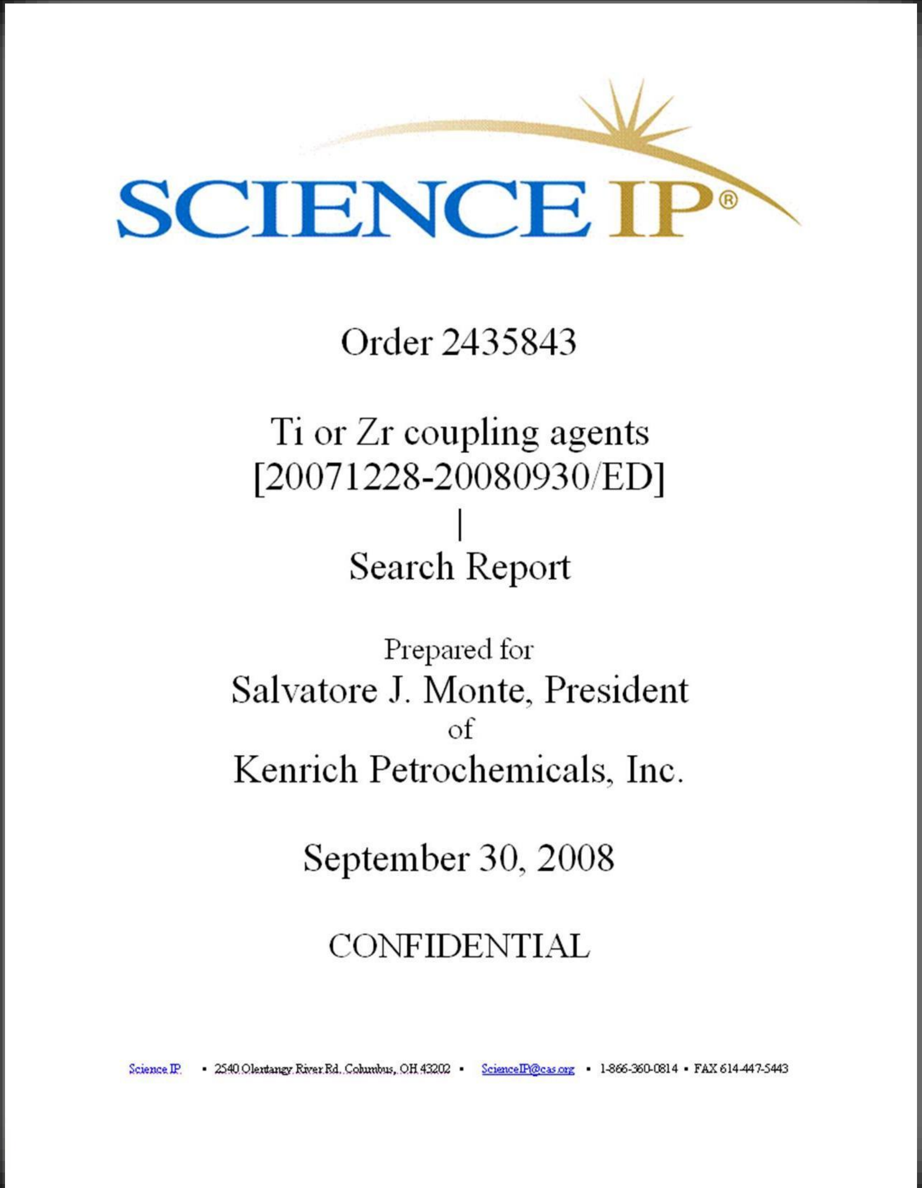
55% ZnO Dispersed In Mineral Oil



55% ZnO Dispersed In Mineral Oil



Patented ZnO Apps


SCIENCE IP®

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

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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

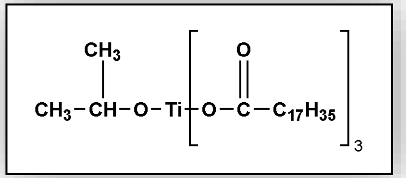
Aluminum or ZnO Heat Conductive Composites
Foxconn Technology Co., Ltd., Taiwan

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

Stone Filled Polyamide, PET, Polyacrylonitrile, and PU
Diamond Polymer Science Co., Ltd., Taiwan

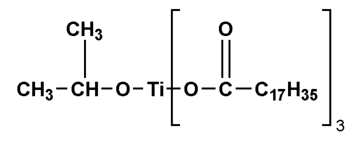
Titanate/Silane ZnO Treatment for Silicone
Kosei Co., Ltd., Japan

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

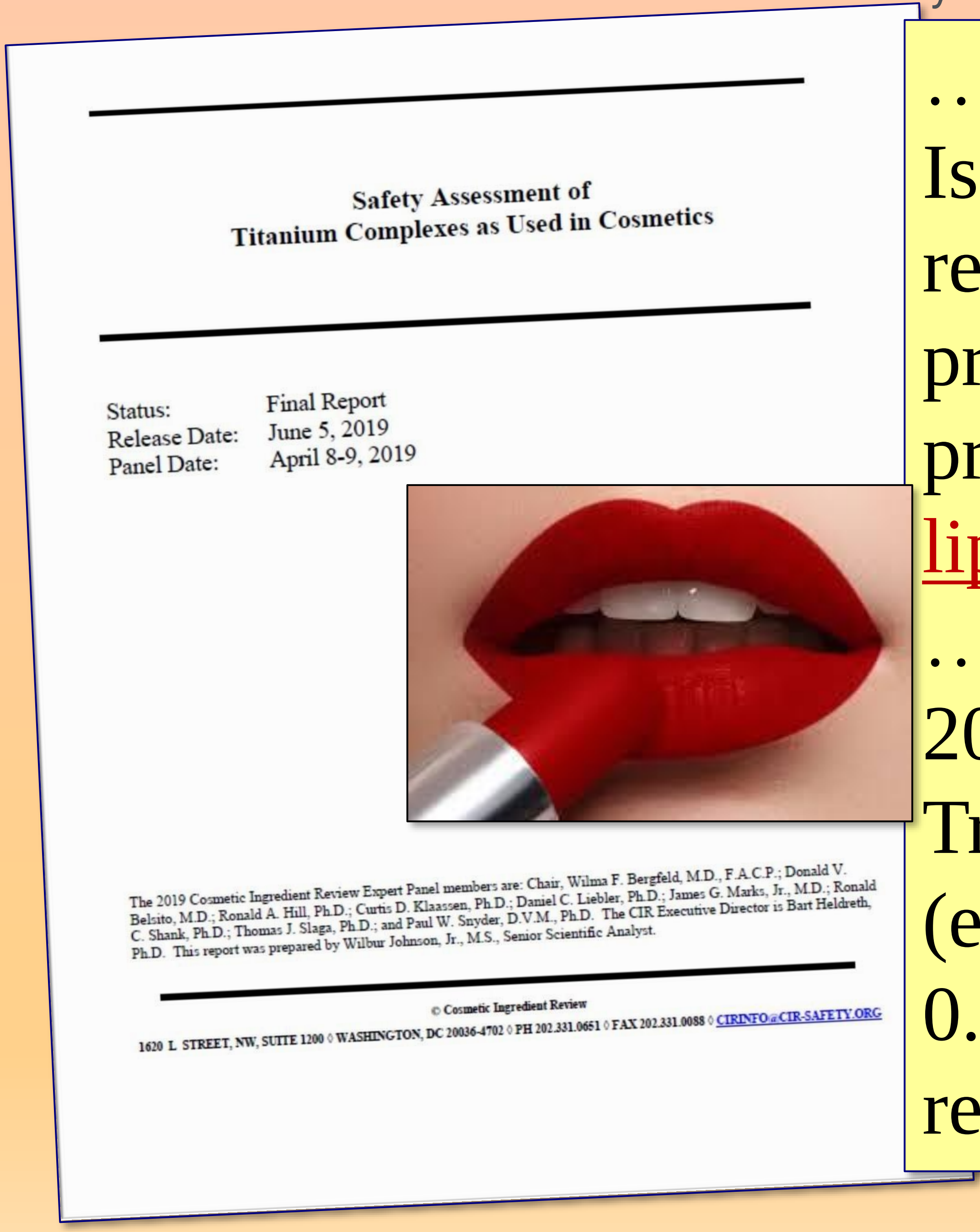
Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents



Improving COLOR & APPEARANCE

FACIAL COSMETICS

FDA's Voluntary Cosmetic Registration Program (**VCRP**)



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.

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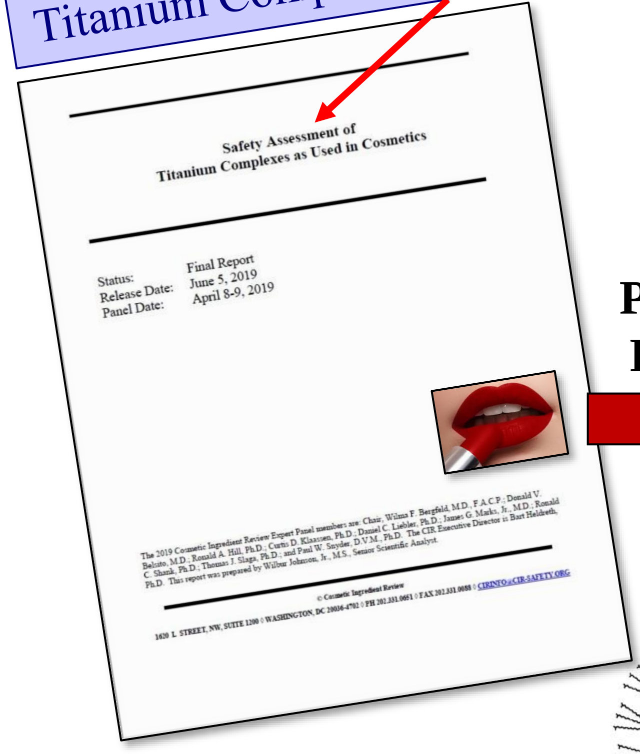
…According to 2019 VCRP data, Isopropyl Titanium Triisostearate is reported as being used in 513 cosmetic products (506 leave-on and 7 rinse-off products); half of the reported uses are in lipstick formulations (253).[8]

…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 2020

Safety Assessment of
Titanium Complexes as Used in Cosmetics



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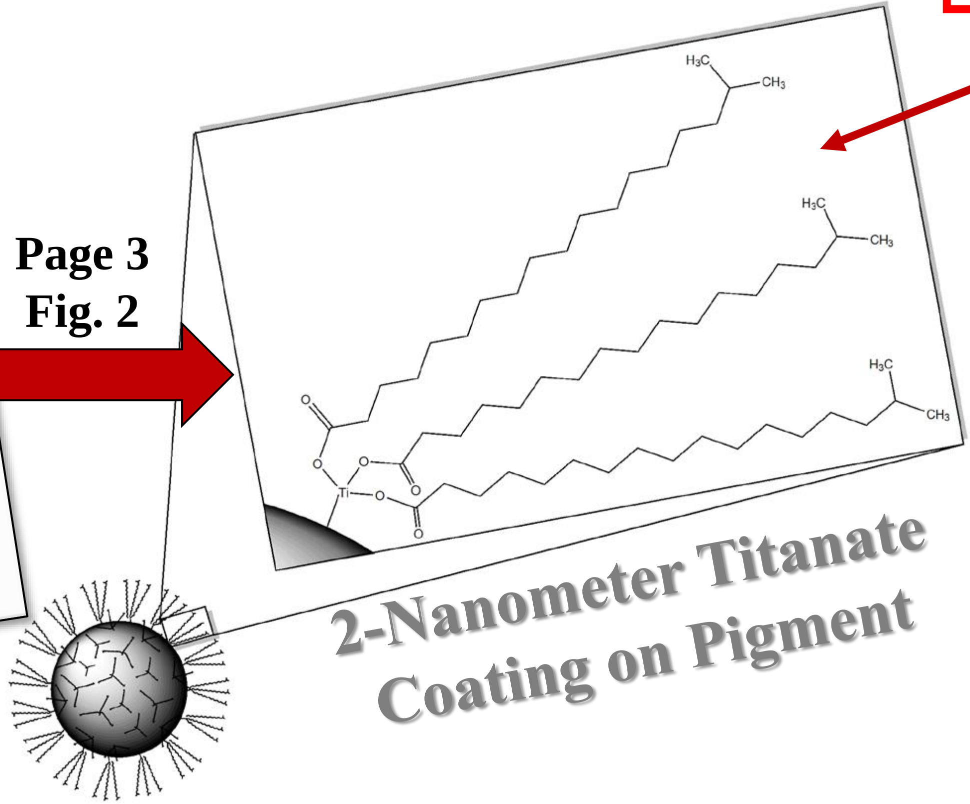
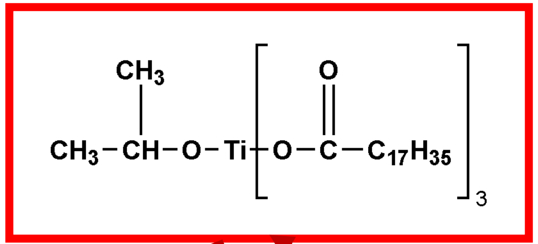
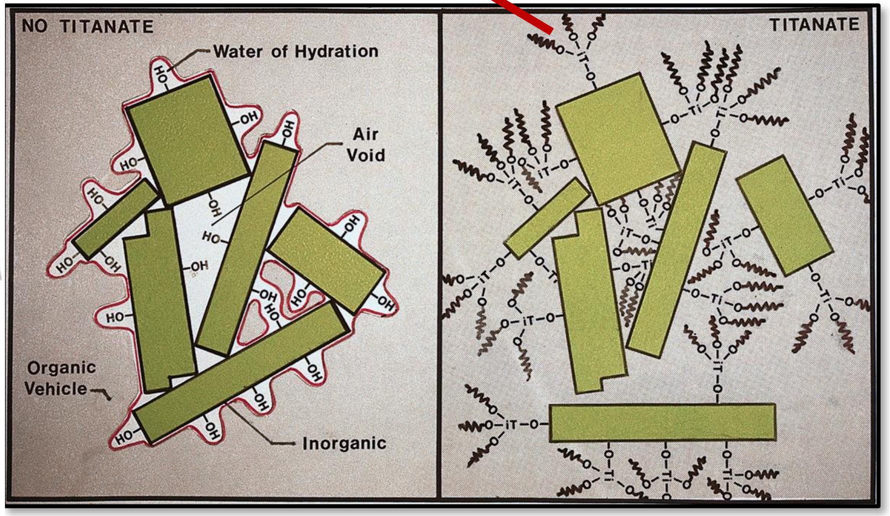
Page 3
Fig. 2



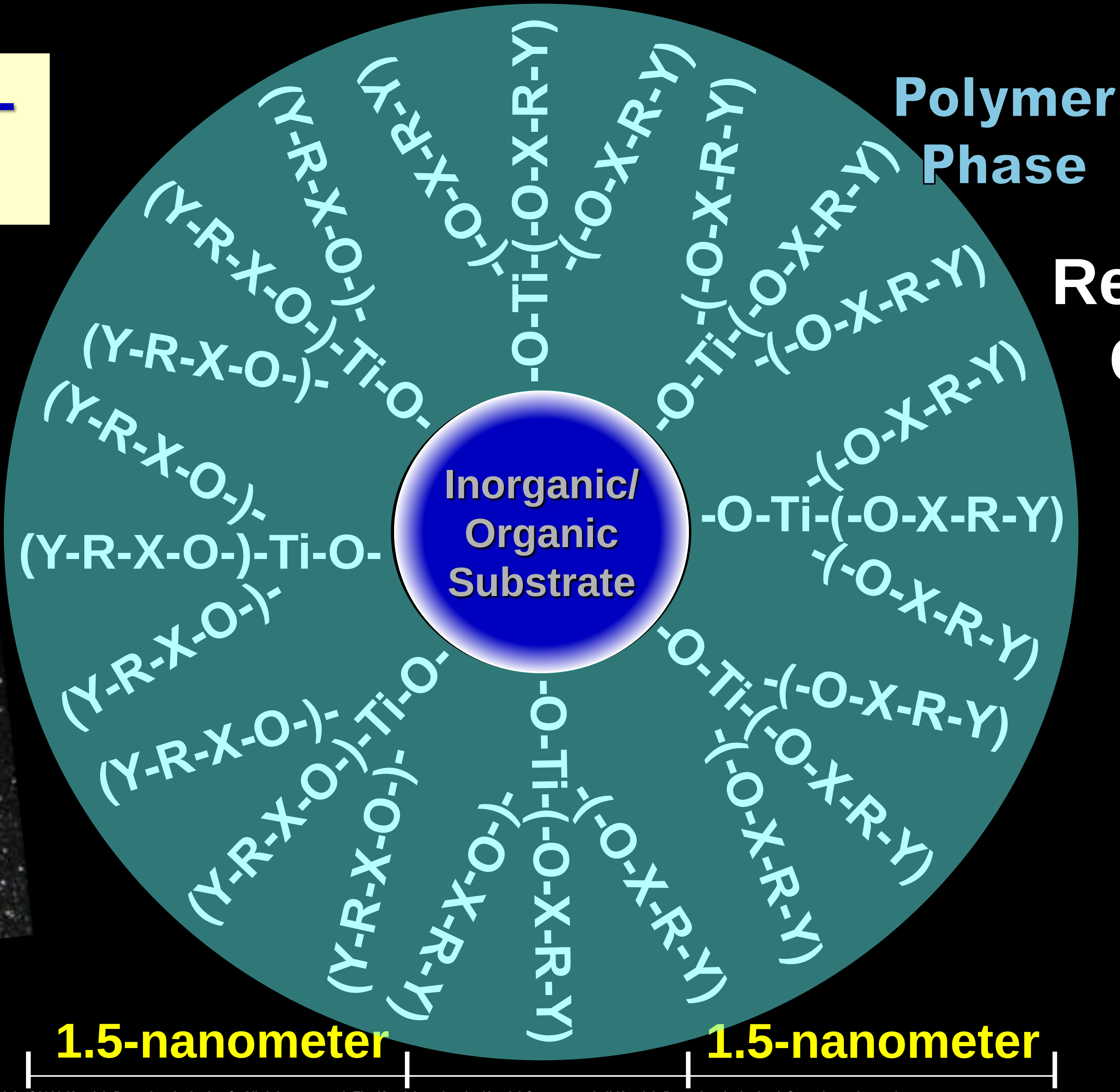




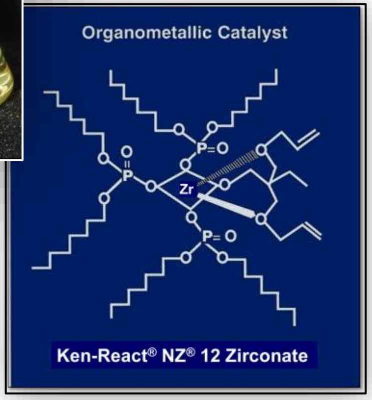
2019 Drawing – Fe2O3/Titanate

1973 Drawing by S. J. Monte

Function 1 – Coupling

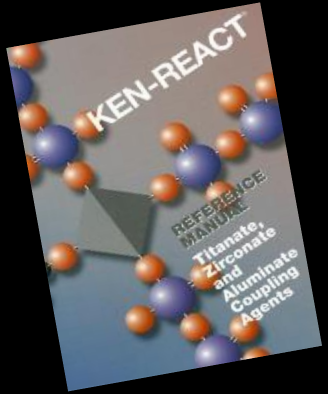


Recycled PVC Compounds Contain A Mixed Bag of Inorganic & Organic Additives

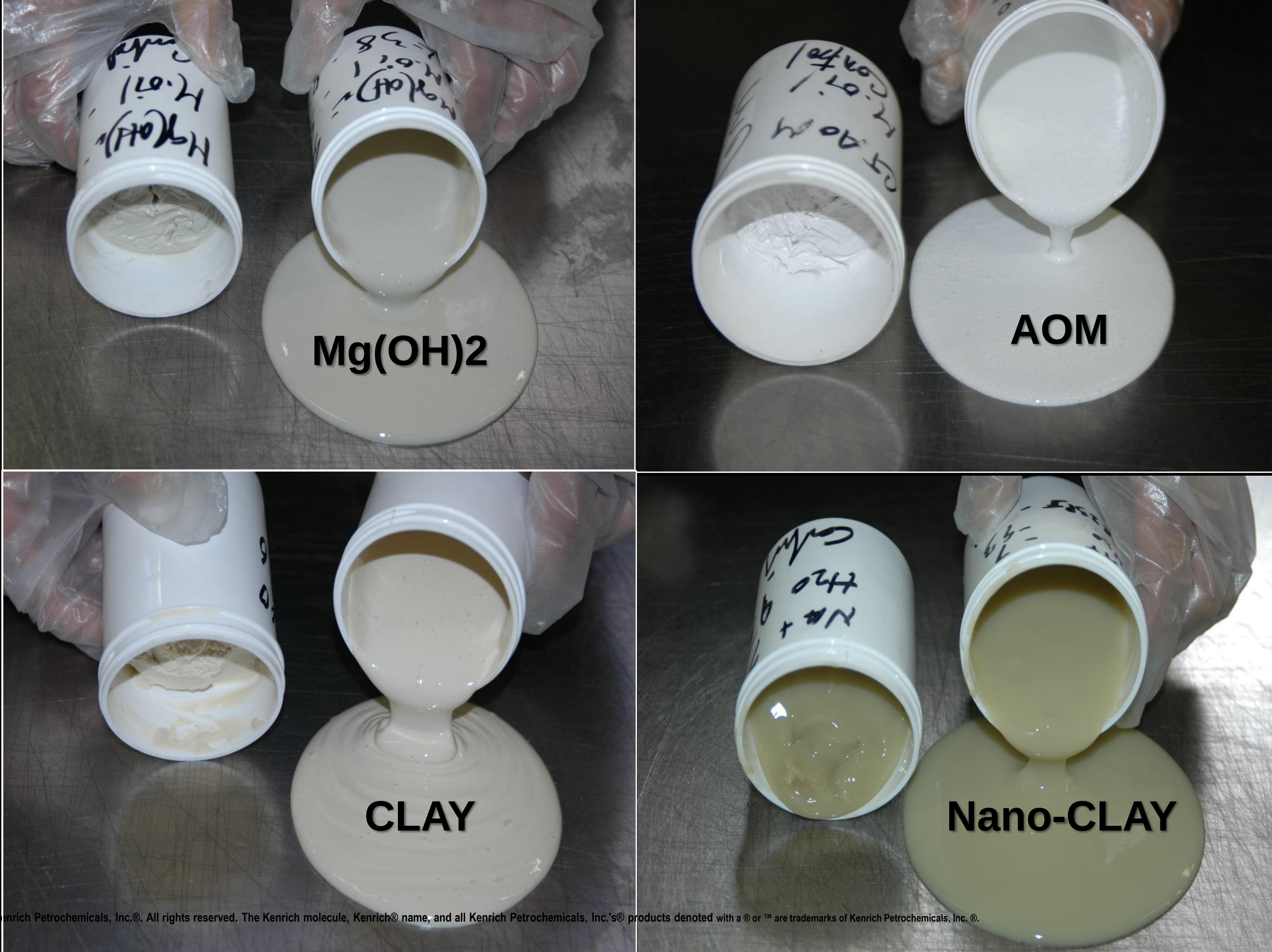


The
LIquid Coupling Agent
can be added to the liqui-color concentrate and then added at the hopper.

