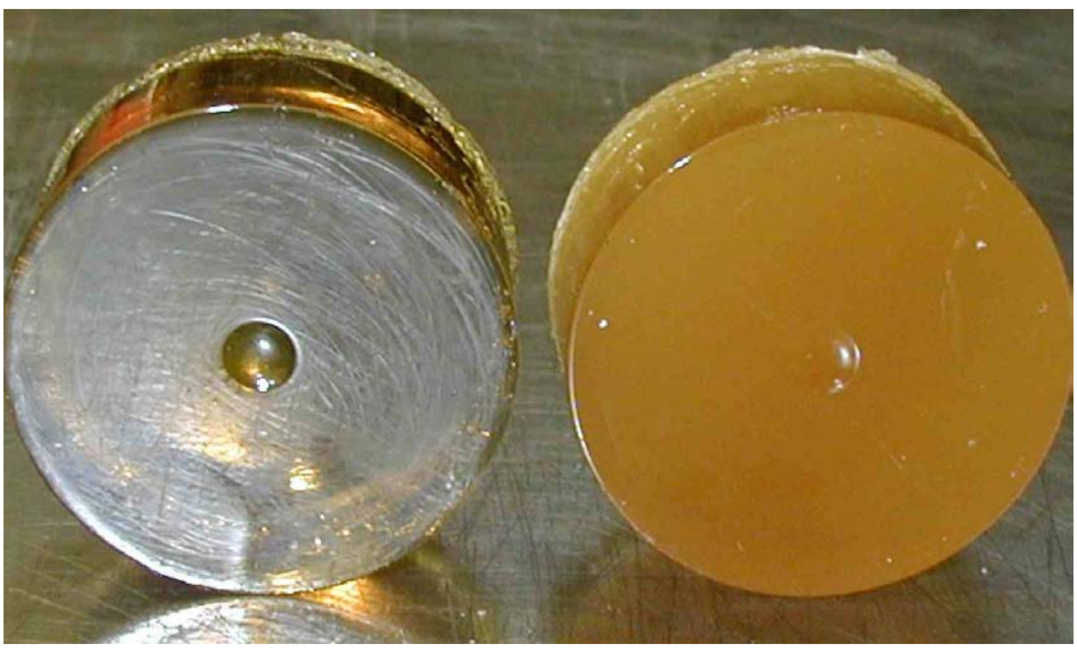
Ken-React® CP-03

Titanate
Coupling Agent
for
Cast Polyester

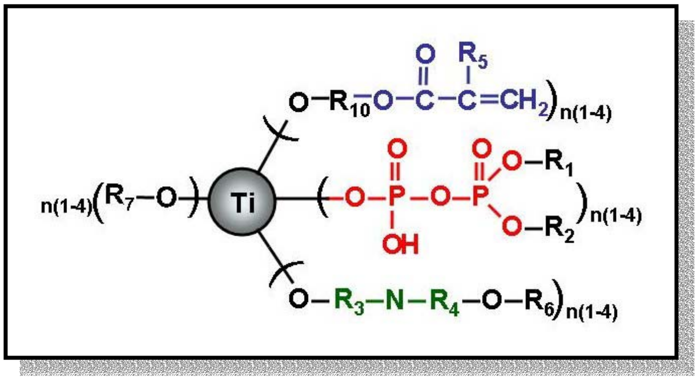


Cast Polyester with Ken-React® CP-03 (left) and without (right)

KENRICH
PETROCHEMICALS, INC.
140 East 22nd Street · 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

Ken-React® CP-03

Product Data Sheet



Ken-React® CP-03 – A Proprietary Mixture of Titanate Coupling Agents Having Phosphato, Amino, and Acrylic Multifunctionality

TYPICAL PROPERTIES:

Physical Form	**Liquid**
Solids (in IPA Solvent), %	**96+**
Color – Descriptive	**Reddish Brown**
Gardner	**16**
Viscosity, cps @ 25ºC (77ºF)	**650**
Specific Gravity @ 16ºC (60ºF)	**1.07**
Flash Point, ºF (TCC)	**120**
pH (saturated solution)	**8**
Solubility	**Soluble in unsaturated polyester, DOP, and IPA. Partially soluble in xylene and toluene. Insoluble in Mineral Oil and H_2O. May be made water soluble via emulsification using surfactants such as sodium dodecylbenzene-sulfonate (anionic), ethoxylated nonyl phenol (non-anionic) or cetyl trimethyl ammonium chloride (cationic).**

All components of Ken-React® CP-03 are US EPA TSCA and EC EINECS registered.