"Silanes"-Plueddemann:
"… Only slight improvement was imparted … titanium dioxide and zinc oxide."



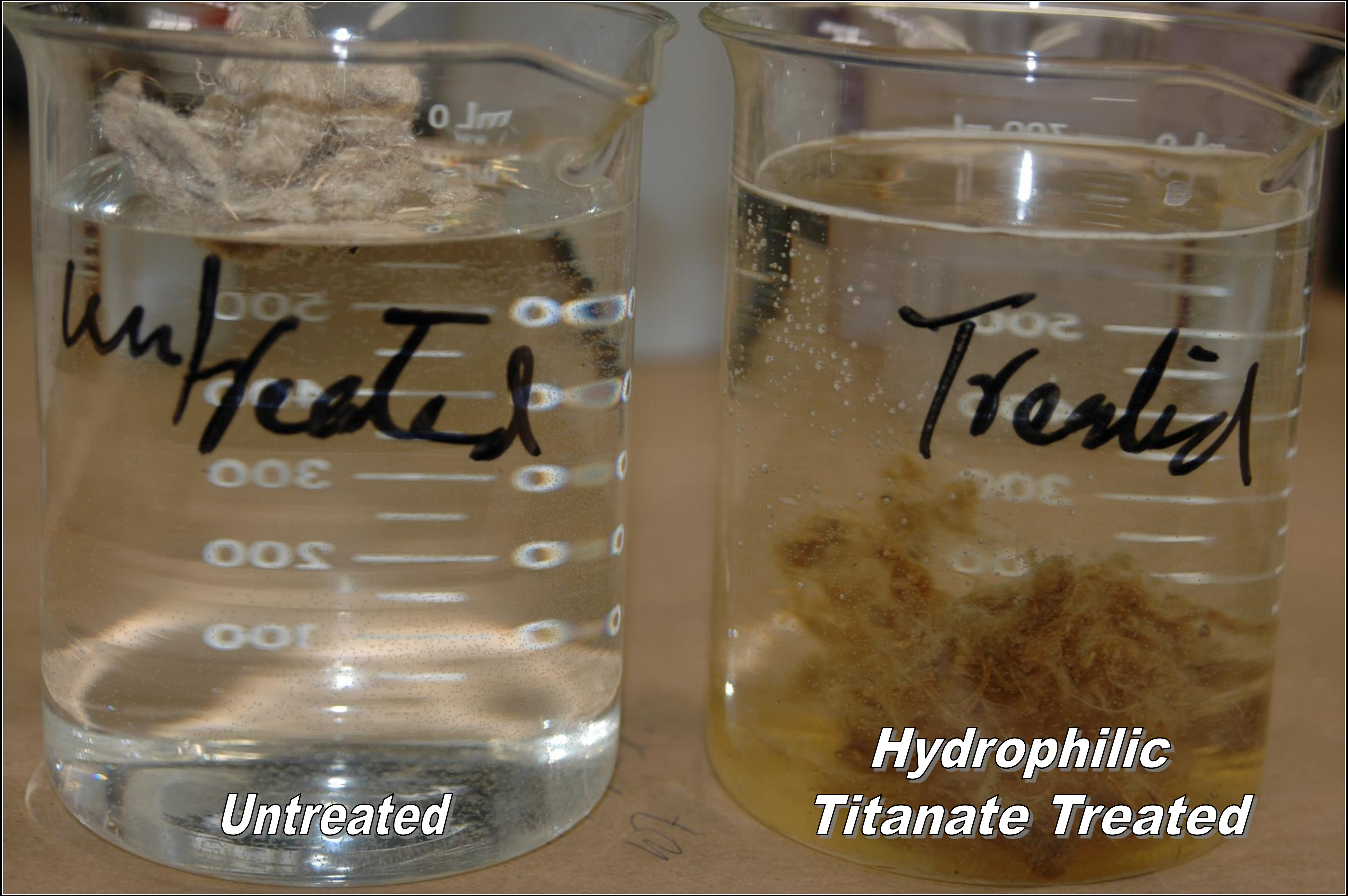
A low dosage of Titanate added in situ into mineral oil followed by filler addition reduces viscosity



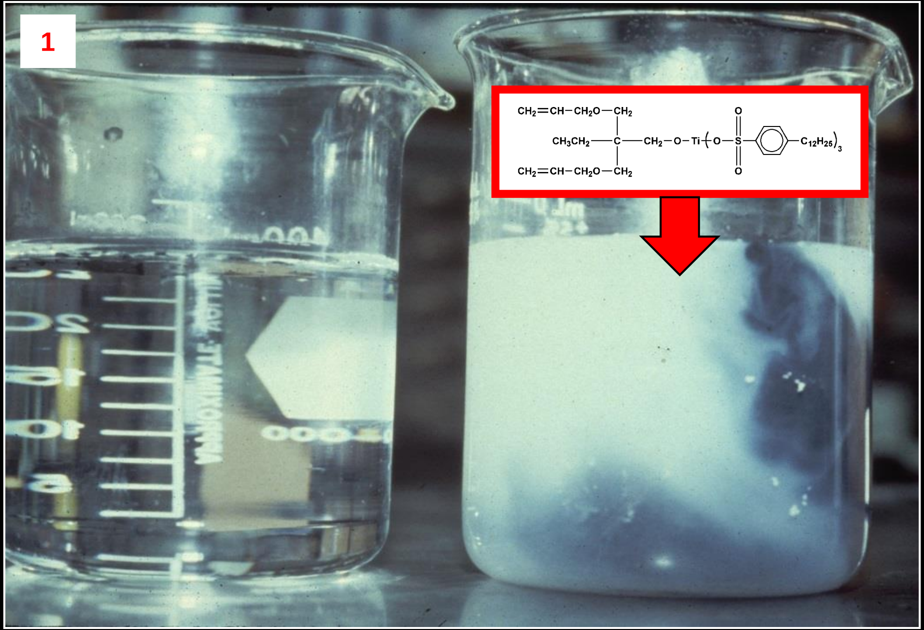
A low dosage of Titanate added in situ into mineral oil followed by filler addition reduces viscosity

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

Reacts with Sustainable Organics such as Flax & Cellulose

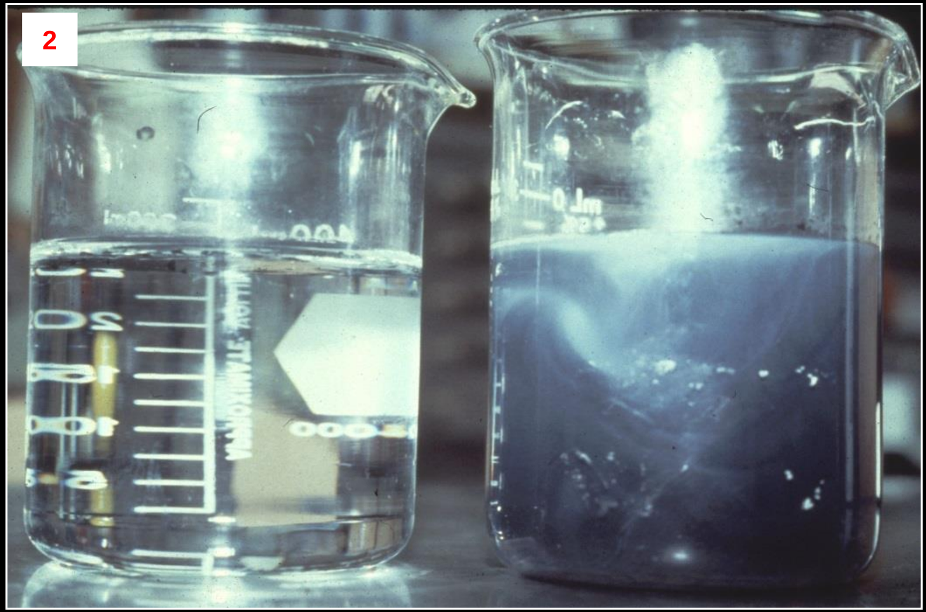


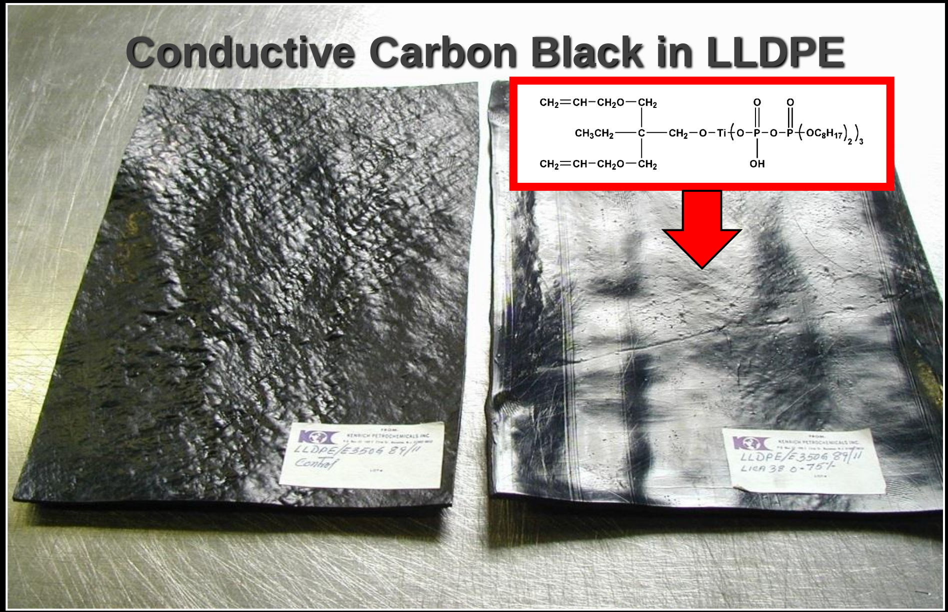
Titanate Coupling to XC-72 Conductive Carbon Black in Water

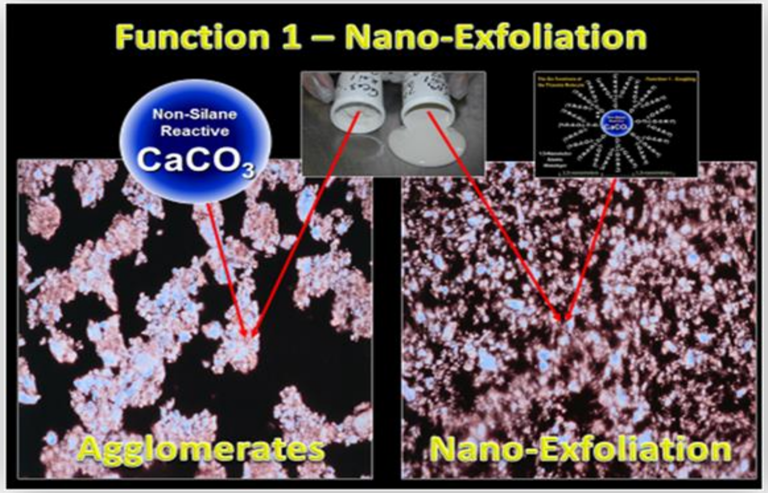


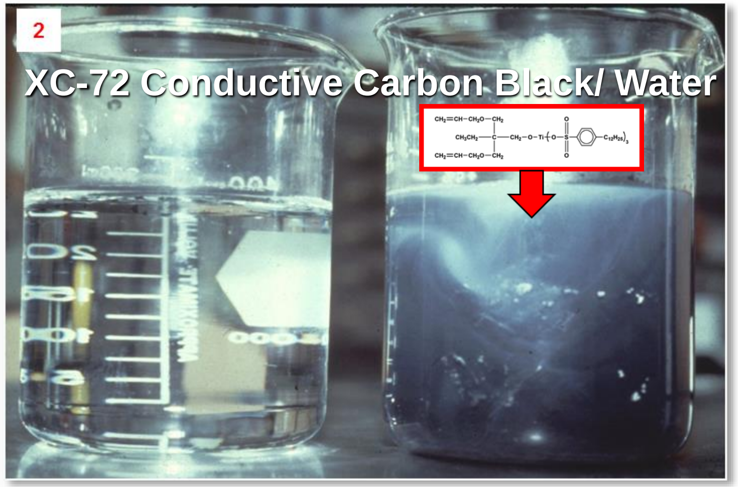
No Titanate | Titanate | No Titanate | Titanate

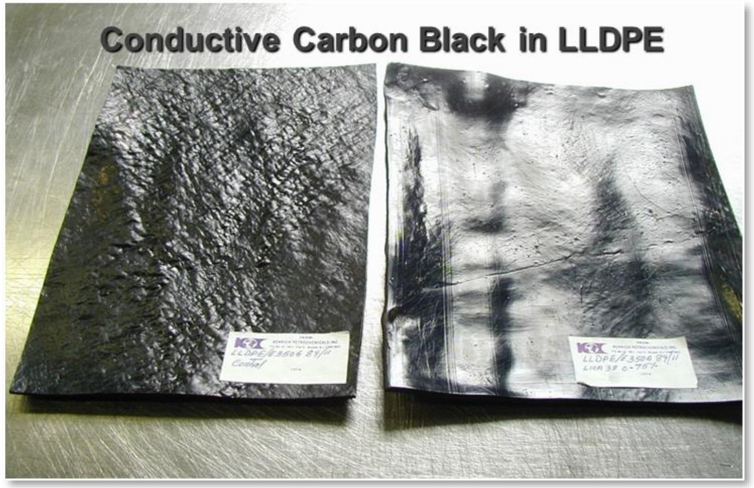
No Mechanical Stirring



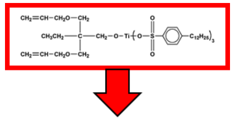






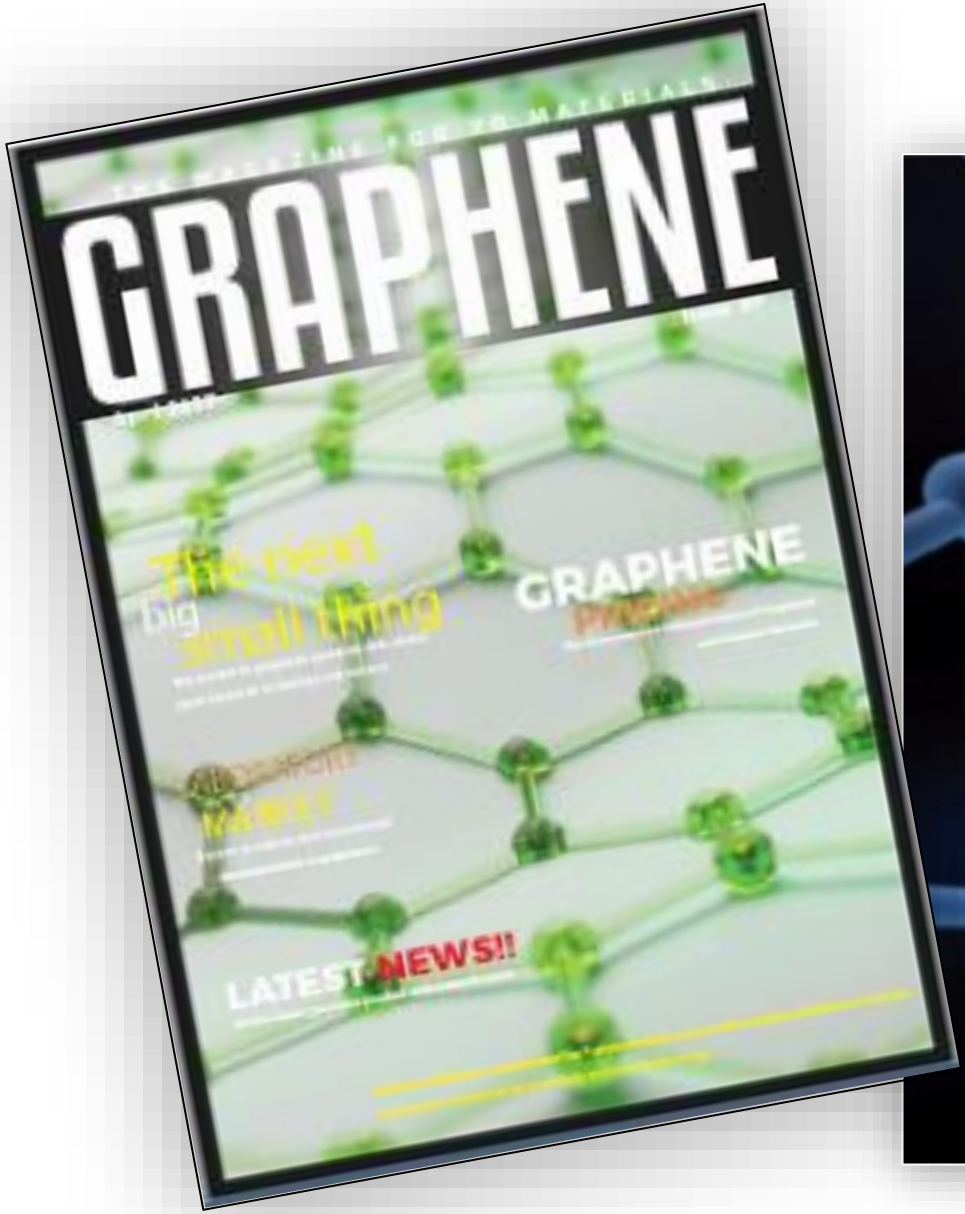


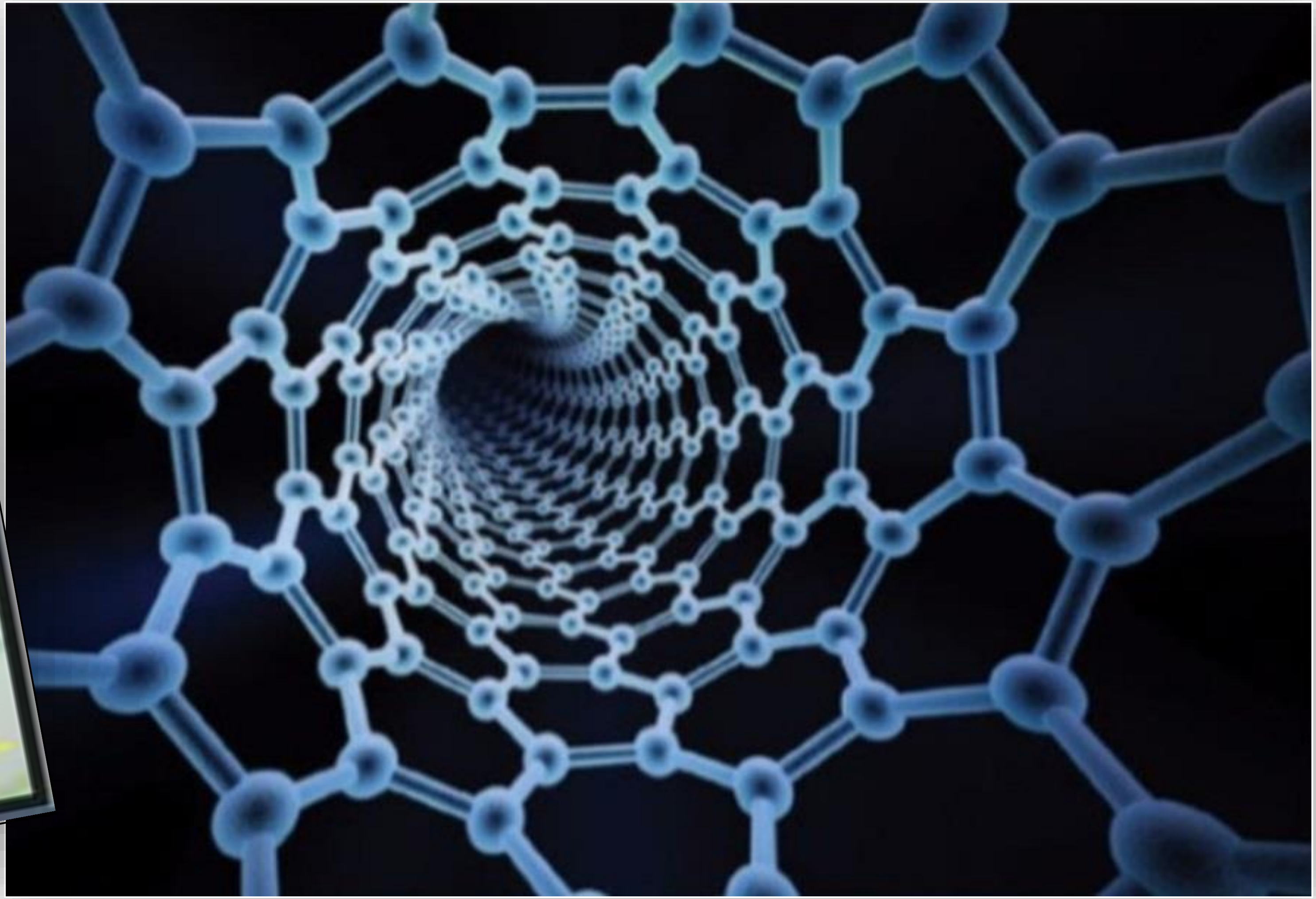
RESISTIVITY OF 3.75% XC-72R CONDUCTIVE BLACK IN STYRENE-BUTADIENE BLOCK COPOLYMER/PS 10mm THICK TEST SLAB



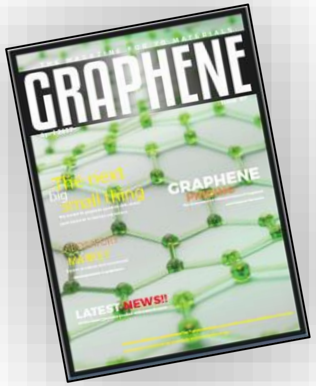
Wt.% LICA 09 Carbon Black	Resistivity Surface, Ω/sq.	Resistivity Volume, Ω·cm
Control	> 10^{16}	7.8×10^{14}
0.67	1.7×10^{12}	3.0×10^{12}
1.00	2.1×10^{8}	4.3×10^{7}
2.00	5.7×10^{7}	3.7×10^{7}

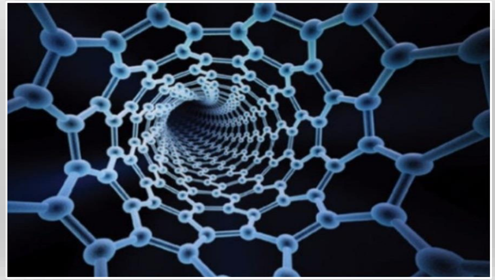
The Next Frontier in Polymer Composite Innovation



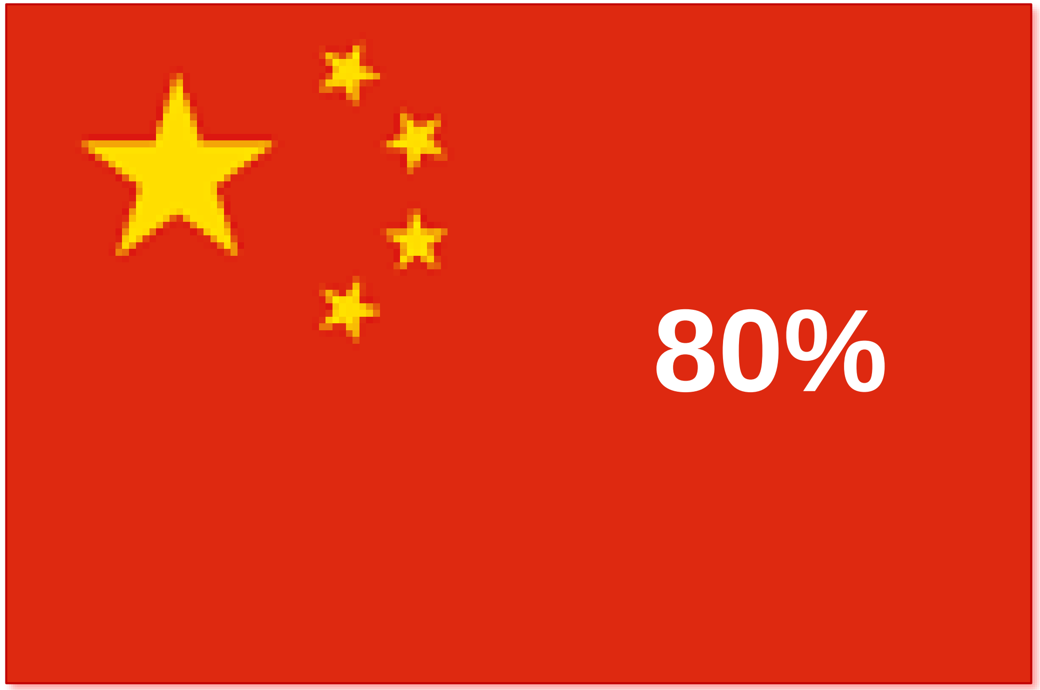


The Next Frontier in Polymer Composite Innovation





391 Abstracts based on Ti/Zr



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Email: kenreact@4kenrich.com · Web Site: www.4kenrich.com

ACS CAS SEARCH **GRAPHENE – GRAPHITE – CARBON NANOTUBES** (Carbon Black Not Included)
From Three ACS CAS Searches

SCIENCE IP
A CAS SOLUTION

Science IP Order: 3189677 TI/ZR COUPLING AGENTS

SCIENCE IP
The CAS Search Service

Science IP Order: 3140835
Ti/Zr Coupling Agents - Modified Update of Science IP Order 3069078

SCIENCE IP
The CAS Search Service

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5=> d a3069078rns/a :d query
A3069078RNS/A
RNS OF KENRICH CHEMICALS