KENRICH PETROCHEMICALS, INC.
140 East 22nd Street · 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

Ken-React® CP-03 Titanate is a specially formulated liquid titanium ester mixture having phosphato/amino/acrylic multifunctionality that:

- Eliminates air bubbles.
- Provides unparalleled surface smoothness.
- Increases thermal shock resistance.
- Lowers viscosity.
- Reduces mold fill time.
- Increases physicals.
- Increases impact strength.
- Enhances flame retardance.
- Wets completely reinforcing fibers, pigments and fillers.
- Eliminates filler filtration, fiber wash and mat fiber deformation.
- Increases stain resistance.
- Increases scratch resistance.
- Increases color stability.
- Resists deterioration of aged properties under salt/water boil.
- Stops aged cracking.
- Increases mold definition.

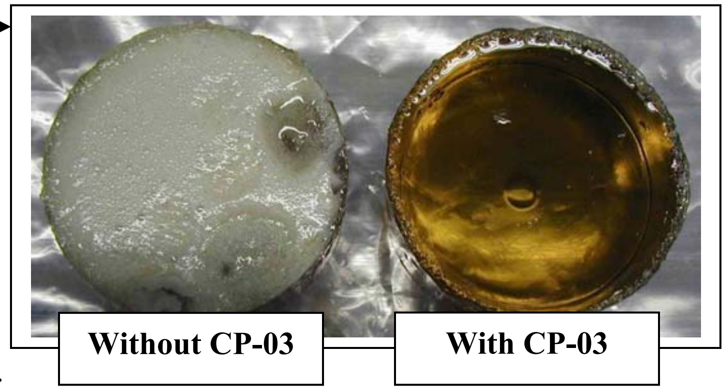


Figure 1 – Drop Impact of Polyester Castings (2¼" x ¼" discs) from 6' Height – Ashland Polaris® MR 20000 SHV Polyester Resin (98.75 parts) cured with Norox® MEKP-925 (1.25 parts) and no Ken-React [left disc] and with Ken-React CP-03 (0.375 parts) [right disc]. The control disc was dropped once and shattered. The Ken-React CP-03 disc bounced on the 1st drop and broke on the 2nd drop.

Patented titanium chemistry provides multifunctional additive benefits
Ken-React CP-03 acts as a “coupling agent” to make fillers hydrophobic and organophilic by forming atomic titanium phosphato/amino/acrylic functional monolayers on the fiber, pigment or filler surface. Particulate and fiber air voids are eliminated and total deagglomeration and complete wetting of the filler, pigment and fiber occurs.

Ken-React CP-03 acts as an “amino” functional adhesion promoter.

Ken-React CP-03 acts as an “acrylic” functional monomer to increase crosslinking.

Ken-React CP-03 acts as a “titanium” catalyst thereby “Repolymerizing” (patented) the polyester to make it stronger by increasing strain strength – important to impact toughness.

Ken-React CP-03 acts as a “phosphatizing” flame retardant synergist.

Coupling, deagglomeration, dispersion and viscosity reduction – The addition of 0.7% Ken-React CP-03 titanate (by weight of $CaCO_3$ or any other filler of fiber) to the liquid polymer phase followed by $CaCO_3$ addition results in electrochemical $CaCO_3$ deagglomeration that no amount of mechanical dispersion can achieve. Unlike silanes, Ken-React CP-03 reacts directly with the filler or fiber surface via proton coordination and needs no hydroxyl groups or water of condensation to achieve atomic monolayer coupling (see Figure 2) and viscosity reduction (see Table 1). CP-03 viscosity effects begin to differentiate from control formulations in the 60 to 75% filler loading range. *Pretreated* filler gives somewhat better results than *in situ* treatment.

Similar coupling, catalysis and intumescent (with pyrophosphato titanates) effects on ATH, $Mg(OH)_2$, glass, graphite and aramid fibers, titanium, zinc and iron oxides, and all manner of inorganic/organic filled thermoplastics and thermosets are noted in the literature. See References 1 to 70 for some of the 1600^+ references on the use of Ken-React’s by others and 355 references on patents, tech papers, journal articles and book chapters attributed to Kenrich Petrochemicals, Inc.