L5    ANSWER 17 OF 374  CA  COPYRIGHT 2019 ACS on STN
AN    170:245595  CA Full-text
TI    High-strength polysulfide rubber with good aging resistance and long
      service life and production process thereof
IN    Zhang, Shixu
PA    Nantong Tongjiang Rubber Products Co., Ltd., Peop. Rep. China
SO    Faming Zhuanli Shenqing, 6pp.
LA    Chinese
FAN.CNT 1
      PATENT NO.          KIND  DATE         APPLICATION NO.        DATE
      ---------------     ----  --------     --------------------   --------
```

- **Graphene – 109x**
- **Graphite – 177x**
- **CNTs – 105x**

March 2019

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

(51) **Int. Cl.**
C04B 20/10 (2006.01)

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

(72) Inventor: Salvatore J. Mo

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

Returned From Darmstadt Mar. 5. 2020

My 32nd Patent Issued 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


US 20200071230A1

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TEC
(US)

(72) Inventor: Salva

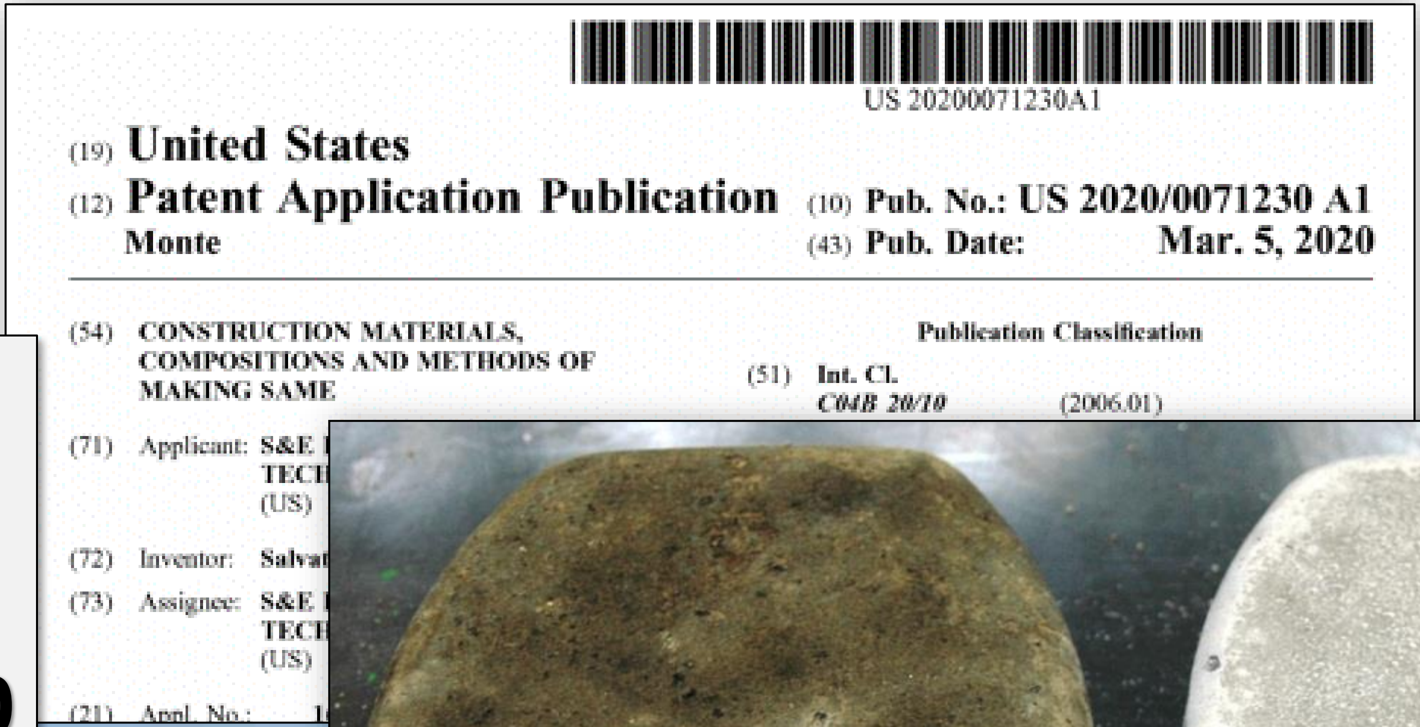
(73) Assignee: S&E
TEC
(US)

(21) Appl. No.:

My 32nd Patent Issued Mar. 5. 2020

Returned From Darmstadt Mar. 5. 2020

Compatibilize Oil Soaked Seawater Sand with OPC


US 20200071230A1

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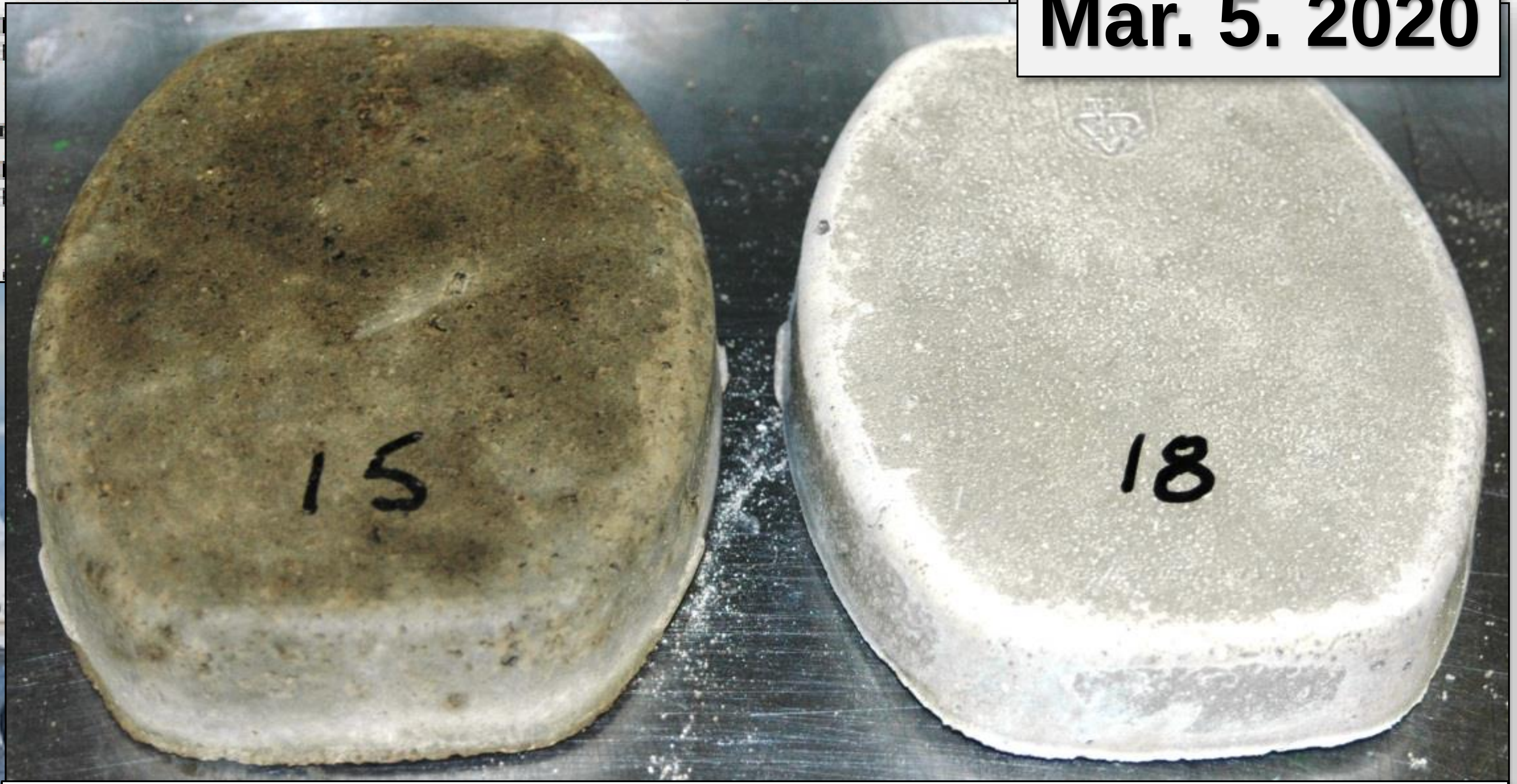
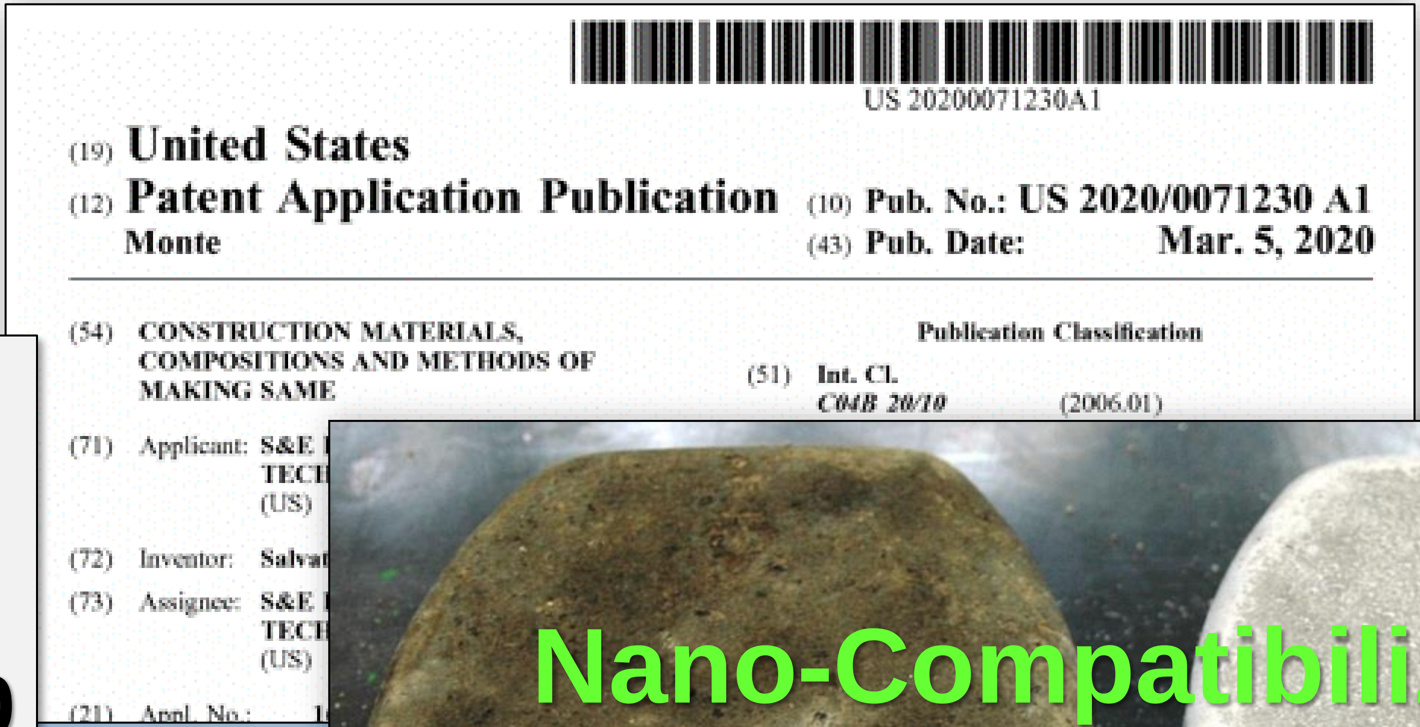


Compatibilize Oil Soaked Seawater Sand with OPC

Returned From Darmstadt Mar. 5. 2020



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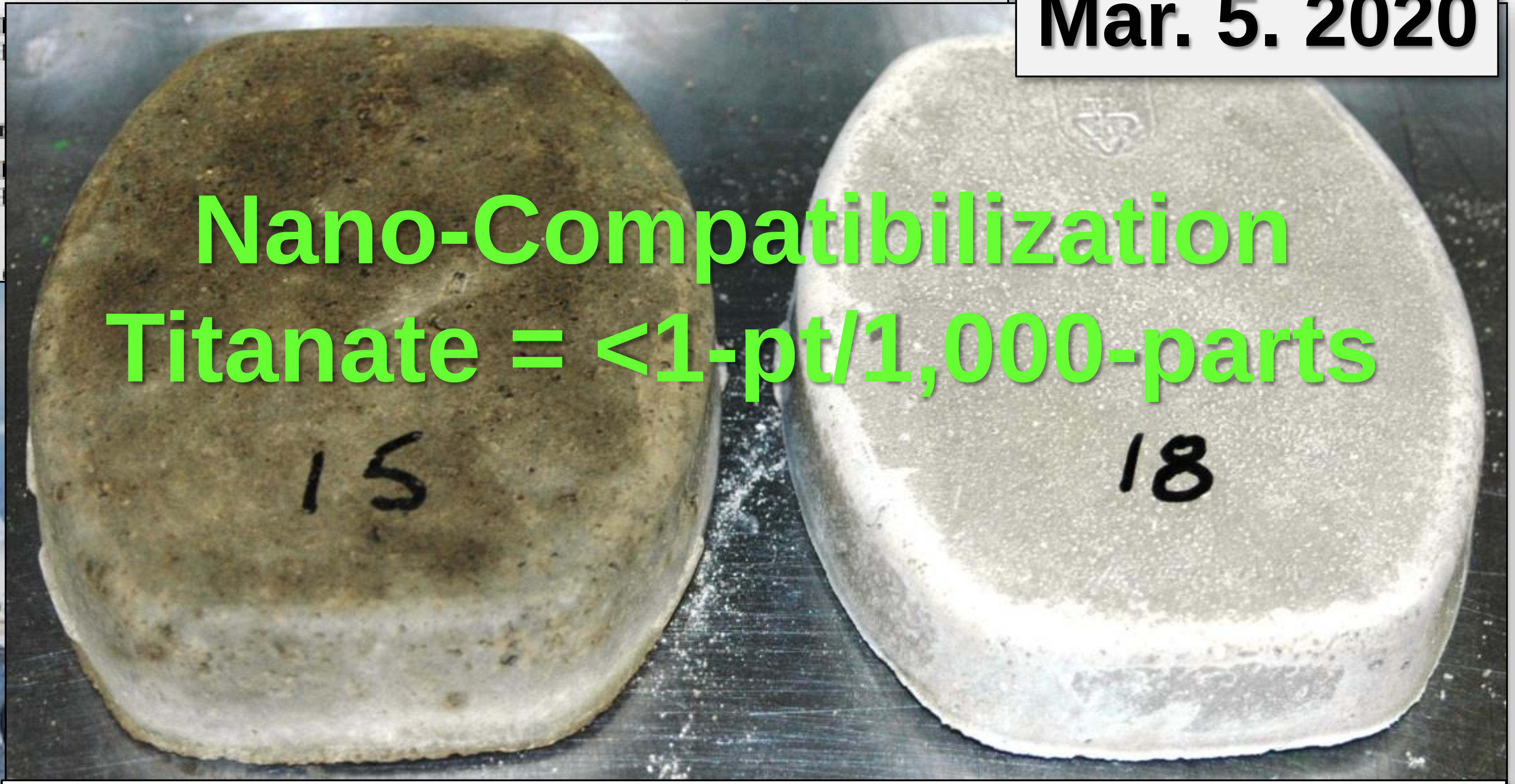
(71) Applicant: S&E I... TECH... (US)

(72) Inventor: Salva...

(73) Assignee: S&E I... TECH... (US)

(21) Appl. No.: 1...

My 32nd Patent Issued Mar. 5. 2020



Nano-Compatibilization Titanate = <1-pt/1,000-parts

Compatibilize Oil Soaked Seawater Sand with OPC

SUSTAINABILITY

Technology Challenge

Add to the mix: Polymers #1 to #7 & Fillers, Fibers, Pigments, etc.

PETE HDPE V LDPE PP PS OTHER

PE & PP are ADDITION POLYMERS

PET is a CONDENSATION POLYMER

Incompatibility PE & PP

Incompatibility PET & PE

LDPE

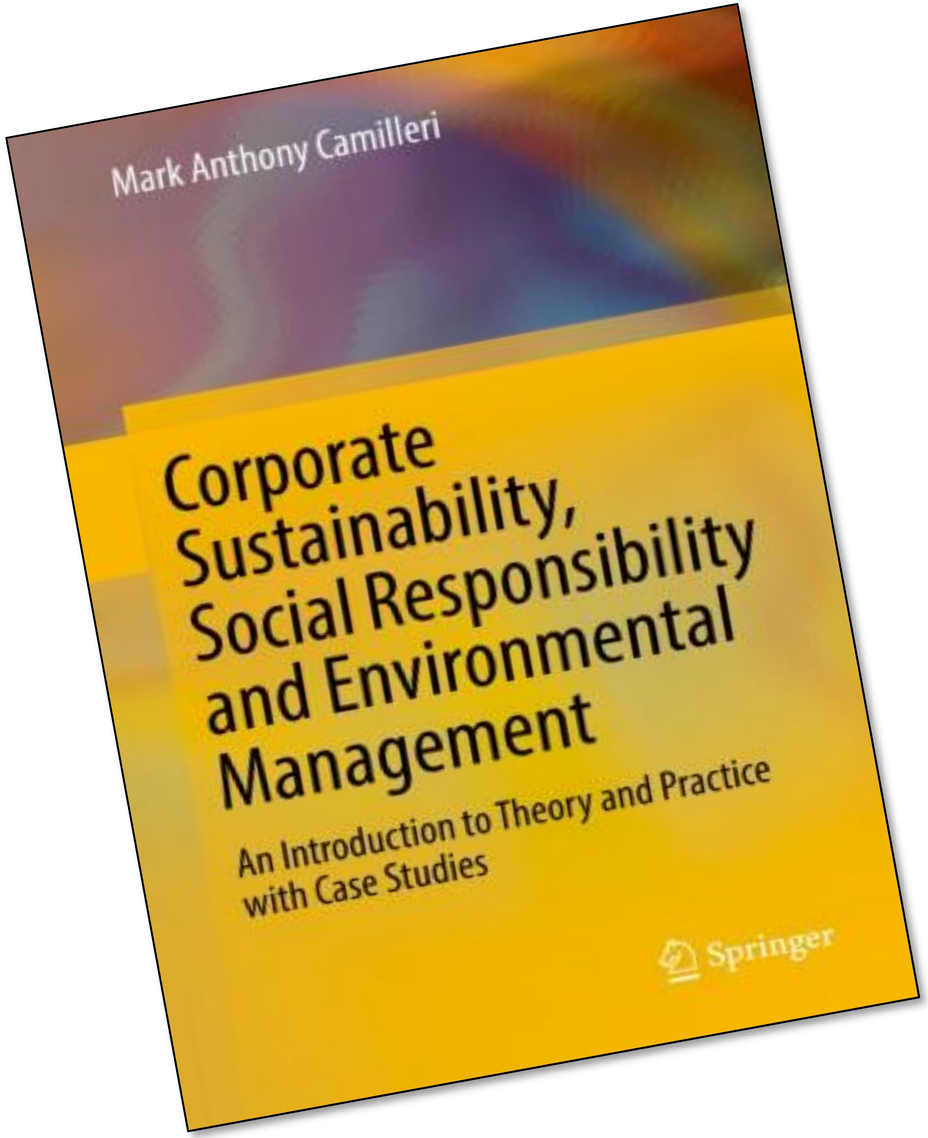
PETE

PP

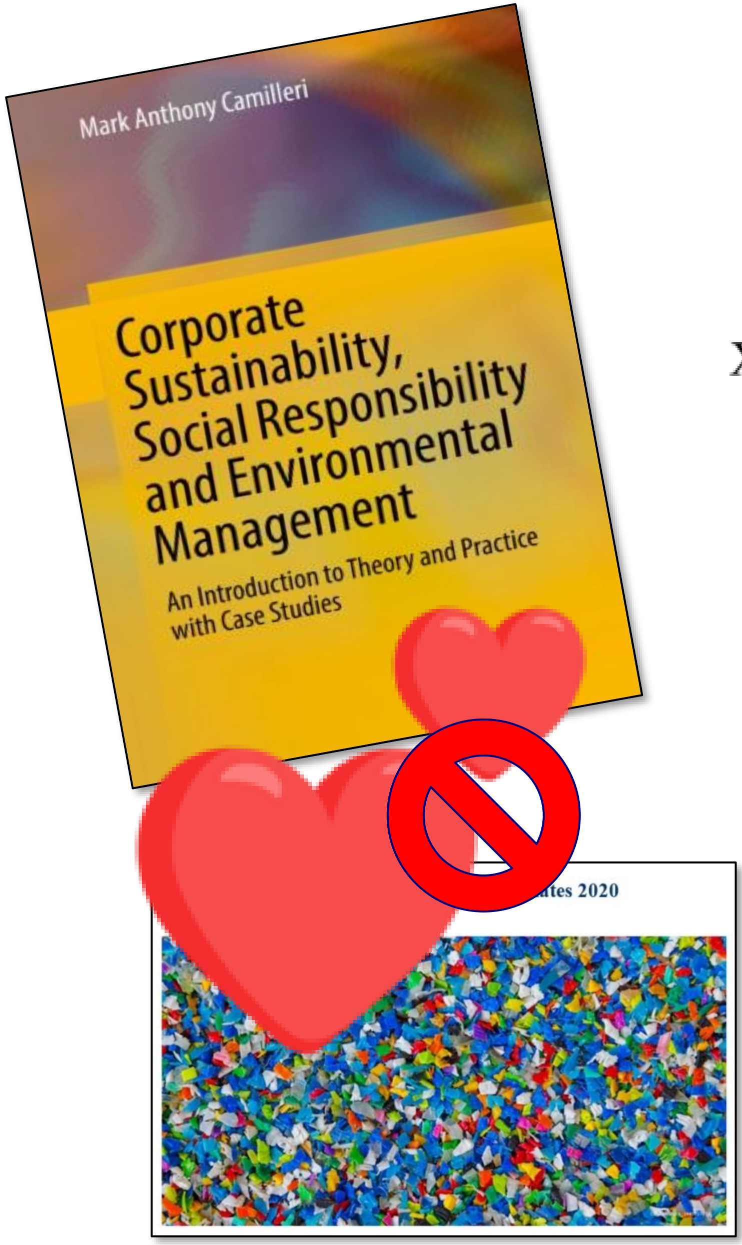
HDPE

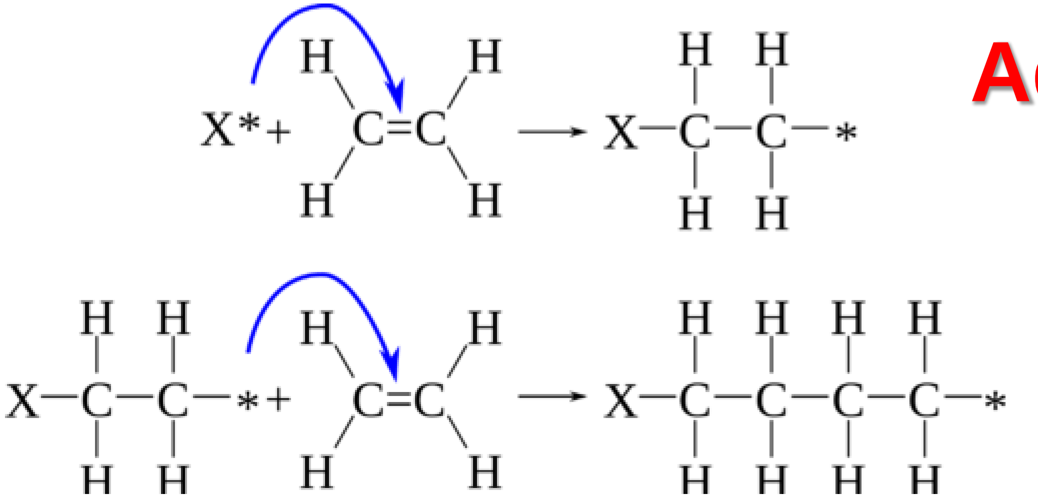
How to Compatibilize?

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents

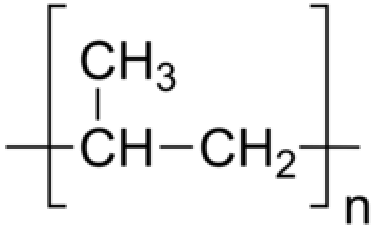


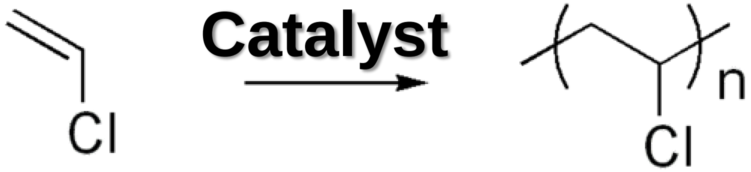
You can't just mix everything together





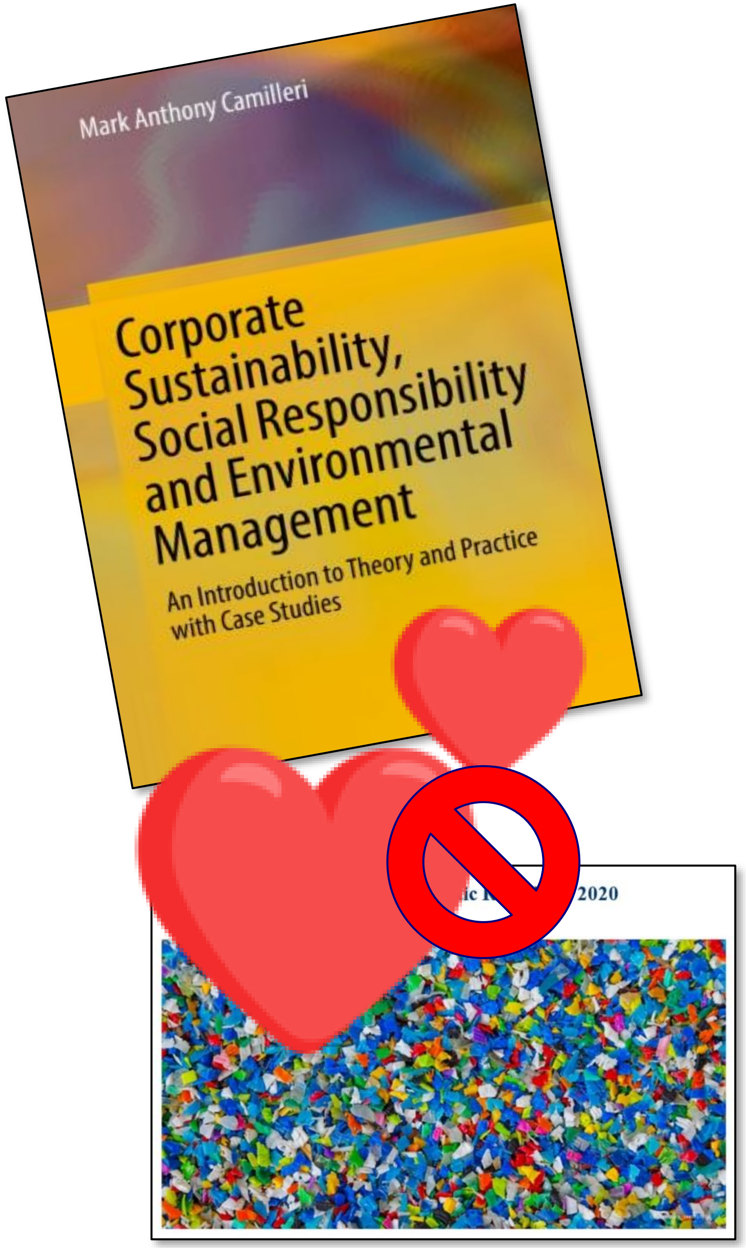
Addition Polymers Are Different

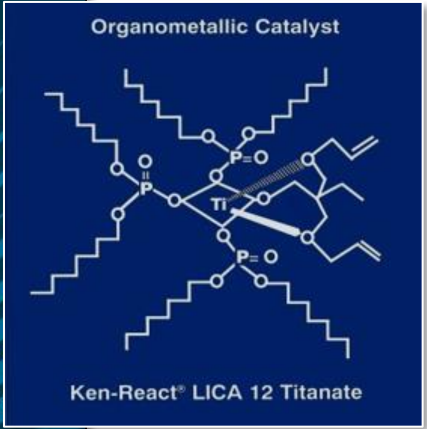




PVC is #3

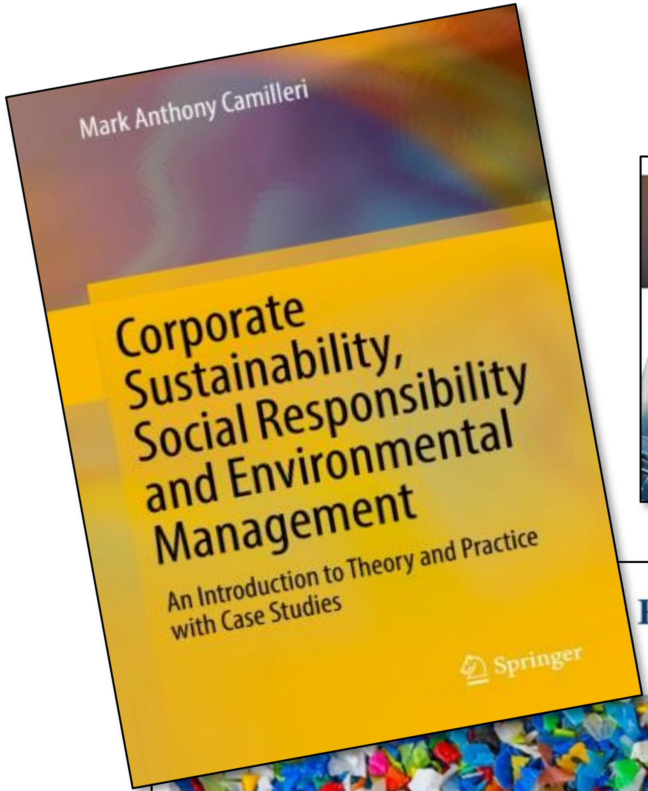
You Need Nano-TITANATE Atomic Compatibilization





Plastics #1 to #7 are incompatible with each other

Advanced Solutions in Vinyl Recycling with Titanate Catalysts/Coupling Agents

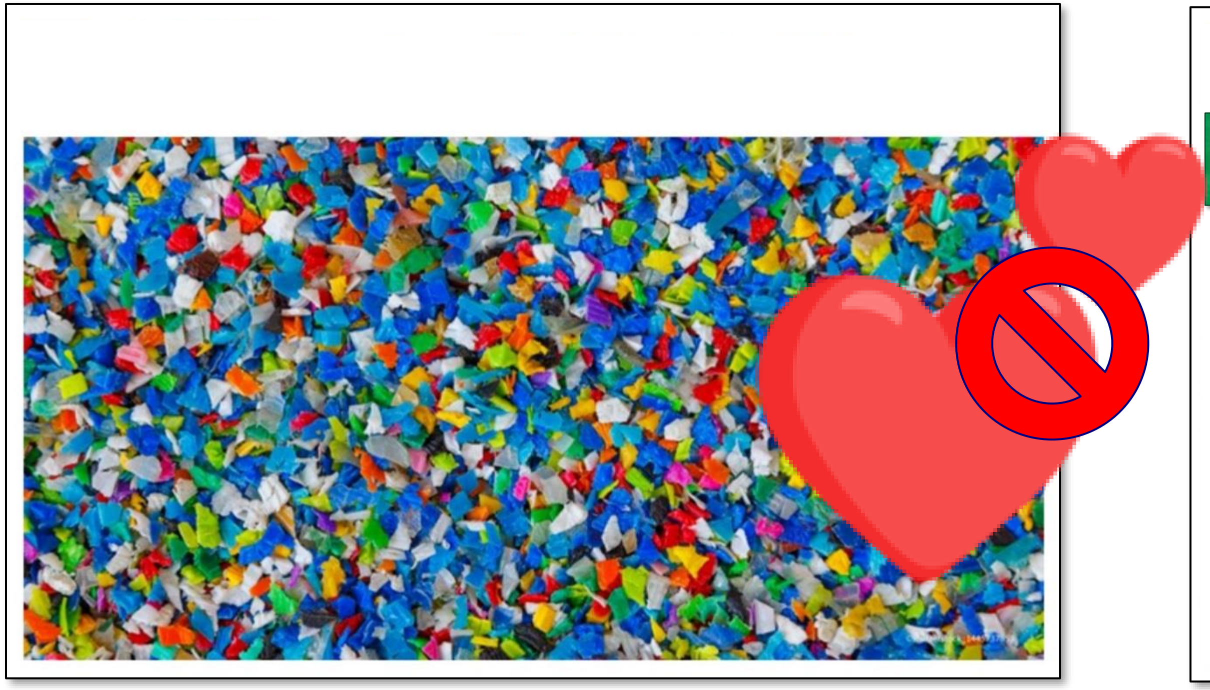


SUSTAINABILITY

Plastics #1 to #7 are incompatible with each other

LDPE
(LOW DENSITY POLYETHYLENE)
PET
(POLYETHYLENE TEREPHTHALATE)

PP
(POLYPROPYLENE)
HDPE
(HIGH DENSITY POLYETHYLENE)



PETE HDPE V LDPE PP PS OTHER
PE & PP are ADDITION POLYMERS
PET is a CONDENSATION POLYMER
Incompatibility PE & PP
Incompatibility PET & PE
LDPE
PP
PETE
HDPE

Add to the mix: Polymers #1 to #7 & Fillers, Fibers, Pigments, etc.

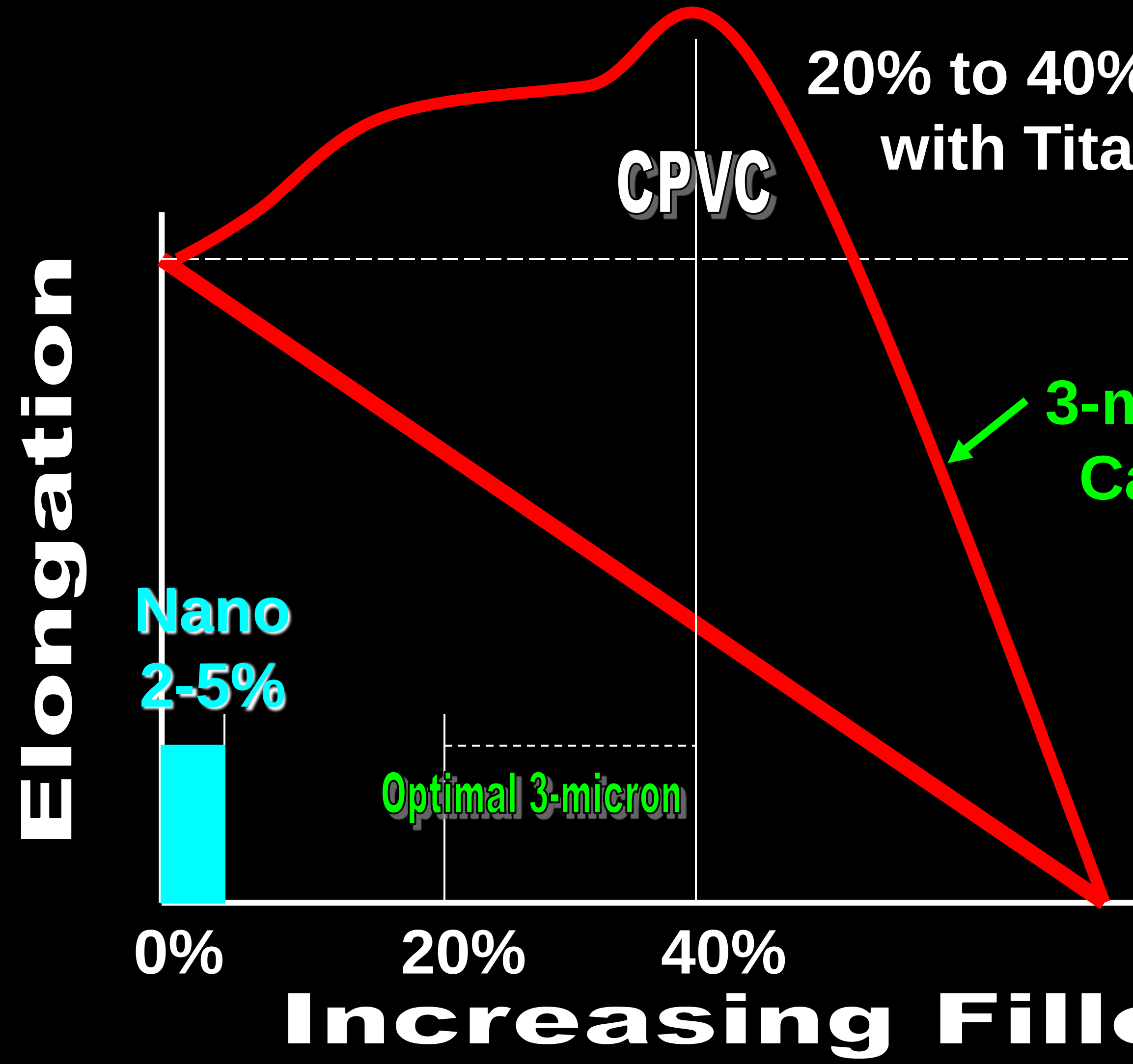
PE & PP are ADDITION POLYMERS

PET is a CONDENSATION POLYMER

Incompatibility PE & PP

Incompatibility PET & PE

Add to the mix: Polymers #1 to #7 & Fillers, Fibers, Pigments, etc.



Functions 1 & 2 – Coupling & Catalysis Elongation

RECYCLE Technology Challenge: Incompatibility of Fillers & Polymers

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

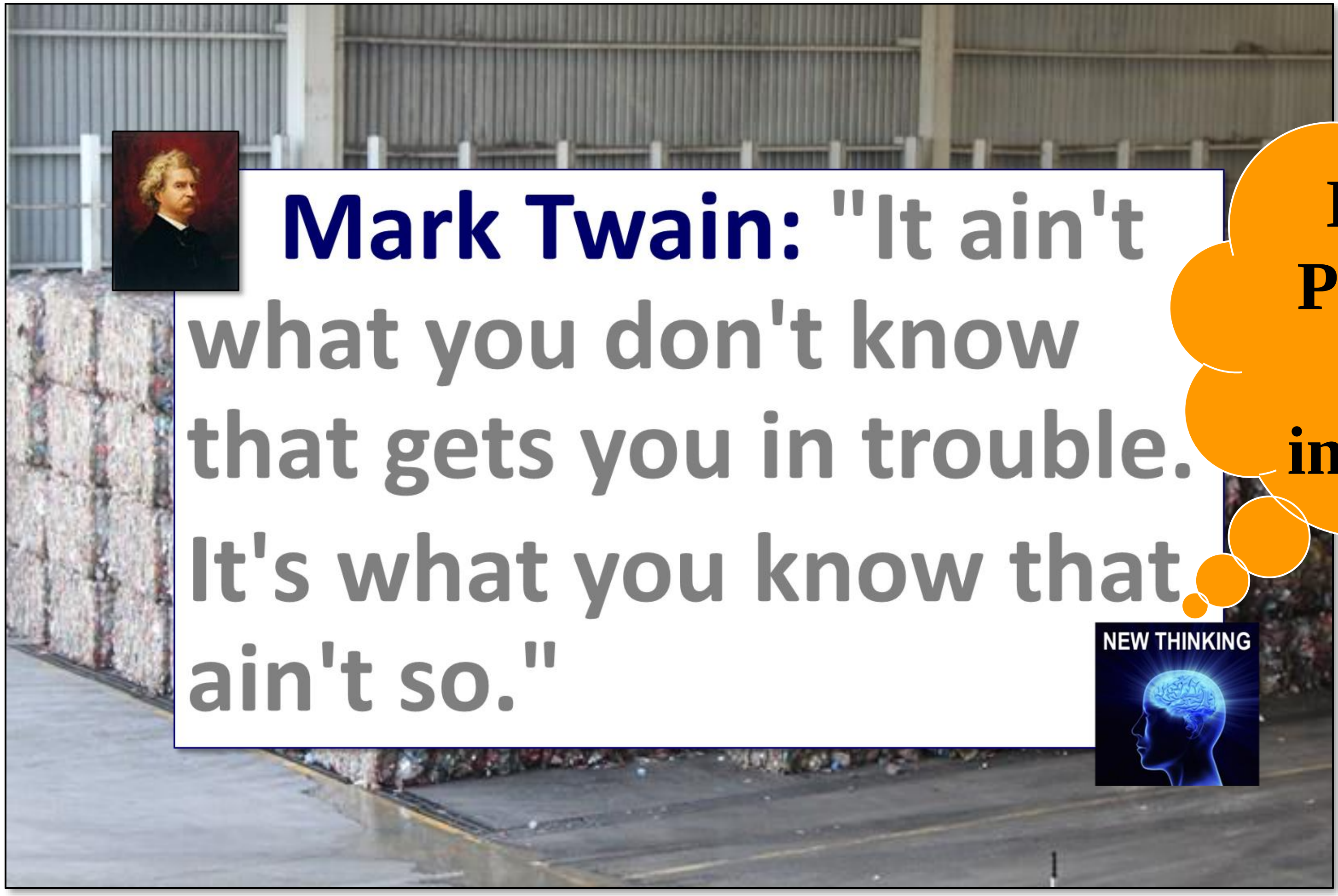
Trouble Shooting for Injection Molding Process

- 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

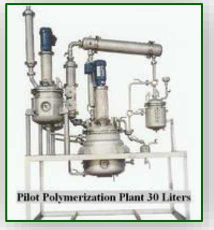
Sustainability Goals such as a Circular Economy using <u>Curbside Recycle</u> in new plastic parts is technically not possible with current industry practices:

Sustainability Goals such as a Circular Economy using <u>Curbside Recycle</u> in new plastic parts is **technically not possible with current industry practices**:



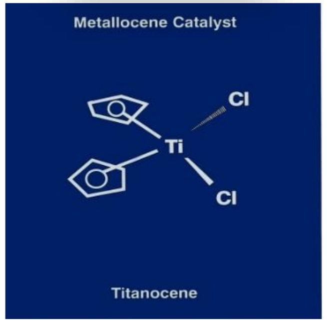
It ain’t so:
PP & HDPE
are
incompatible

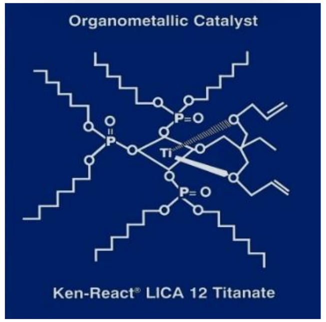
Reactor
Titanocene Polymerization - Ethylene Monomer



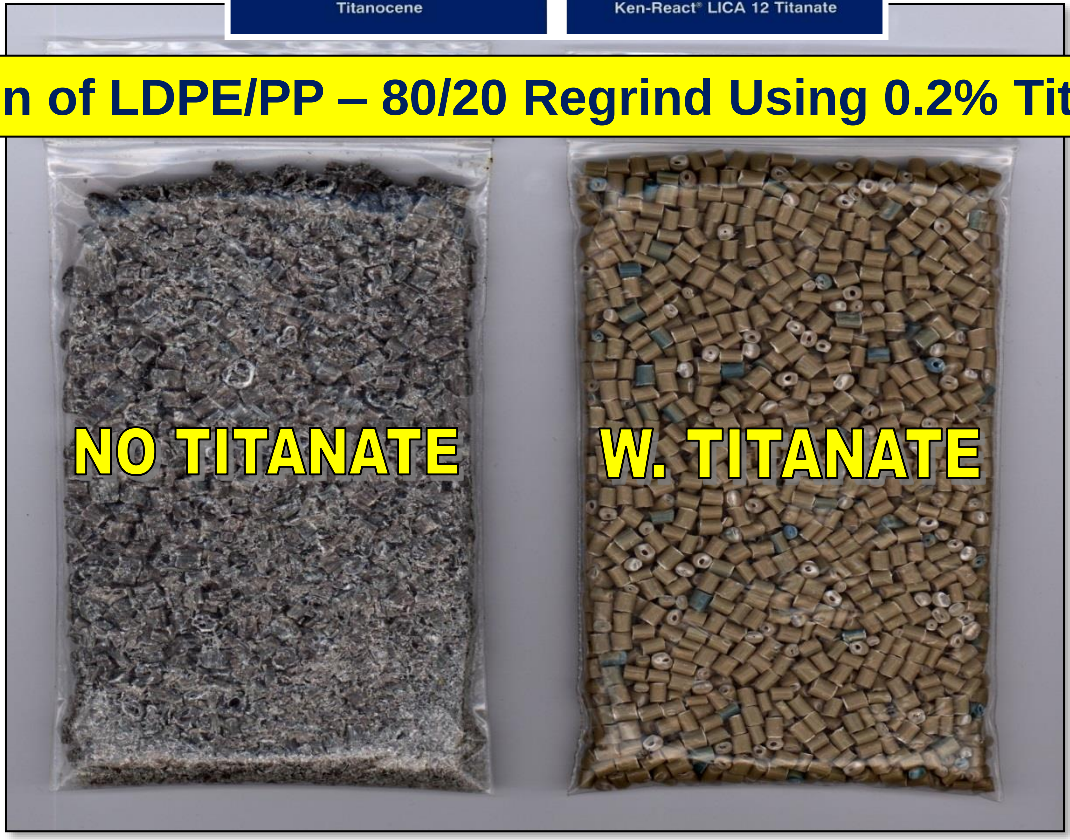
Extruder
Titanate Copolymerization - Ethylene Polymers

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

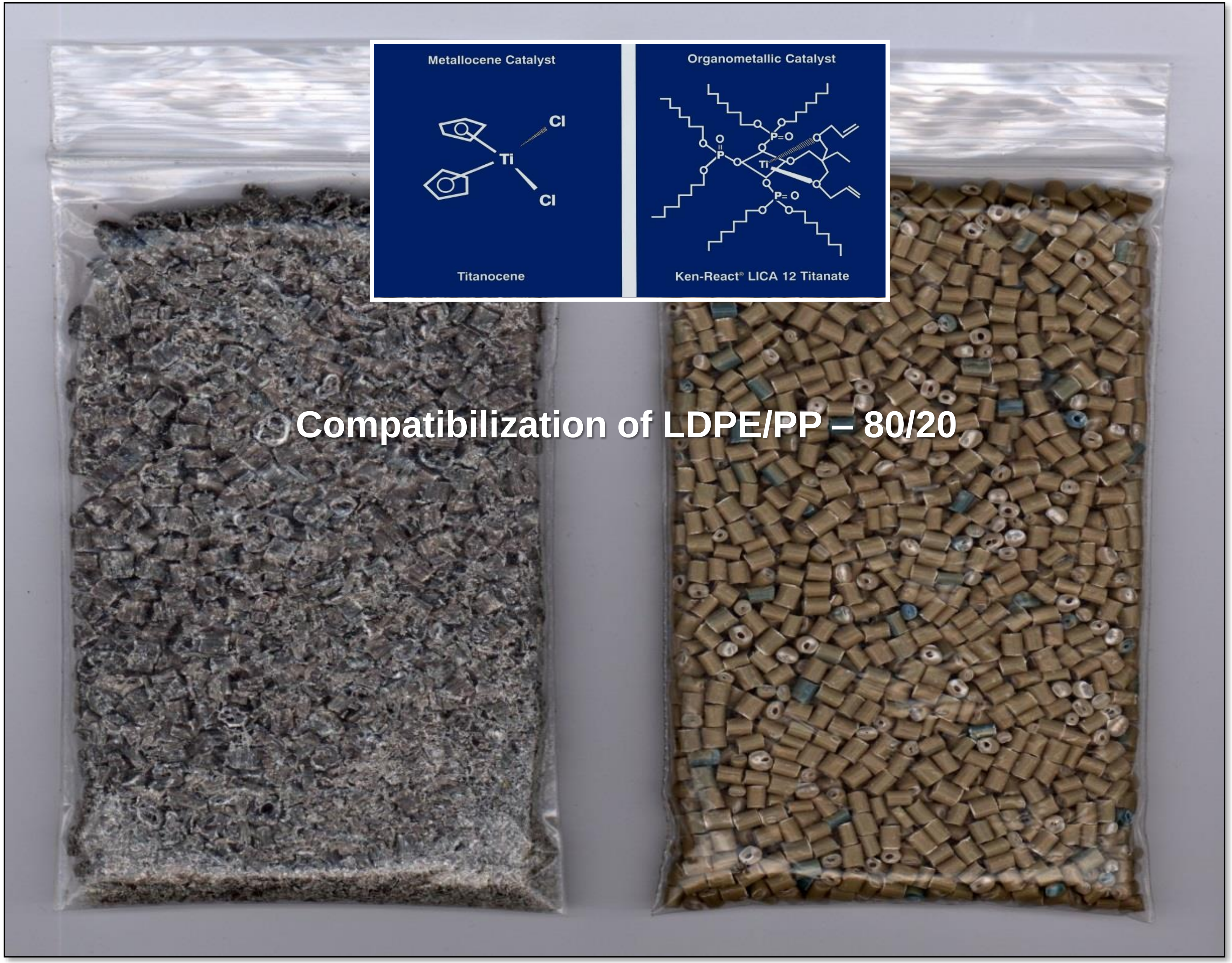




Compatibilization of LDPE/PP – 80/20 Regrind Using 0.2% Titanate Catalyst



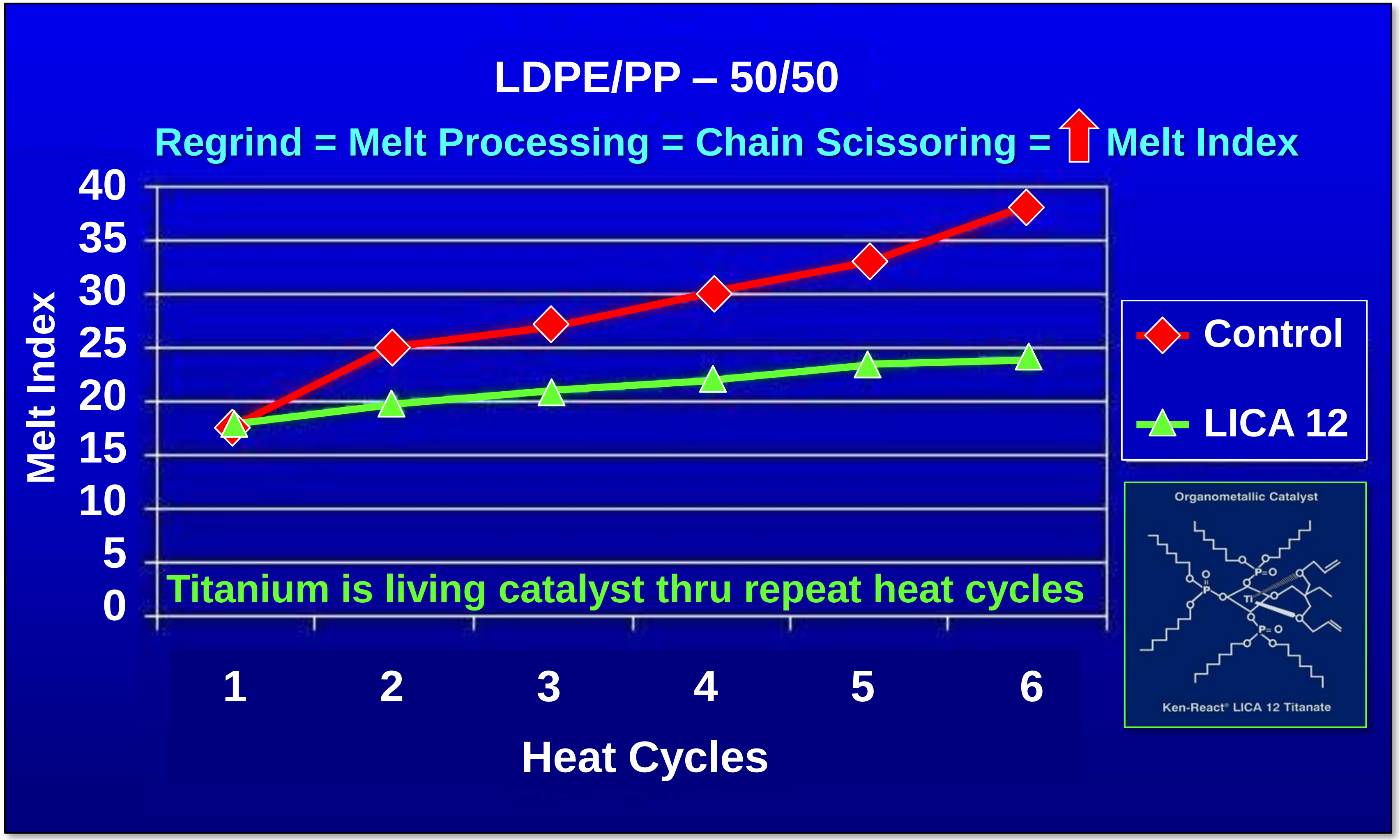
PE & PP are COMPATIBLE



Chain Scissoring Effect - 6 Heat Cycles on LDPE/PP – 50/50 Regrind

REPOLYMERIZATION of LDPE/PP – 50/50 Regrind

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



New thinking in Compatibilization & Polymer Regeneration via Ti / Zr Coupling & Catalysis to reduce the need & cost to sort materials so as to broaden Recycling Compounding Capability