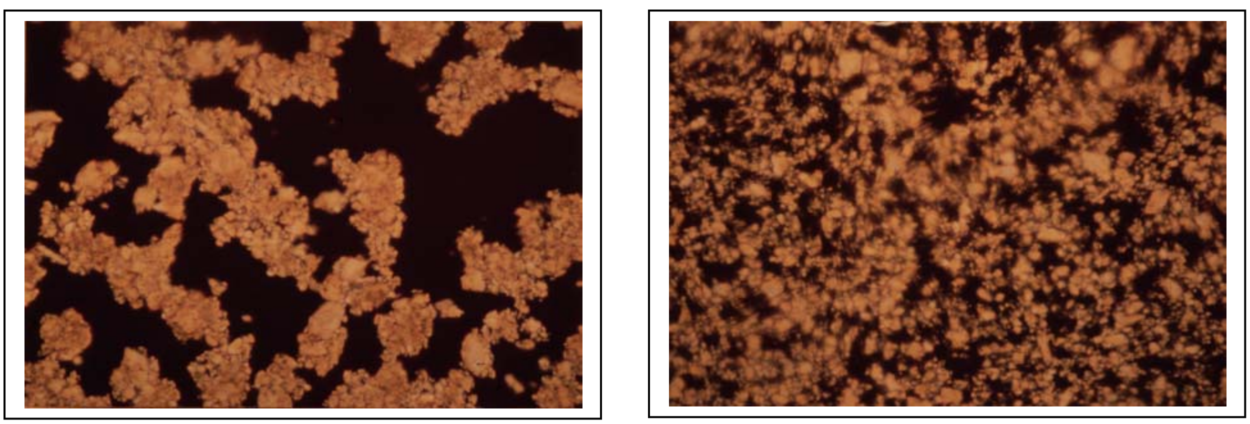


Figure 2 – The SEM on the left is $CaCO_3$ dispersed mechanically in a non-polar vehicle without Ken-React. The SEM on the right is the same $CaCO_3$ dispersed electrochemically in a non-polar vehicle to which had been added a Ken-React titanate prior to addition of the $CaCO_3$.

Table 1 – The viscosity reduction effect of Ken-React CP-03 at 0.7% by weight of varying amounts of $CaCO_3$ in cast polyester resin – In Situ and Pretreated.

Polyester MR 20000 SHV (Ashland)	$CaCO_3$ (OMYA 3)	No Additive - Brookfield Viscosity, cps @ 25°C	0.7% Additive Ken-React CP-03 In Situ[a]	With Additive - Brookfield Viscosity, cps @ 25°C	$CaCO_3$ OMYA 3 – Pretreated[b] with 0.7% Additive Ken-React CP-03	Brookfield Viscosity, cps @ 25°C
25	75	4,800,000	0.525	4,000,000	75	3,600,000
30	70	576,000	0.490	544,000	70	384,000
35	65	160,000	0.455	144,000	65	112,000
40	60	80,000	0.420	67,200	60	57,600
50	50	22,400	0.350	22,400	50	22,400
60	40	12,800	0.280	12,800	40	12,800
70	30	8,000	0.210	8,000	30	8,000
80	20	6,400	0.160	6,400	20	6,400

a) In Situ: The Ken-React CP-03 dosage was calculated at 0.7% by weight of the anticipated % loading of $CaCO_3$. The CP-03 was dispersed into the Ashland Polaris® MR 20000 SHV Polyester Resin followed immediately by addition and drill mix dispersion of the OMYA 3 (3-micron) $CaCO_3$. MEKP withheld for measurements.

b) Pretreated: Ken-React CP-03 was added to the $CaCO_3$ dropwise over a one-minute period to a fluidized bed of the $CaCO_3$ using a Henschel mixer operating at low speed (1800 rpm) followed by a post-mix for one-minute and then discharged for later addition to the liquid polyester resin.

Complete Wetting of Glass Fiber – Figure 3 shows the complete wetting effect of a pyrophosphato titanate having similar pyrophosphato chemistry as is incorporated into Ken-React CP-03. Note the titanate wets the fiberglass so completely that the fiber seems to "disappear". This because there are no air voids at the FG/polyester interface.

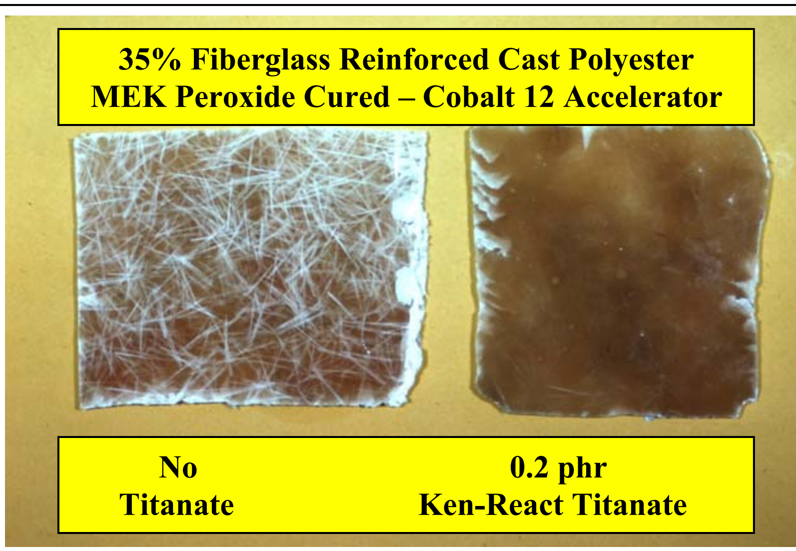


Figure 3 – The cast polyester (left) has un-wetted silane-sized fiberglass and no titanate. The same casting (right) containing pyrophosphato titanate shows a smooth surface with no fibers showing due to complete coupling & wetting.

Complete Wetting of Glass Fiber (continued)

As a result, cast polyester composites using Ken-React CP-03 titanate can have more filler, lower viscosity and can be up to four to eight times stronger and seventeen times better on drop impact than controls without the additive. Cast polyester problems such as filler filtration, surface finish, part definition, fiber mat deformation, fiber wash, pigment dispersion, mold fill time and final part gloss are diminished significantly. Laser surface profilometry data shows CP-03 imparts a class "A" automotive finish to filled and fiber reinforced polyester composites.

The effect is not limited to just cast polyester and applies to other thermoset and thermoplastic resins such as epoxy, vinyl ester, urethanes and elastomers. For example, Figure 4 shows similar effects in fiberglass/epoxy. See References 1 and 2 for complete data.

Figure 4 – The silane-sized fiberglass wound epoxy pipe on the left without titanate shows fiberglass while the pipe with 0.2 phr Ken-React added to the resin with the same fiberglass cause complete wet-out and "disappearance" of the fiber with a subsequent significant increase in resistance to hydrostatic pressure.

Surface Smoothness of RTM Molded W/R-$CaCO_3$ filled Polyester Using Benzoyl Peroxide Comparing Ken-React CP-03 to BYK-W 995 – Ken-React CP-03 was added to unsaturated polyester resin (proprietary gel coat type - Rheichhold) at 0.5% by weight of $CaCO_3$, while the BYK-W 995 was added at the recommended 1.25% by weight for this type of silicone-based additive. $CaCO_3$ was filled to 38% and 55% by weight of polyester resin. The compounds were RTM molded using Woven Roving glass mat having a surface area equal to 567 g/m^2 (38% volume). The conditions for injection molding are shown in the Table 2. Tests show CP-03 to injection mold two to four times faster than BYK-W 995 with surface smoothness to be generally superior as determined by laser surface profileometry.

Surface Smoothness (continued)

Table 2 – Surface Smoothness of RTM Molded W/R-$CaCO_3$ filled Polyester Using Benzoyl Peroxide Comparing Ken-React CP-03 to BYK-W 995 Via Laser Surface Profilemetry

FORMULATION	
Unsaturated Polyester (Rheichhold)	100
$CaCO_3$	As Shown
Ken-React CP-03, 0.5% by weight of $CaCO_3$	As Shown
BYK-W 995, 1.25% by weight of $CaCO_3$	As Shown
Woven Roving Glass Mat (567 g/m^2)	38% Resin Volume
Benzoyl Peroxide Curative (Atofina)	3
Cobalt Octoate Accelerator (1% in Styrene - CCP)*	3

RESULTS

Additive	**RTM Injection Time, Min:Sec @ 3.8 bar**	**RTM Injection Temp. (°F)**	**Filler Content % by Weight of Resin**	**Filler Filtration**	**Surface Roughness (µm) as Measured by Laser Profilemetry[a]**
CP-03	1:52	120	38	Low	9.5
CP-03	1:19	140	38	Low	9.5
CP-03	2:32	120	55	Low	0.2
CP-03	1:00	140	55	Low	1.6
W 995	2:32	120	38	High	13.5
W 995	2:17	140	38	High	12.0
W 995	5:23	120	55	High	1.9
W 995	4:09	140	55	High	1.1

Note a): Profilemetry Measurement Ratings

Surface Roughness (µm)	**Surface Finish Rating**
≤1	Very good
≥1-3	Good
≥3-10	Average
≥10-13	Below Average
≥13	Poor

* According to BYK-Chemie's website:
http://www.byk-chemie.com/gbn/frame.cfm?idx=21
"BYK-W 995 is a wetting and dispersing additive for molding compounds such as SMC and BMC. It is recommended to use BYK-W 995 for filler dispersion to reduce viscosity in LP- and LS-systems. BYK-W 995 cannot be used in cobalt accelerated resins! BYK-W 995 is often used in amine accelerated cont. laminating processes to lower viscosity, allowing more efficient production and/or higher filler loading."