***

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

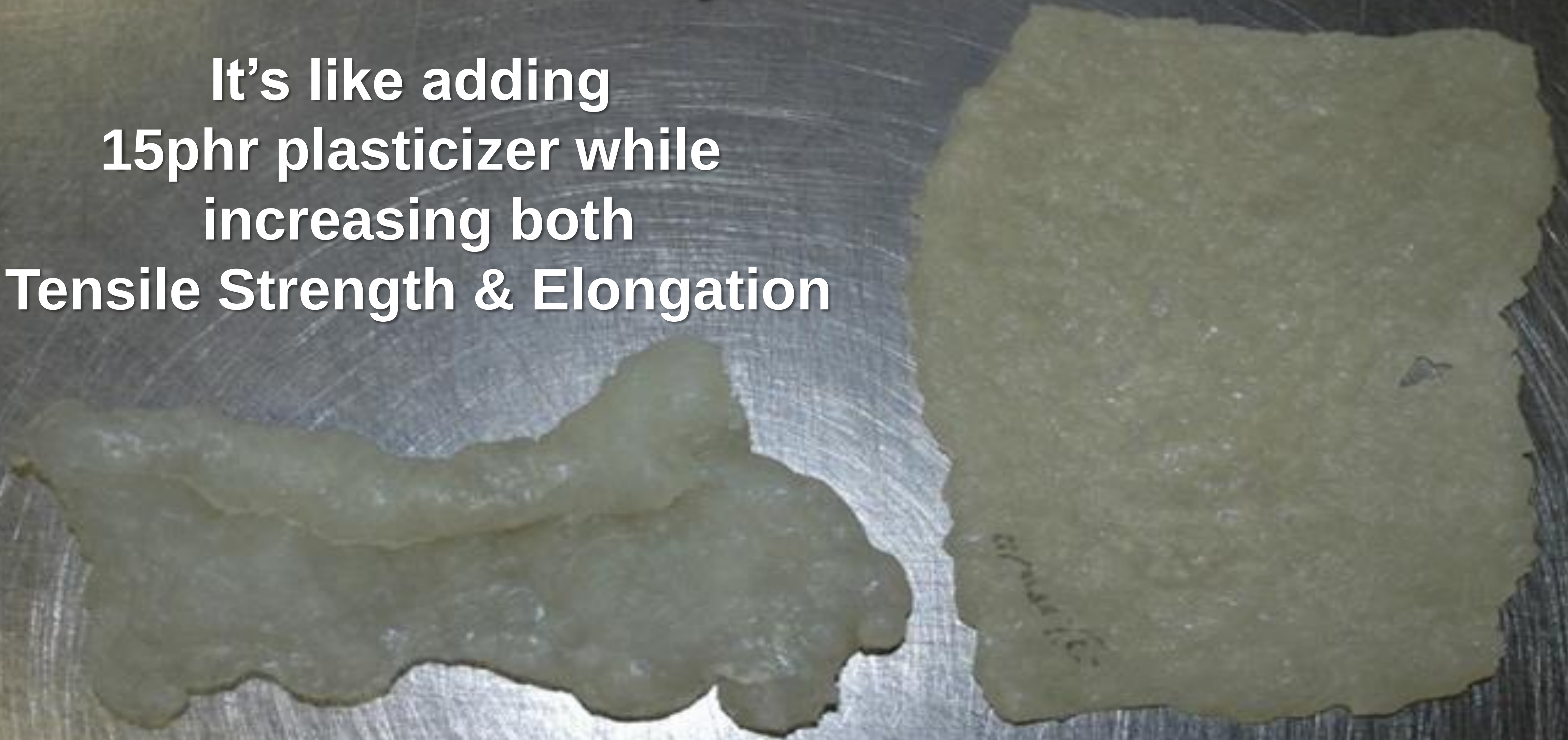
PC IS A CONDENSATION POLYMER
Molded @100°C lower Temp. (188°C vs. 304°C)

- **Maleated polymer compatibilizers work on Addition Polymers but depolymerize Condensation Polymers.**

- **Maleated polymers couple polymers but not fillers.**

Titanate Catalysis Unfilled EPR

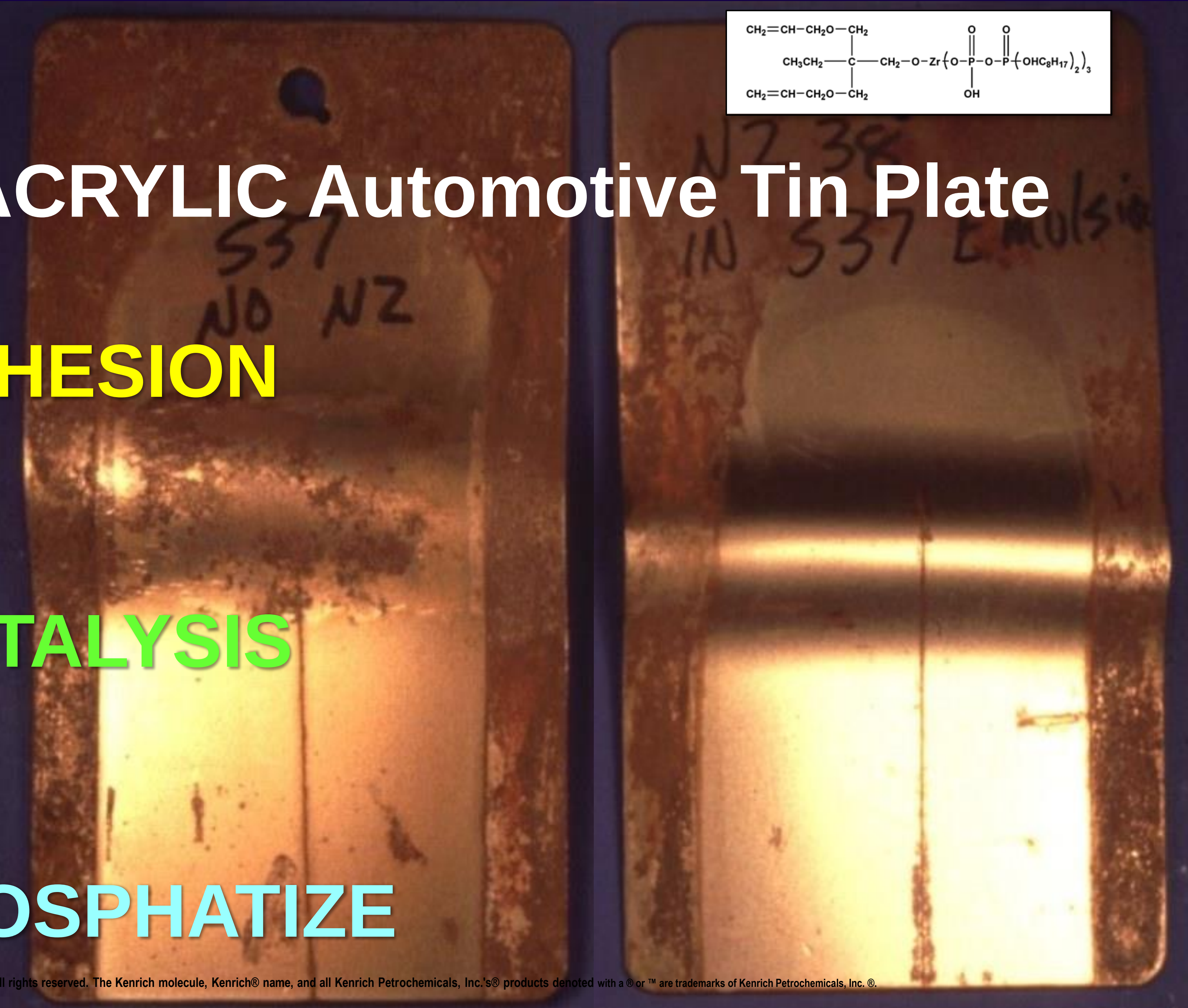
It's like adding
15phr plasticizer while
increasing both
Tensile Strength & Elongation



1000g off 2-roll mill

0.2% Titanate

UNFILLED WB ACRYLIC Automotive Tin Plate



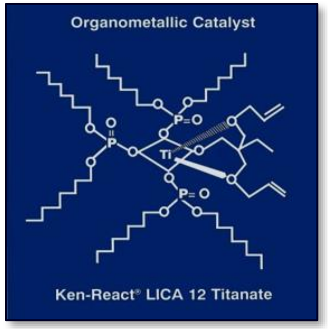
Function 1 – ADHESION

Function 2 – CATALYSIS

Function 3 - PHOSPHATIZE

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

Copolymerization of Two Dissimilar Condensation Polymers



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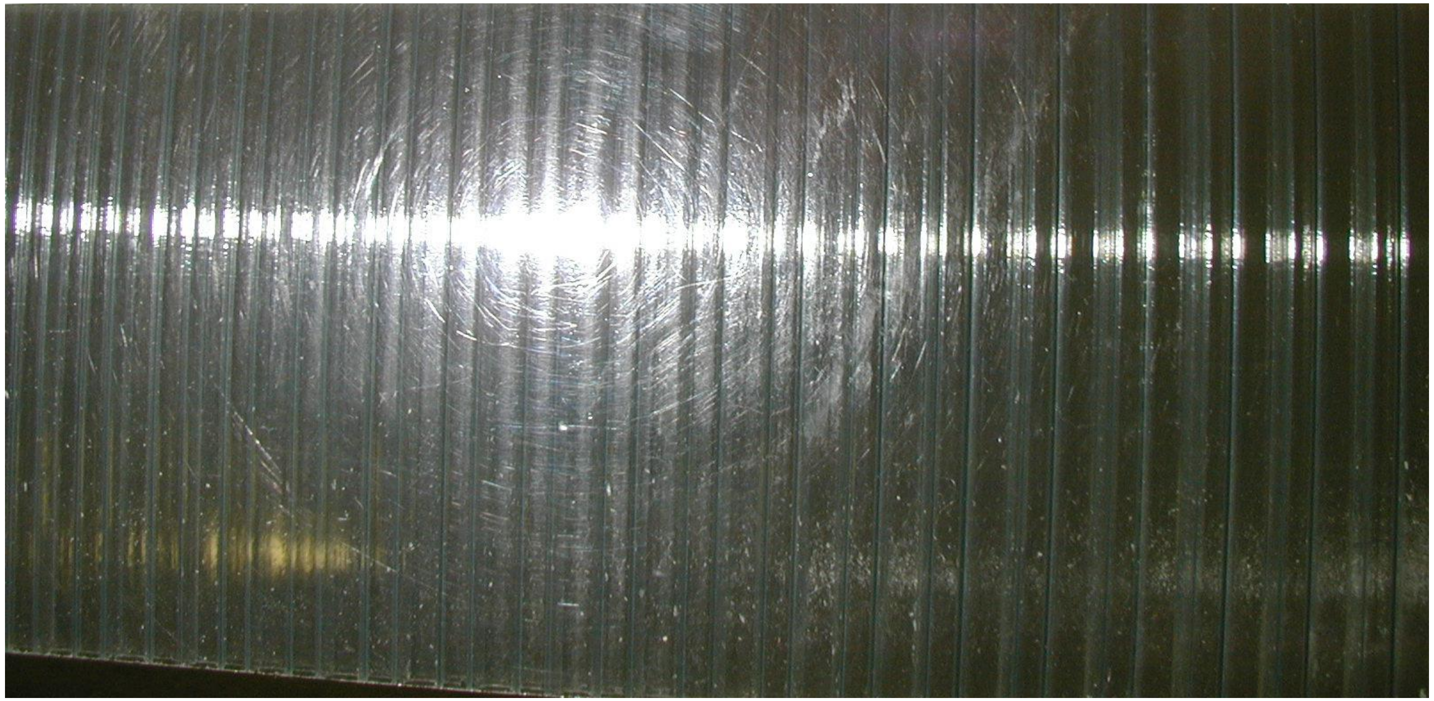
Extruded@ 180ºC using 0.3% CAPOW® L®12/H Titanate Catalyst vs. 280ºC without the Additive



Regrind: Compatibilizing HDPE / Nylon Film

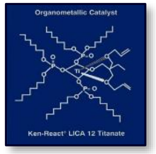
Using 0.2% Titanate Catalyst

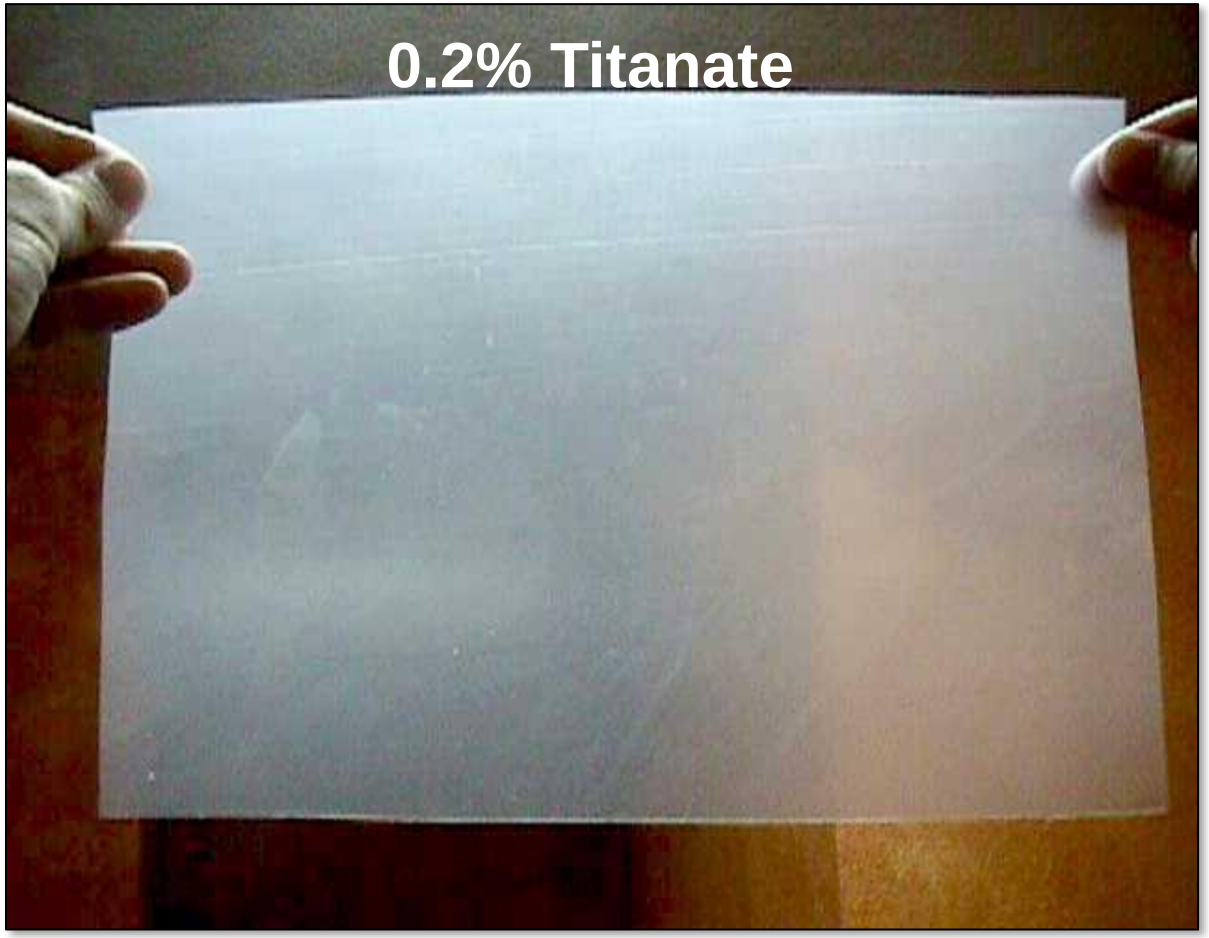
HDPE – Addition Polymer

+

NYLON – Condensation Polymer

+



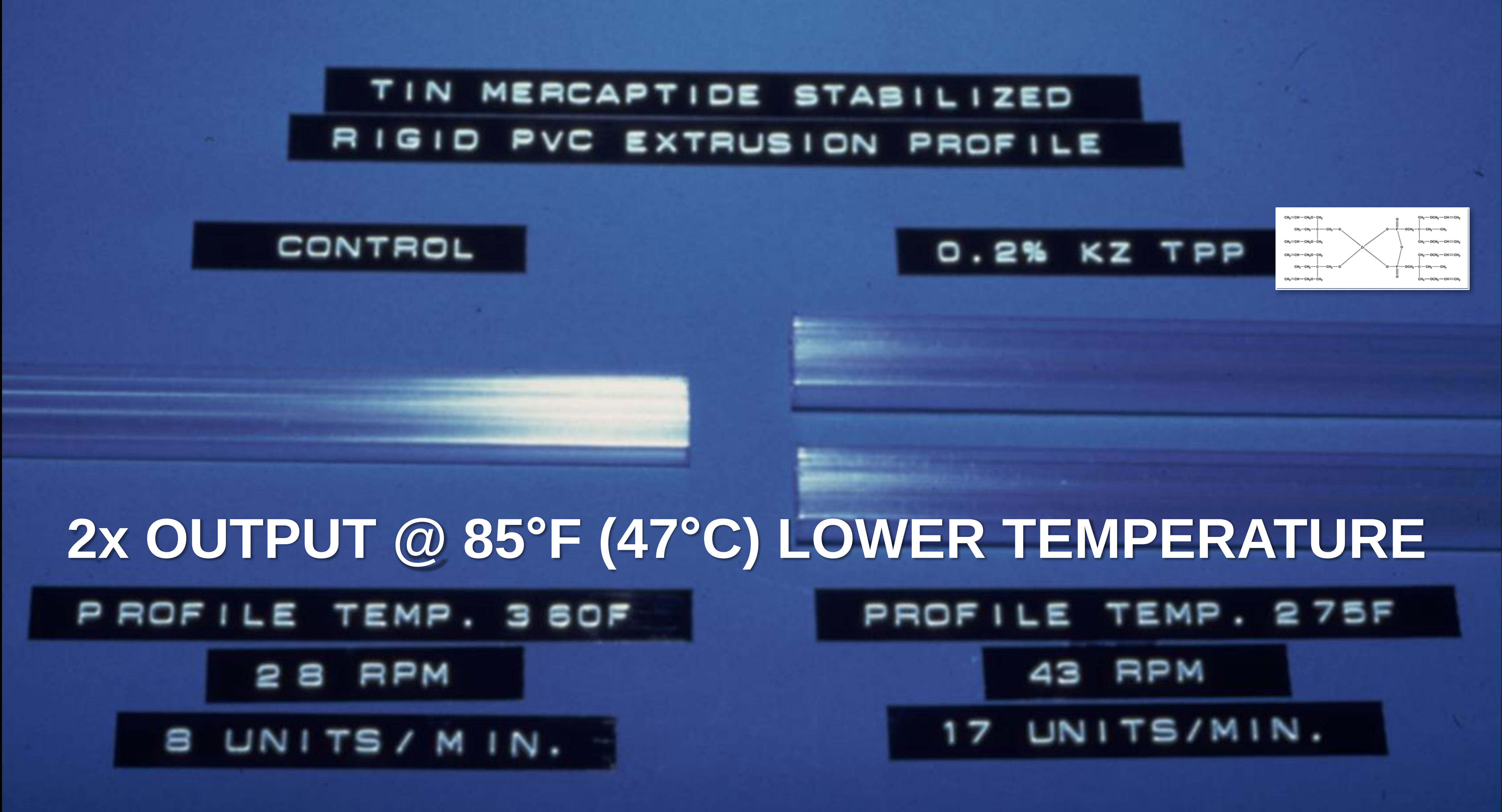


71-ABSTRACTS on POLYBLENDS – sjmonte@4kenrich.com

SCIENCE IP
The CAS Search Service

KEY SEARCH WORD: “BLEND”

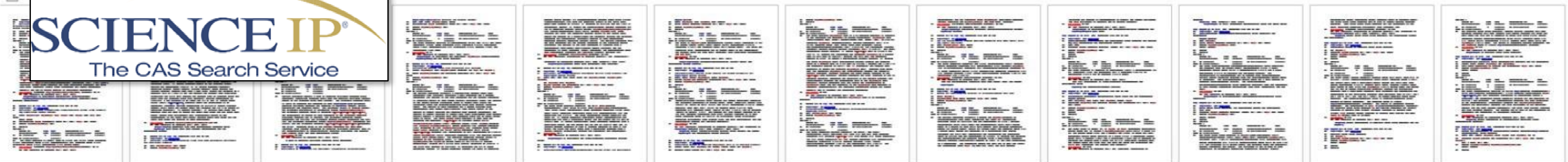
44 References to “PVC”

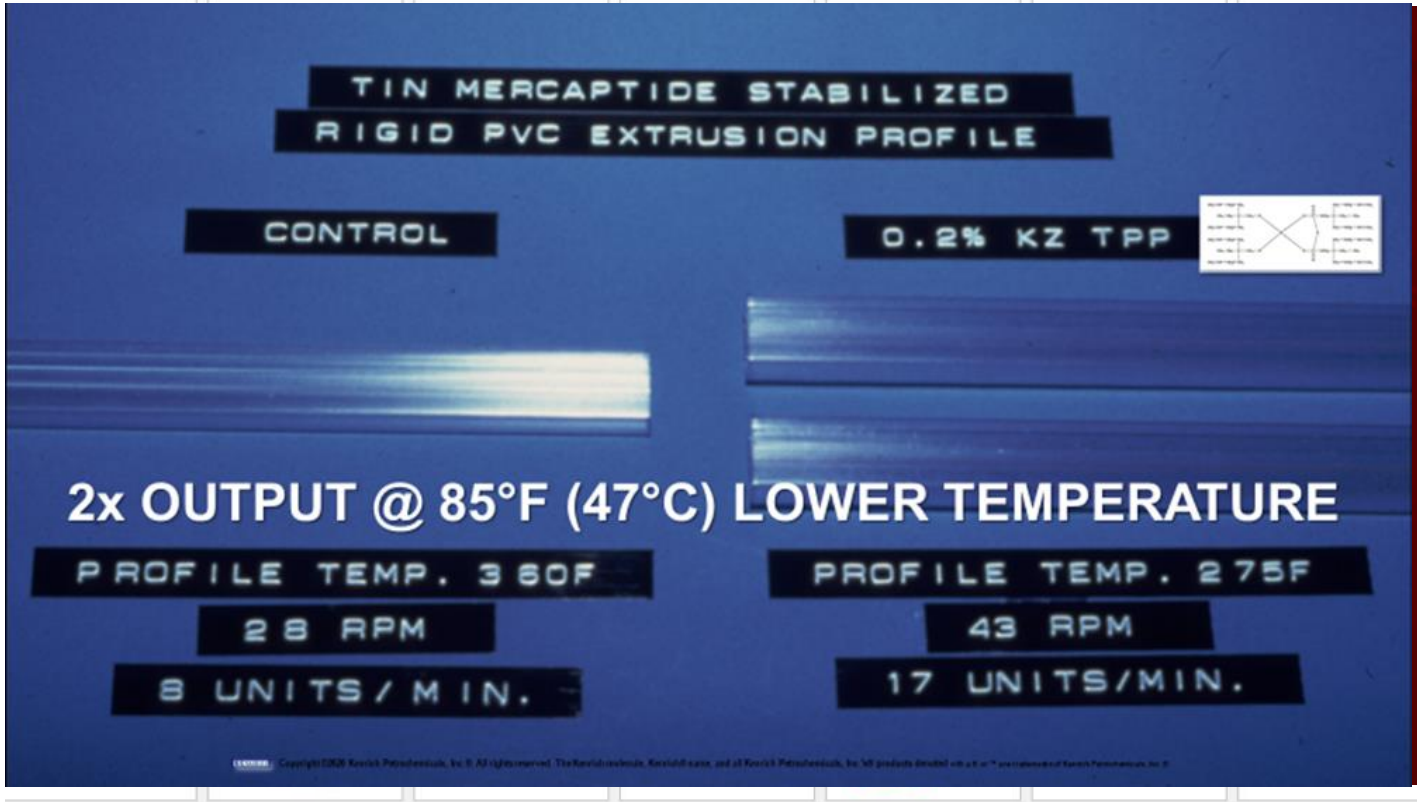


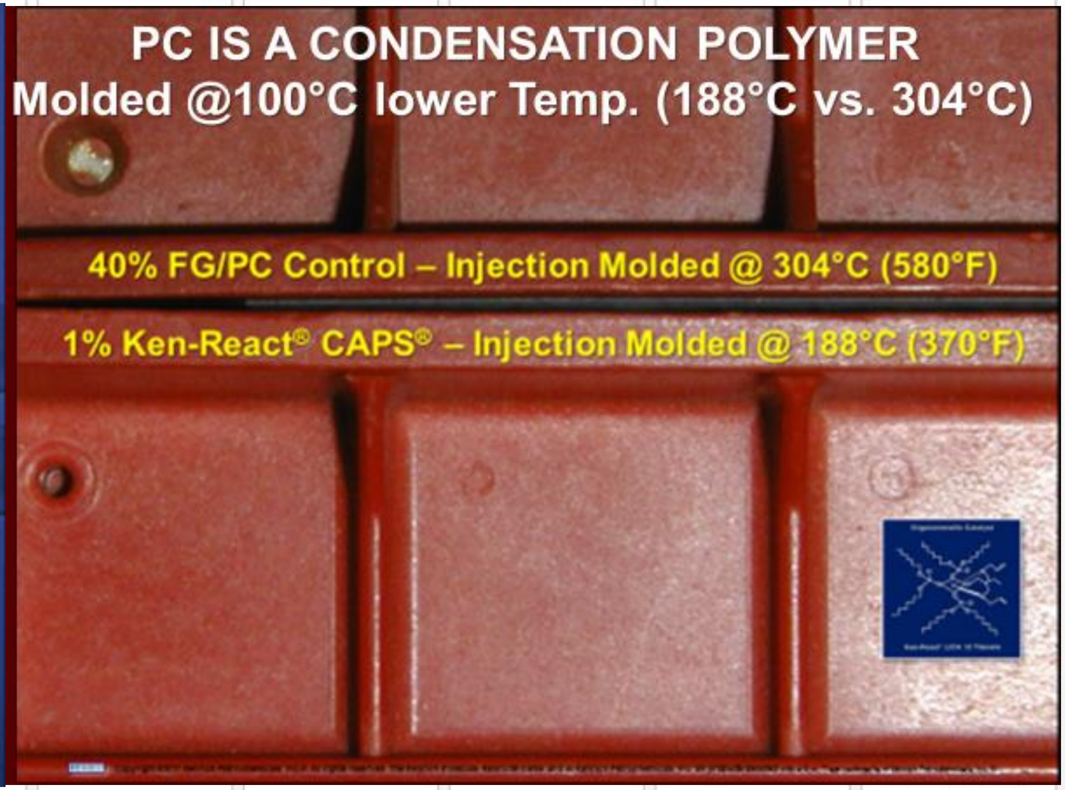
2x OUTPUT @ 85°F (47°C) LOWER TEMPERATURE

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

SCIENCE IP
The CAS Search Service







L5 ANSWER 155 OF 439 CA COPYRIGHT 2016 ACS on STN
AN 163:386816 CA Full-text <<LOGINID::20160920>>

SCIENCE IP The CAS Search Service

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		

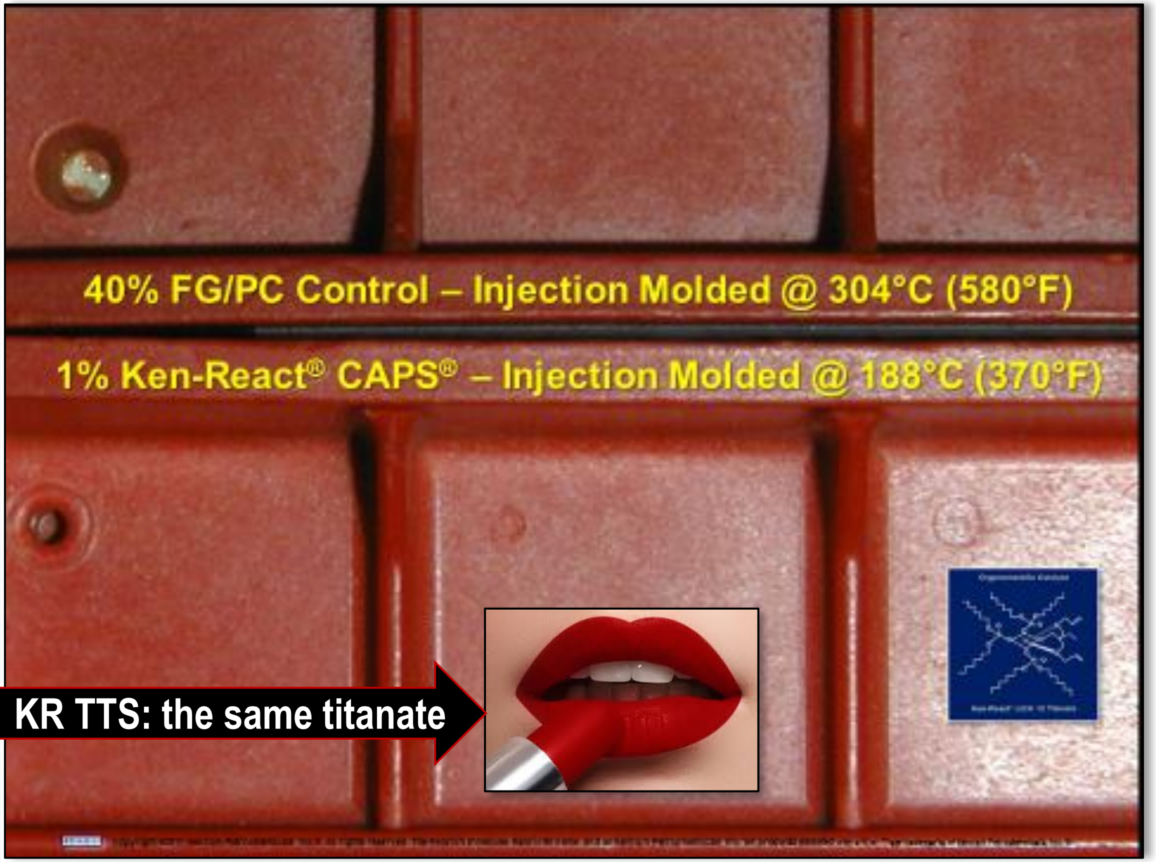
AB The present invention provides polyvinyl chloride (PVC)-polycarbonate alloy with good weathering resistance and antistatic property, comprising the following components by mass percentages: PVC 45-55, polycarbonate 20-25, SMA 2-4, ACR 3-6, attapulgite 2-8, melamine cyanurate 4-7, dioctyl phthalate 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)

KR TTS: the same titanate

PVC 45-55, polycarbonate 20-25

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 155 OF 439 CA COPYRIGHT 2016 ACS on STN