A Stronger Cure with Fewer Bubbles and Surface Pinholes – Some investigators speculate that the higher modulus and impact strength (see Figure 1) using CP-03 comes from the catalytic effect of *Titanium* on slowing the rate of cure, which is different from the rapid cure and exotherm caused by conventional cast polyester cures without *Titanium*. In unfilled systems, it is apparent that while conventional MEKP cures occur in 40-minutes with peak exotherms of 282ºF (138ºC) – the rapid cure creates aeration bubbles in the cured part. On the other hand, Ken-React CP-03 flows into the mold faster but generates less heat over its ~7-hour cure period. In fact, during the first five-and-a-half hours, there is little or no exotherm with CP-03. Then the temperature of cure rises slowly from 77ºF (25ºC) to 90ºF (32ºC) at the six hours, then rises to 94ºF (34ºC) in the next half hour, then to 96ºF (35.5ºC) in the next half hour (hour 7) where it peeks and then begins to cool down. The result is a clear, aeration free composite with superior gloss and clarity and much greater strength than the control (see Figure 5).

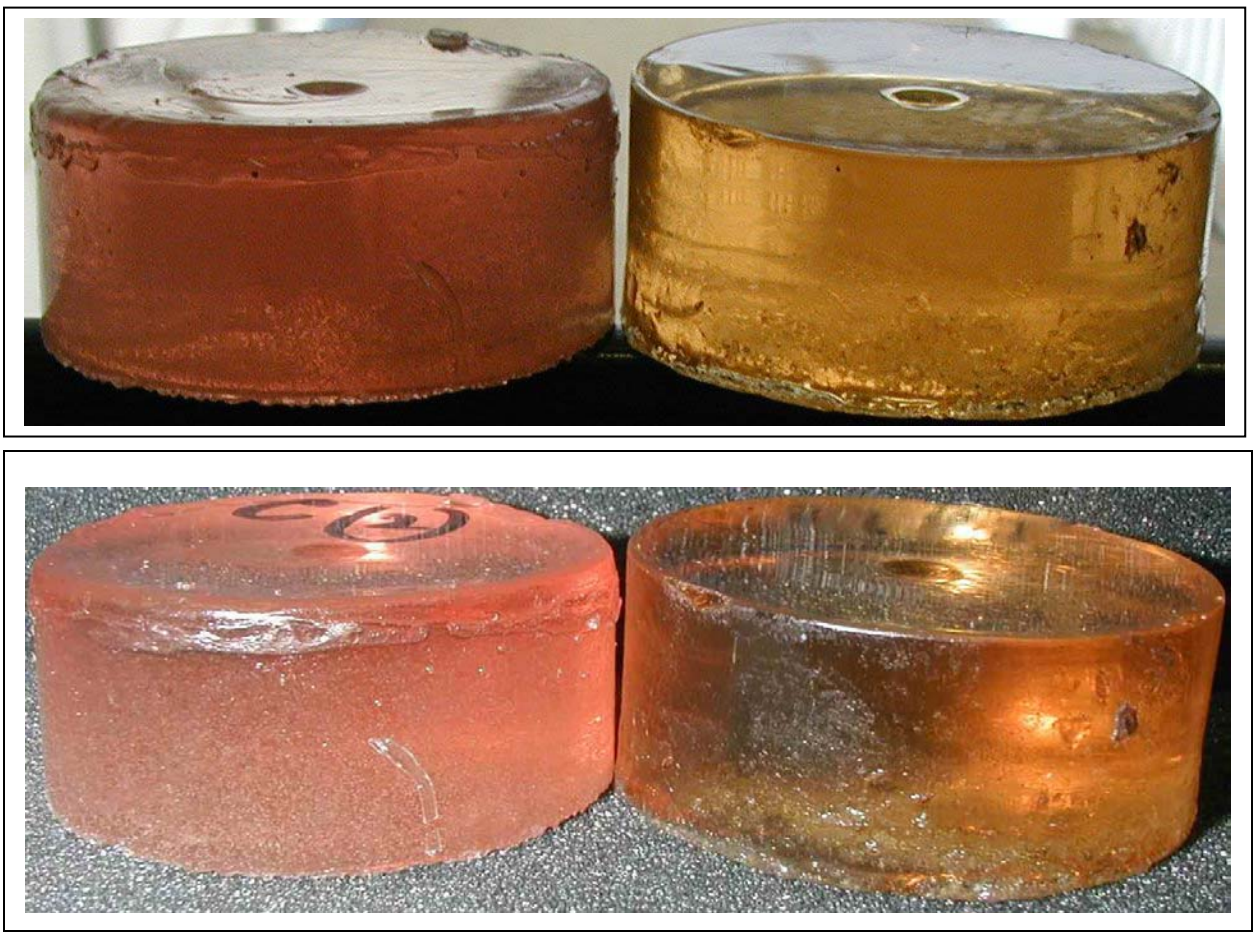


Figure 5 – Polyester Castings (2¼" x 1" discs) – Top Photo with sun light background and Bottom Photo with black foam background. Discs cast with Ashland Polaris® MR 20000 SHV Polyester Resin (98.75 parts) cured with Norox® MEKP-925 (1.25 parts) and no Ken-React [left disc] and with Ken-React CP-03 (0.375 parts) [right disc]. The control disc shows dullness (left-top) and aeration bubbles (left bottom) caused by cure exotherm [282ºF (138ºC)] while the CP-03 disc (right-top) is free of bubbles and has sharper part definition. The control disc (left-bottom) is pink and translucent and cured in 40-minutes while the CP-03 disc (right-bottom) is light tan and transparent and cured in 7-hours with 66% less exotherm.