AN 163:386816 CA Full-text <<LOGINID::20160920>>

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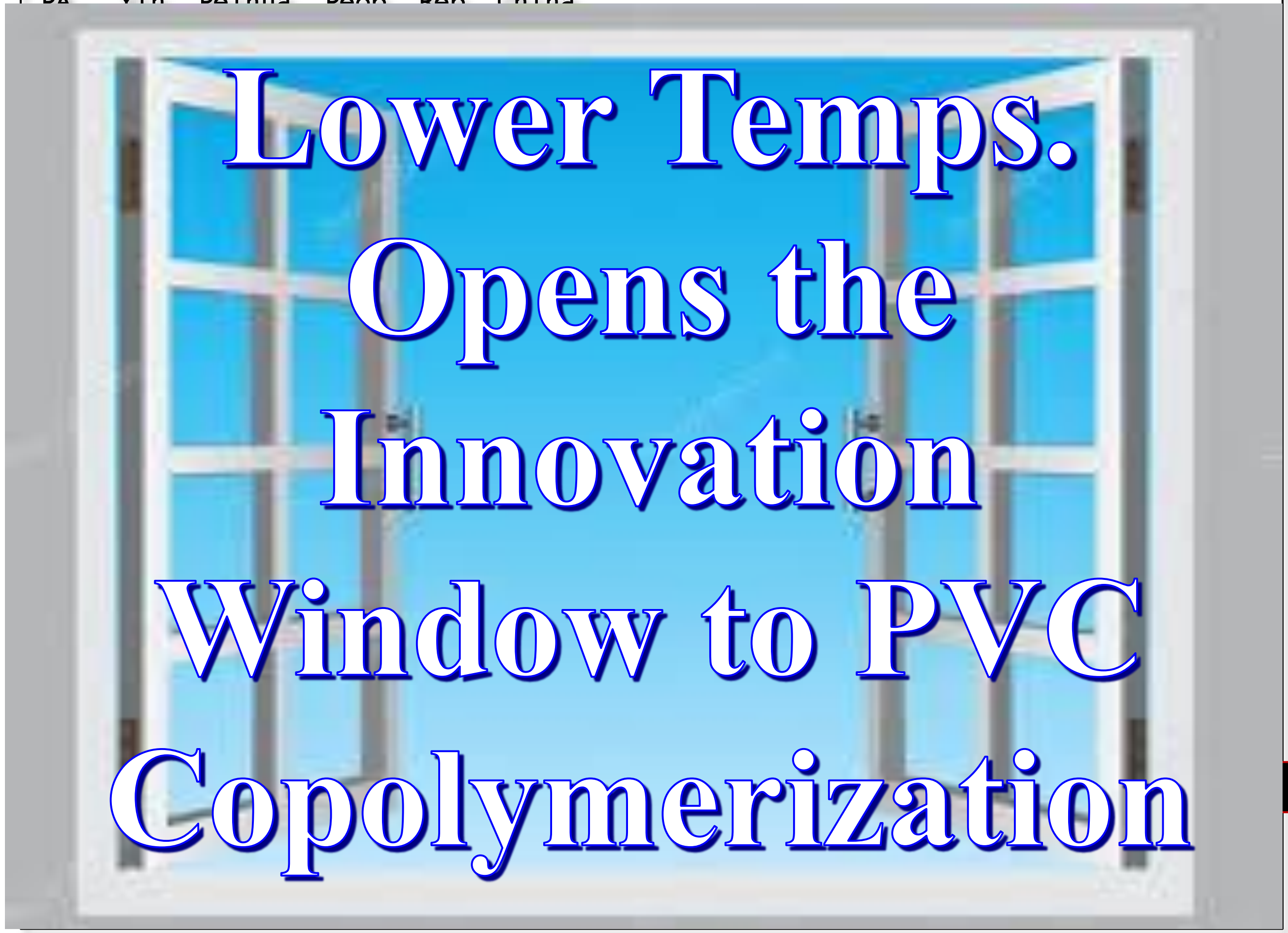
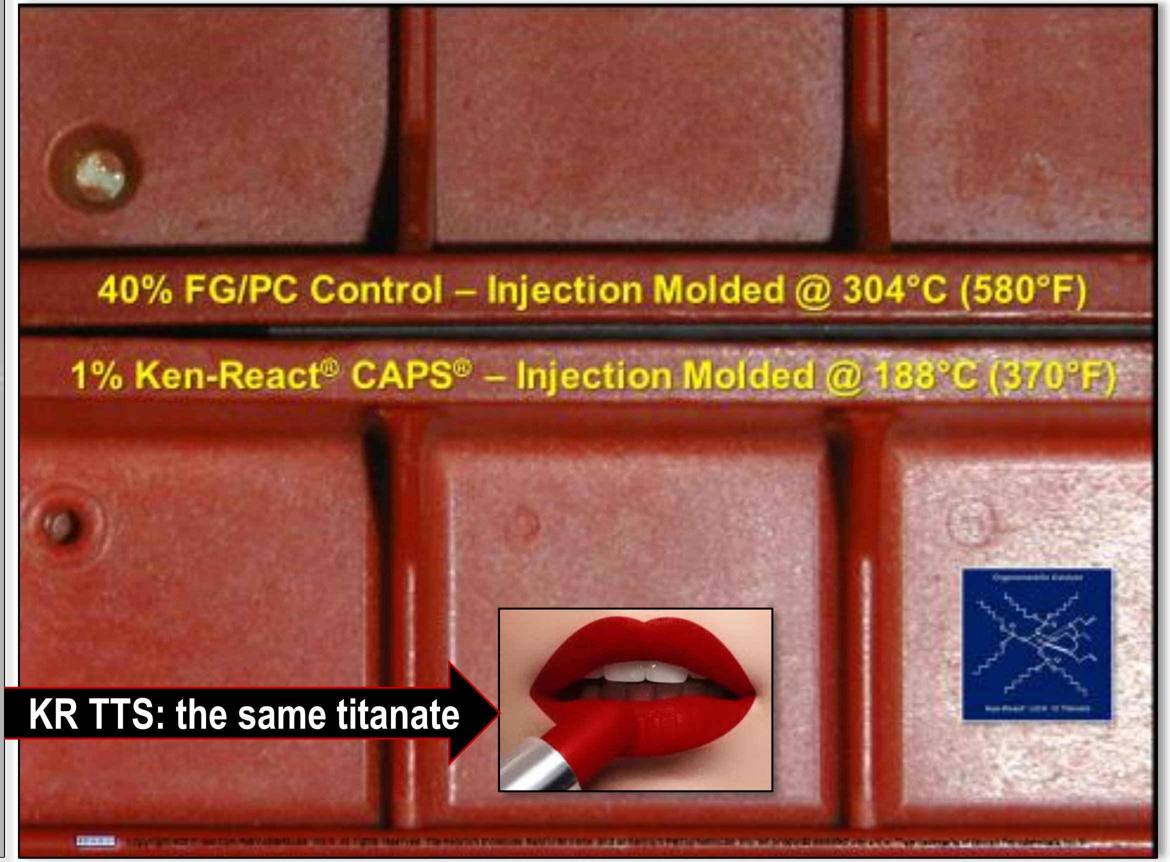




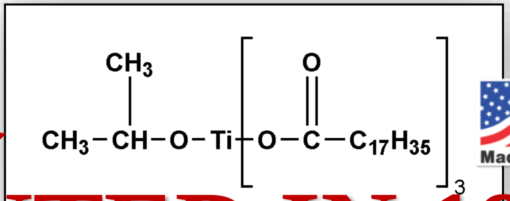
L5 ANSWER 152 OF 439 CA COPYRIGHT 2016 ACS on STN
AN 163:386826 CA Full-text <<LOGINID::20160920>>

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

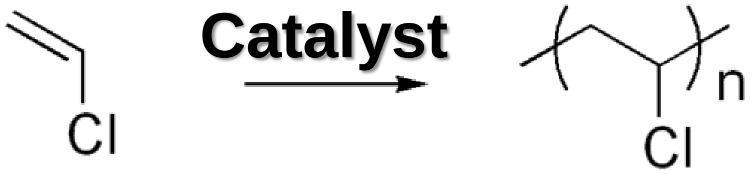
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	CN 104861353	A	20150826	CN 2014-10838685	20141230
PRAI	CN 2014-10838685		20141230		



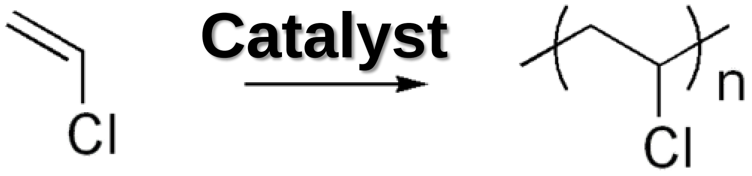
INVENTED IN 1973

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.**

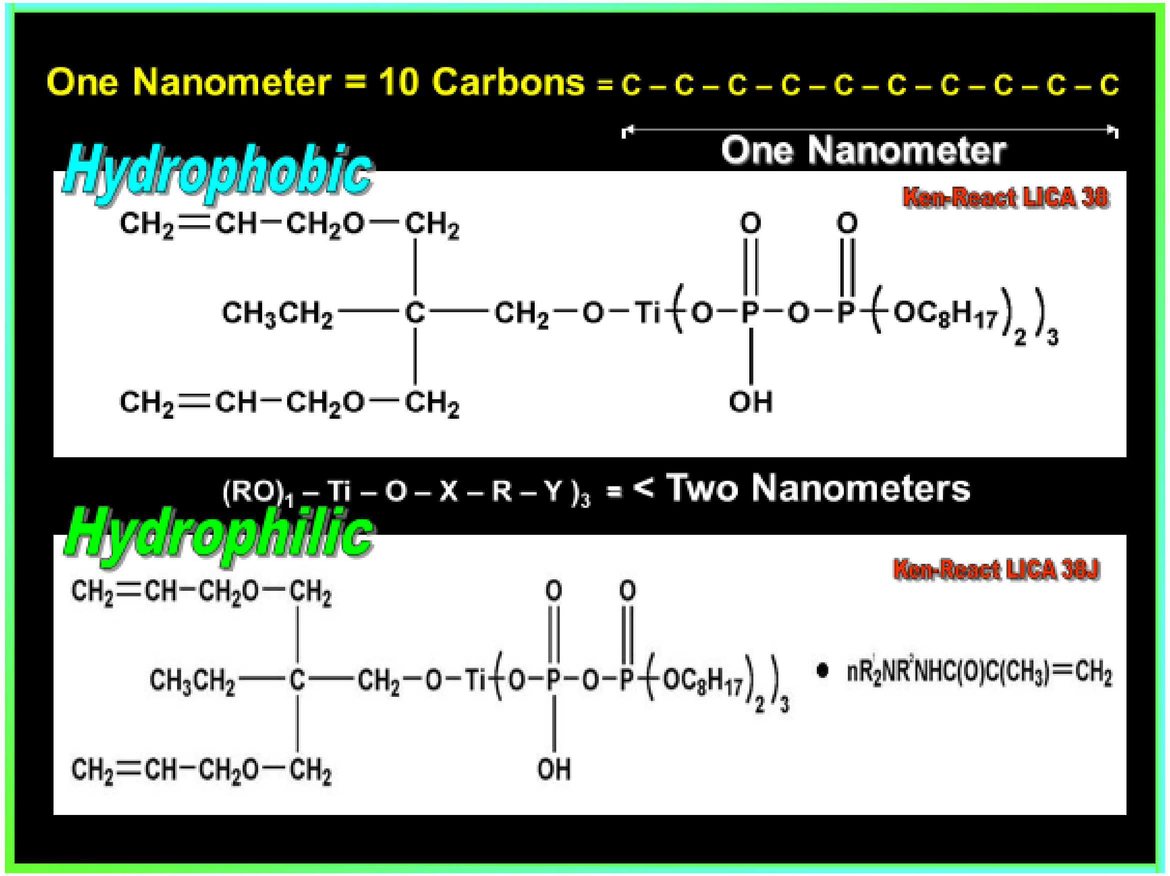
IT 61417-49-0, Iso-propyl triisostearoyl titanate, KR TTS
RL: MOA (Modifier or additive use); USES (Uses)
(flame-retardant anti-aging polyvinyl chloride-polyethylene blended composite plastic)

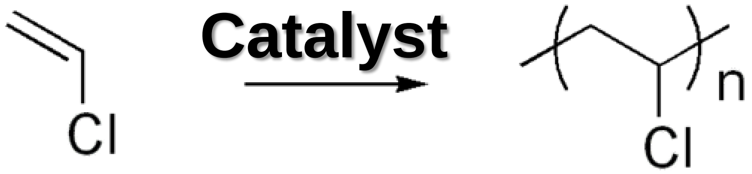


PVC can be: Polymerized, Co-Polymerized, Re-Polymerized or De-Polymerized

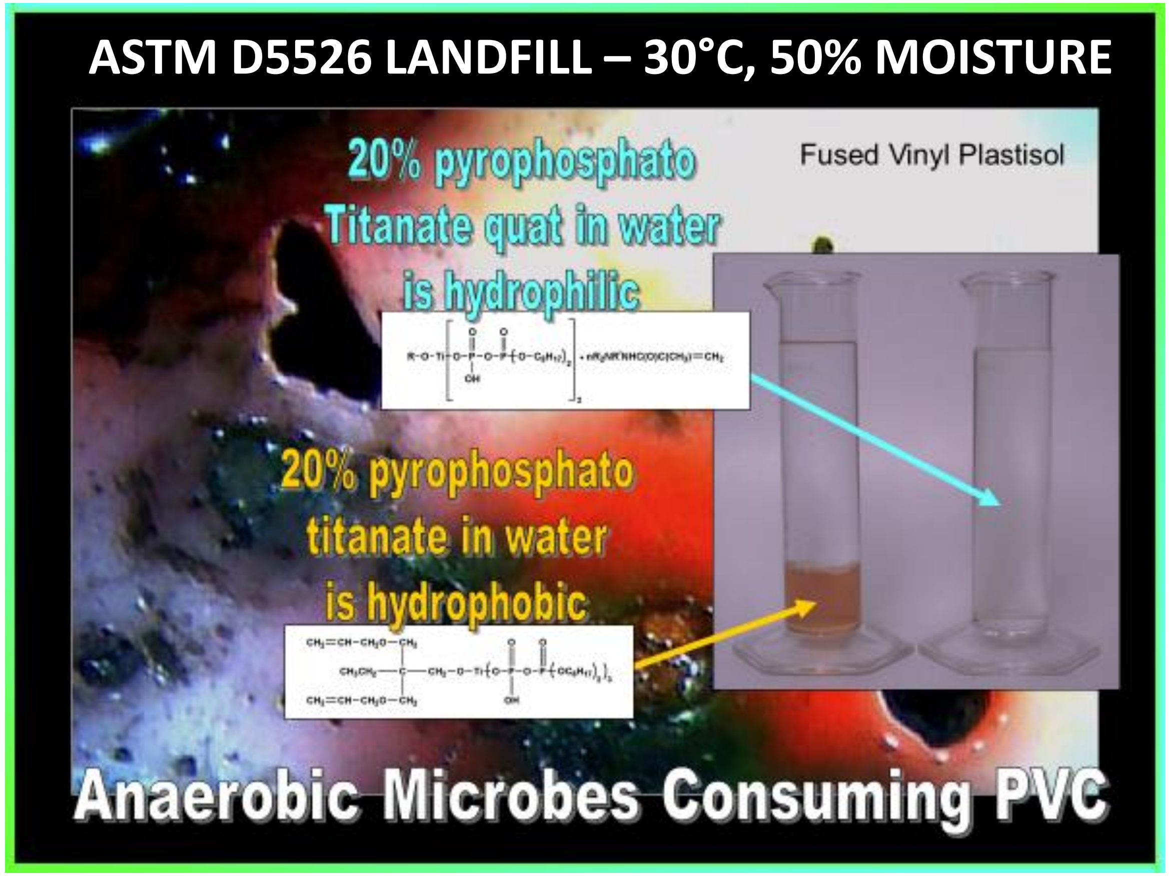


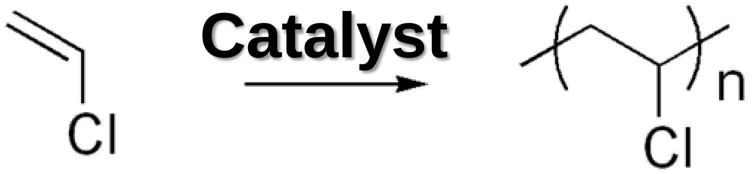
PVC can be: **Polymerized, Co-Polymerized, Re-Polymerized or De-Polymerized**





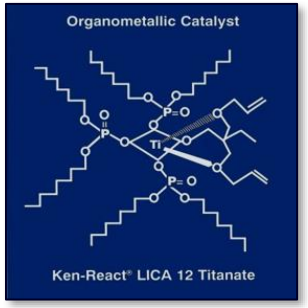
PVC can be: **Polymerized, Co-Polymerized, Re-Polymerized or De-Polymerized**





PVC can be: Polymerized, Co-Polymerized, Re-Polymerized or De-Polymerized

Compatibilization of Addition & Condensation Polymers



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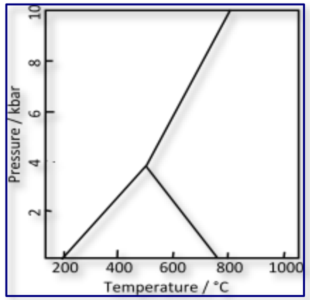

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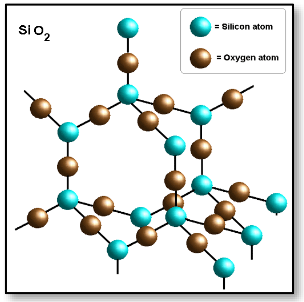

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Ken-React®
CAPS®
KPR® 12/LV

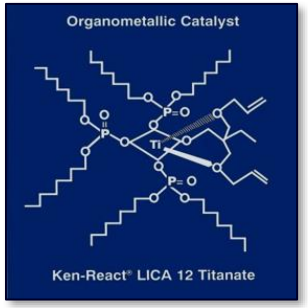
Incompatibility PP & PET & PE

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



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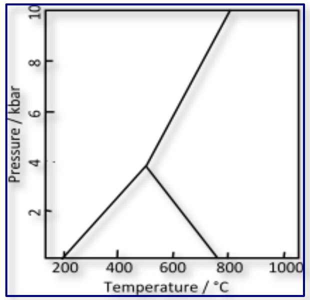

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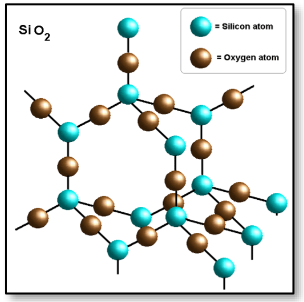

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Ken-React®
CAPS®
KPR® 12/LV

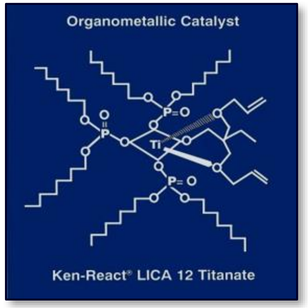
Incompatibility PP & PET & PE

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-<u>industrial waste streams</u>:

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

Compatibilization of Addition & Condensation Polymers



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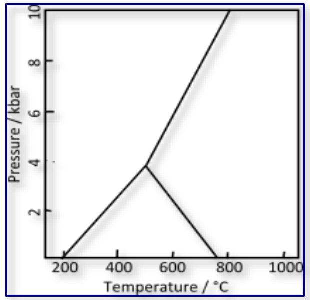