Shortening the CP-03 Cure Time Using Cobalt, Heat or More Peroxide – Table 3 shows the Ken-React CP-03 formulations can have their cure times shortened by using heat – and to a lesser amount by increasing the peroxide dosage. The 7-hour cure time of the CP-03 formulation can be reduced to the control 50-minute cure time if heated to ~110ºF to125ºF. As can be seen in Table 4, the addition of 0.4 parts of 6% Cobalt Naphthenate reduces the cure time to about 45-minutes vs. 50-minutes for the control, but the 6% Cobalt Naphthenate increases the heat of exotherm and subsequent bubble formation while turning the polyester composite from bright amber to deep purple. Table 4 also shows similar effects with 60% $CaCO_3$ filler.

Table 3 – Effect of MEK Peroxide Amount and Cure Temperature On Polyester Cure Time

	Amount – In Order of Increasing MEKP-925				
Ingredients	**Increase Heat**		**Increase MEK Peroxide →**		
Polyester Resin[a]	98.750	98.750	98.750	98.750	98.750
Ken-React KR CP-03[b]	-	1.086	1.086	1.086	1.086
MEKP-925[c]	1.25	1.250	1.875	2.500	2.500
Cure Time, minutes:hours – In Order of Increasing Temperature ↓					
25ºC (77ºF)	0:50	7:00	2:50	2:41	2:10
38ºC (100ºF)	0:22[d]	1:04[e]	-	-	-
66ºC (150ºF)	-	0:16[f]	-	-	-

Notes:

a) Polyester Resin = Ashland Polaris® MR 20000 SHV Polyester Resin.
b) Ken-React KR CP-03 = 1.1% by weight of Polyester Resin.
c) Norox® MEKP-925
d) 18-min halfway cure – breakdown. 22-min. complete cure – color change to purplish – 45 minutes later color back to normal.
e) Complete cure 1:04 – color change to purple.
f) Color change to purple to green.

Table 4 – Effect of Varying Amounts of 6% Cobalt Naphthenate on Polyester Cure Time

	Amounts							
Ingredients	**Unfilled**					**Filled**		
Polyester Resin[a]	98.750	98.750	98.750	98.750	98.750	40	40	40
Ken-React CP-03	-	1.086	1.086	1.086	1.086	0.42	0.42	0.42
3μ-$CaCO_3$	-	-	-	-	-	60	60	60
6% Co Naphthenate[b]	-	-	0.20	0.30	0.40	-	-	0.4
MEKP-925[a]	1.250	1.250	1.250	1.250	1.250	1.250	1.250	1.250
Cure Time, minutes:hours								
25ºC (77ºF)	0:45	7:00	1:20[c]	1:15	0:45	0:50	7:00	0:50

Notes:

a) Polyester and MEKP-925 the same as Table 3.
b) 6% Cobalt Naphthenate = The Shepherd Chemical Company.
c) All cobalt containing composites turn a deep purple.