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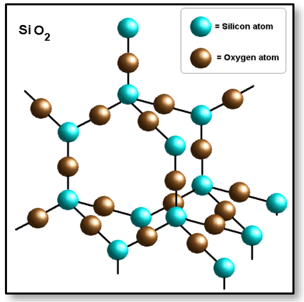

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Ken-React®
CAPS®
KPR® 12/LV

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.

Materials obtained from post-industrial waste streams:

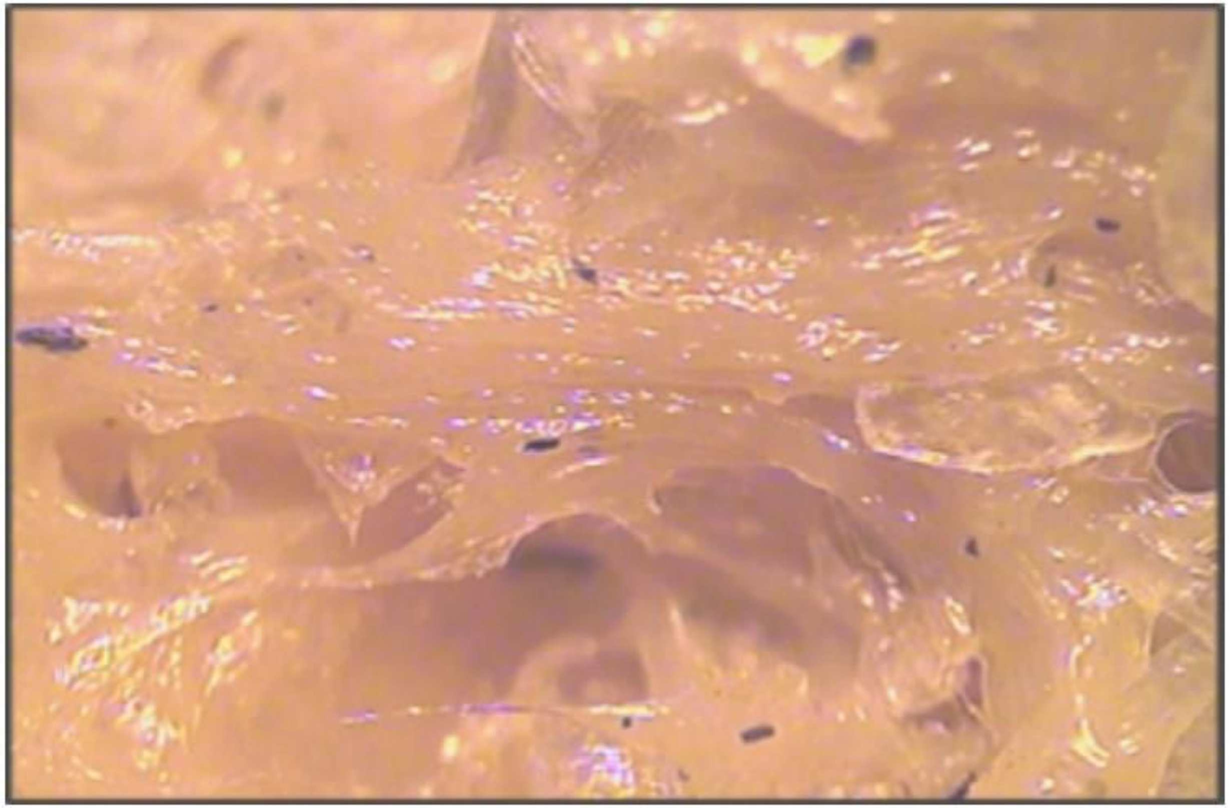
1. **LLDPE from a fractional melt film,**
2. **PP Copolymer from mixed 20-35 MFI injection molded caps,**
3. **PET from thermoformed clamshell food packaging.**

Compatibilization of Addition & Condensation Polymers

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

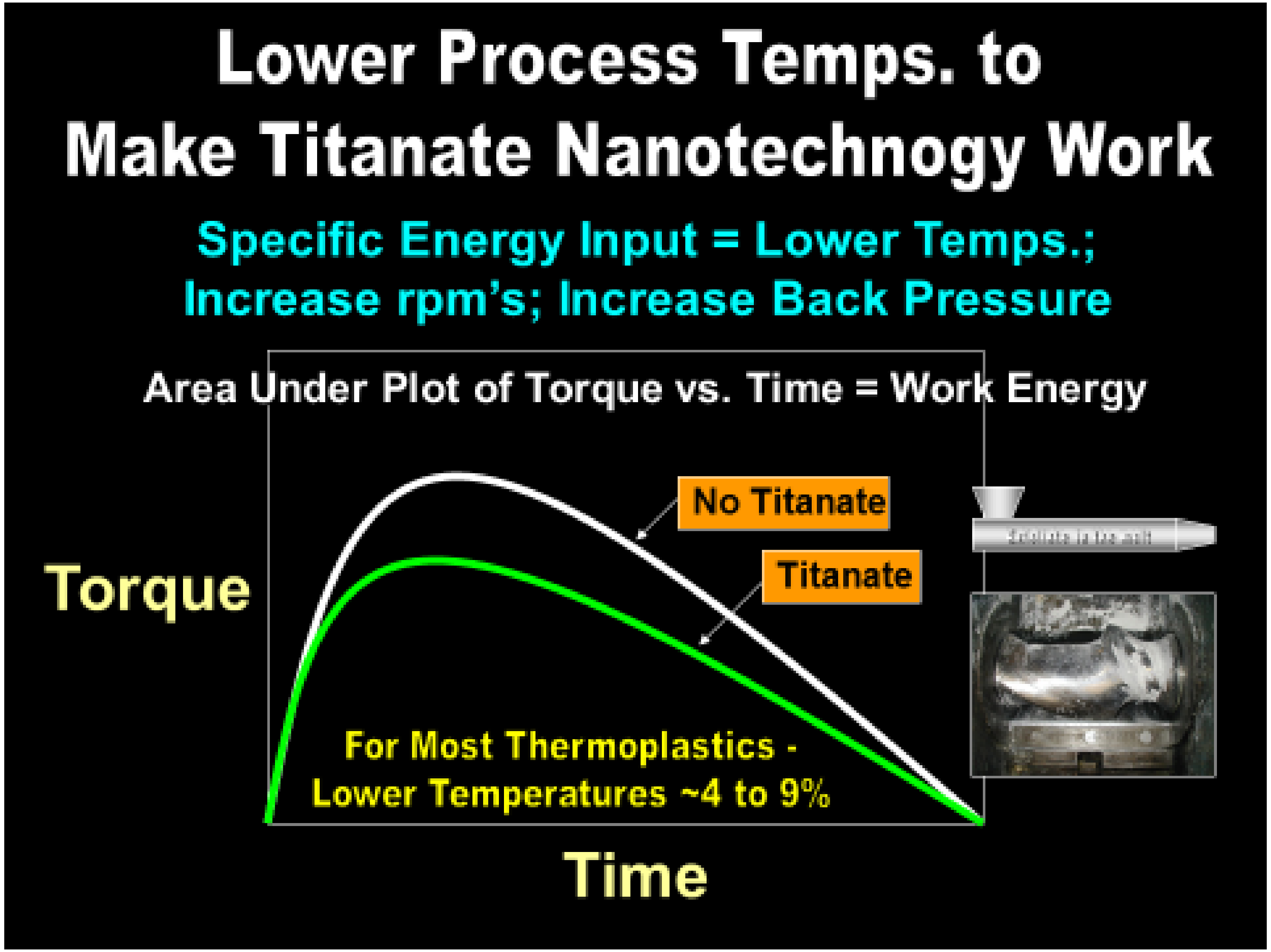
One Nanometer = 10 Carbons = C – C – C – C – C – C – C – C – C – C

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

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

Compatibilization of Addition/Condensation Polymers – Lower Temps.

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



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

University of Waterloo
Chemical Engineering Dept.

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

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?

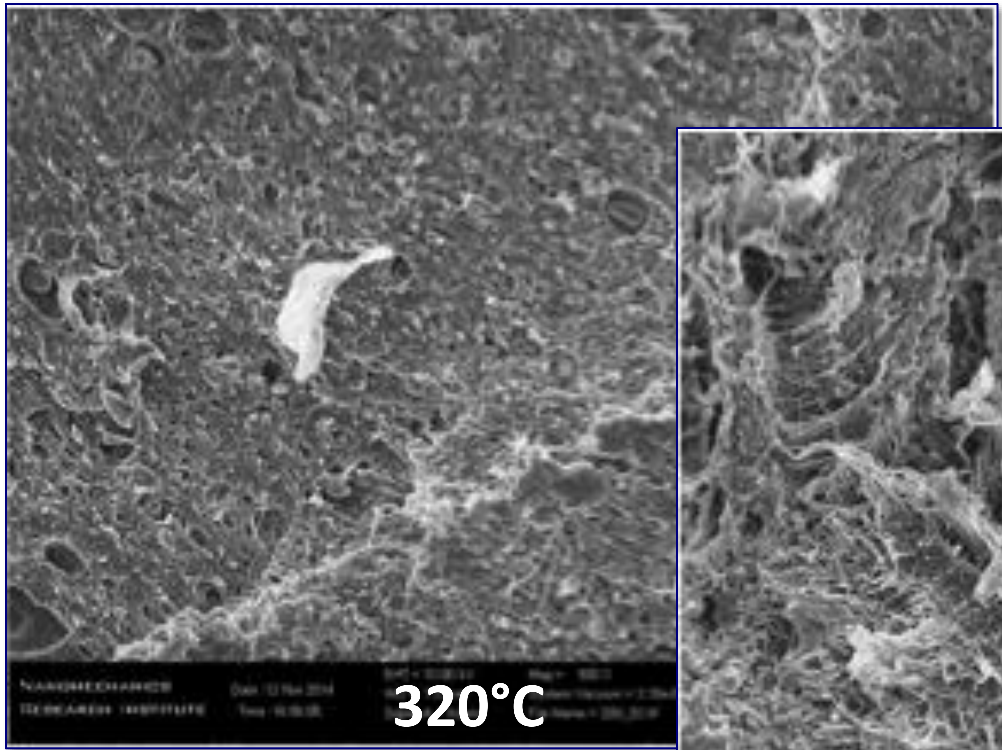
The surface of the extrudate exiting the die became significantly smoother. Upon further analysis with SEM and Izod, it was clear that the increasing the shear dramatically improved the dispersion and physical properties of the compound.

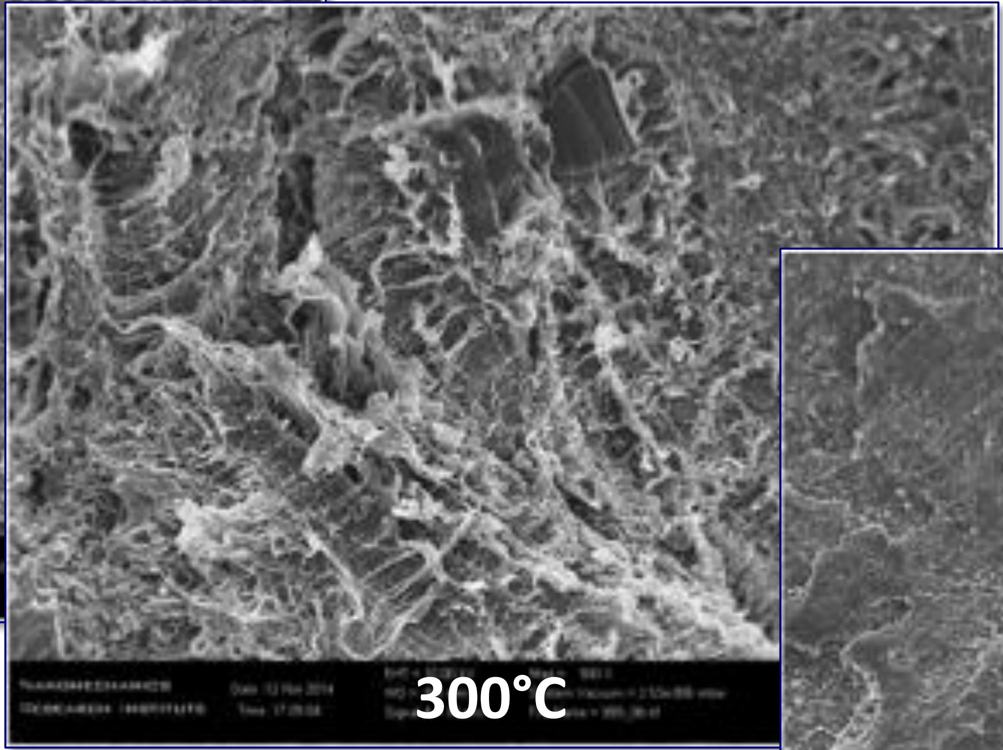
Compatibilization of Addition & Condensation Polymers

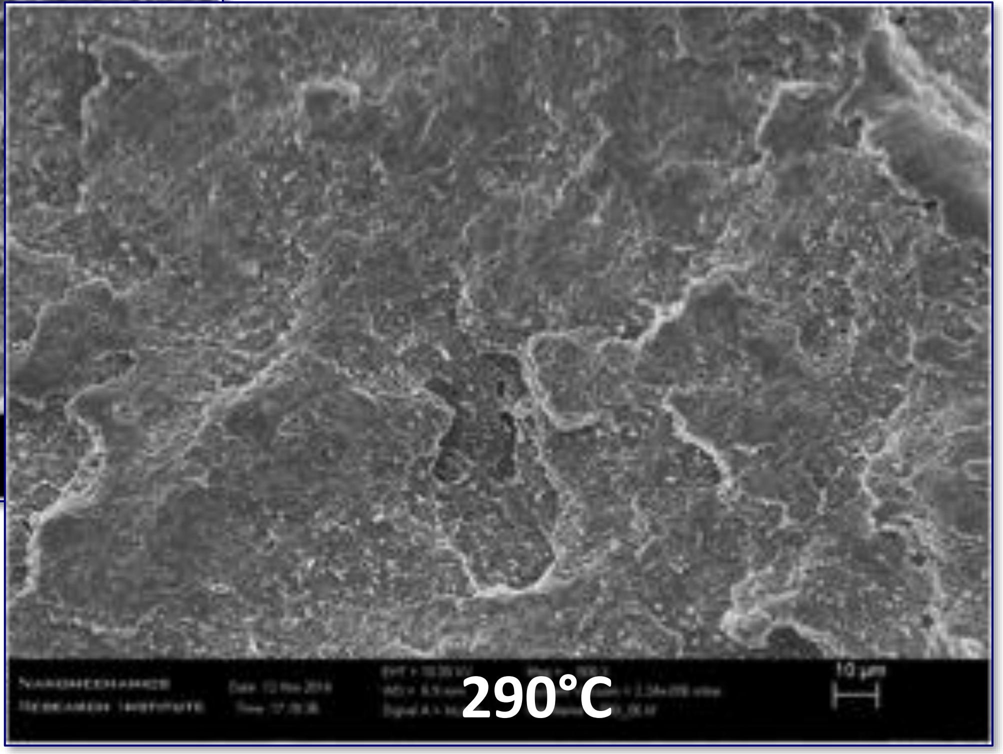
LOWERING THE PROCESS TEMPERATURE FOR REACTIVE COMPOUNDING SHEAR IS CRITICAL

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

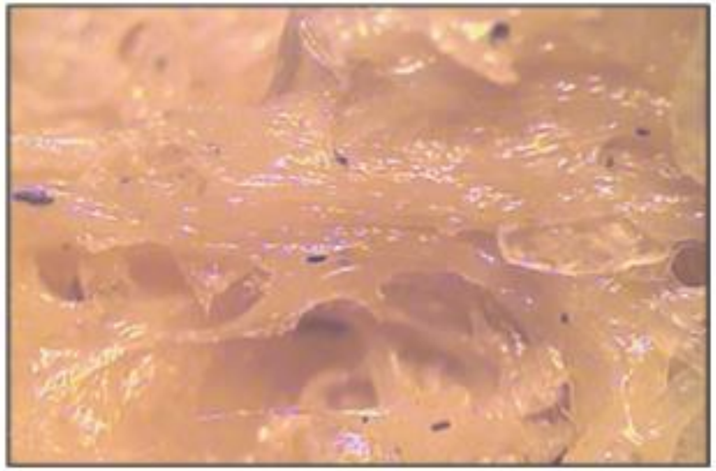
We have shown In Situ Macromolecule Titanate/Al (KPR®) Coupling & Catalysis is a significant strategic approach to reach VINYL RECYCLING sustainability goals.

Compatibilization of Addition & Condensation Polymers

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

Incompatible PP/PET/PE—

No Additive

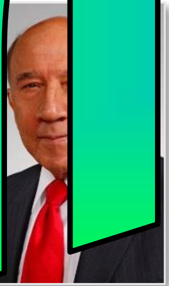


Compatibilized PP/PET/PE—

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

Thank You

Advanced Solu s i nyl Recy ing n Tita C a st upling A ents



J onte – Kenrich Petrochemicals, Inc.

July 20, 2021 – 2:00-4:00pm

sjmonte@4kenrich.com

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

www.4kenrich.com

The End

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