The Effect of Cobalt on CP-03 Cast Polyester Clarity – Figure 6 shows the negative effect of 0.4 parts of 6% cobalt naphthenate accelerator on cast polyester appearance.

A

B

C

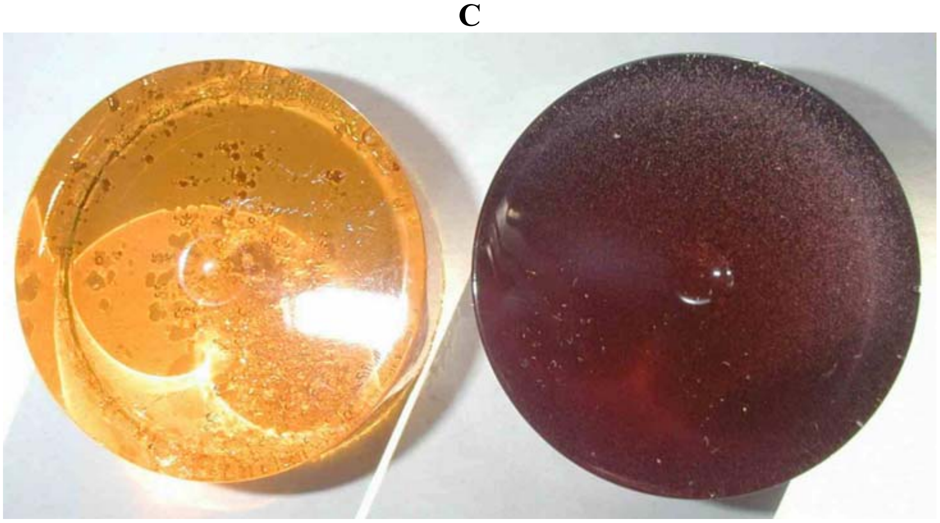


Figure 6 – Photo A is a side view of clear cast polyester containing CP-03. Photo B is top view of the "bubble side up" of cast polyester with CP-03 alone (left) and with CP-03 and Cobalt (right) as per Table 4. Photo C is top view of the same casting "bubble side down".

Pinhole Elimination – Figure 7 shows that CP-03 eliminates pinholes in cast polyester.

Figure 7 – Photos [(upper-left = top-side of poured in mold) and (upper-right = bottom-side of poured in mold)] show the results of the cast polyester formulations in Table 4 for Unfilled (Casting 1 = Control; Casting 2 = CP-03; and Casting 3 = CP-03 + 0.4 parts of 6% Co Naphthenate) and 60% $CaCO_3$ Filled (Casting 6 = Control; Casting 5 = CP-03; and Casting 4 = CP-03 + 0.4 parts of 6% Co Naphthenate). The larger lower photo is a close-up of the bottom-side of castings 6 (left – Control with pinholes) and 5 (right – CP-03 without pinholes) demonstrating the use of CP-03 eliminates pinholes.

Ken-React CP-03 Evolution – Ken-React titanates were introduced commercially in 1974. Ken-React CP-03 is the result of years of testing various zirconates and other titanates to obtain $CaCO_3$ viscosity reduction in polyester while providing superior cast polyester part smoothness and strength. Table 5 demonstrates the superior viscosity reduction effects of CP-03 over the other Ken-React Zirconates tested. Also, although zirconates such as Ken-React NZ 33 will reduce viscosity and the cure time vs. CP-03 for a 60% $CaCO_3$ polyester from ~5-hours to 2.5-hours, the resultant composite is not bubble free and exhibits higher exotherm during the cure.

Table 5 – Effect of 0.5% by weight of filler of Various Titanates and Zirconates In Situ on 3µ-$CaCO_3$ 70% Filled Polyester Viscosity

Ken-React Item	Polyester MR 20000 SHV	$CaCO_3$ OMYA 3	KR Amount % by weight of Filler	Brookfield Viscosity, cps @ 25°C
Control	30	70	0.0	888,000
NZ 33	30	70	0.5	592,000
KZ TPP	30	70	0.5	528,000
NZ 38J	30	70	0.5	624,000
KZ 55	30	70	0.5	640,000
CP-03	30	70	0.5	416,000

Recommended Ken-React CP-03 Dosage – Tables 6 and 7 show a ladder study of increasing CP-03 dosage – *in situ* and *pretreated*. A dosage of 0.7 % Ken-React CP-03 by weight of 3µ-$CaCO_3$ is about the right balance of viscosity reduction and subsequent length of cure times.

Table 6 – Effect of Varying Amounts of Ken-React CP-03 *In Situ* on 3µ-$CaCO_3$ 70% Filled Polyester Viscosity

Item	Polyester MR 20000 SHV	$CaCO_3$ OMYA 3	KR Amount % by weight of Filler	Brookfield Viscosity, cps @ 25°C
Control	30	70	0.0	560,000
CP-03	30	70	0.25	432,000
CP-03	30	70	0.50	288,000
CP-03	30	70	0.75	272,000
CP-03	30	70	1.0	256,000

Table 7 – Effect of Various Levels of Ken-React CP-03 Henschel *Pretreatment* of 3µ-CaCO on 60% Filled Polyester Viscosity and MEKP Cure Time

Ingredients	Polyester MR 20000 SHV	3µ-$CaCO_3$	% CP-03 Pretreat.	MEKP	Viscosity, Cps	Cure Time Hr:Min
Control	40	60	-	1.25	576,000	0:45
CP-03	40	60	0.35	1.25	384,000	3:50
CP-03	40	60	0.70	1.25	384,000	4:50

Amino and Pyrophosphato Ken-React Organometallic Adhesion to Fiberglass in Peroxide Cured Polyester Thermoset Composites – Table 8 shows the adhesion – original and after aging 240 hr. in boiling 10% aqueous salt solution of a long strand of fiberglass embedded in benzoyl peroxide cured polyester and the viscosity and mechanical properties of the corresponding short glass fiber. Note the control tensile strength without coupling agent drops from 42 Joules (J) original to 27 J after aging. While the tensile strength of an aromatic amino zirconate (Ken-React NZ 37) increases original tensile strength from 42 to 62 J – and exhibits only a 6.5% drop-off in tensile to 58 J - compared to the 27 J after aging for the control. In other words, after aging, the aromatic amino zirconate fiberglass reinforced polyester composite interface adhesion property is twice as strong as the control.

Note also, that a pyrophosphato zirconate has a 40% viscosity reduction effect on the short fiber filled polyester. Mechanical properties, heat deflection temperature and notched izod data all point to a stronger polyester composite. The hybrid Ken-React CP-03 product has all of these attributes – plus synergistic pyrophosphato and acrylic functionality benefits.

Table 8 – Evaluation of Various Coupling Agents in Fiberglass Reinforced, Bis t-butylperoxycyclohexane Cured, Polyester (Original/Aged Properties)

Formulation	**Parts by Weight**
Resin, (Stypol 40-1029 – Freeman Chemical)	100
Curatives: Benzoyl peroxide	0.5
bis t-butylperoxycyclohexane	0.5
Short (5 mm) and long fiber (Fiberglass - Certainteed)	40
Additive(s)	as shown

Brookfield Viscosity measured @ 25°C. Cure 20 min. @ 150°C followed by postcure of 2 hr. @ 180°C. Aging 240 hr. in boiling 10% aqueous salt solution.

Additive (PBW)	**Long Fiber**	**Short Fiber Vehicle Only**				
	Tensile Pullout Energy J	Viscosity 0.2 rpm/2 rpm Megapoise	Flexural Modulus gPa	Flexural Strength gPa	HDT 1.18 mPa ° C	N.I. kJ/m
Control	42/27	0.89/0.62	16/11	0.83/0.49	201/169	1.15/0.89
A-1100:0.4	49/41	0.84/0.71	19/14	1.05/0.88	218/194	1.32/0.97
A-174:0.4	50/44	0.82/0.66	18/16	1.06/1.01	217/203	1.28/1.10
NZ 97:0.4	59/56	0.71/0.60	21/17	1.14/1.12	221/216	1.56/1.47
KZ TPP:0.4	46/41	0.53/0.42	17/16	1.03/0.96	206/203	1.72/1.63
KZ 55:0.4	44/43	0.59/0.45	18/16	0.91/0.86	201/200	1.41/1.28
NZ 37:0.4	62/58	0.83/0.71	23/21	1.27/1.19	229/216	1.23/1.09
NZ 37:0.2+ KZ TPP:0.2	59/55	0.54/0.44	24/23	1.34/1.27	242/228	1.29/1.17
NZ 37:0.2+ A-174:0.2	71/69	0.83/0.71	28/26	1.46/1.42	279/257	1.42/1.38

References

[1]. Monte, S.J., Kenrich Petrochemicals, Inc., "Ken-React® Reference Manual - Titanate, Zirconate and Aluminate Coupling Agents", Third Revised Edition, March 1995, 340 pgs.

[2]. Monte, S.J. and Sugerman, G., Kenrich Petrochemicals, Inc.: S.M. Gabayson and W.E. Chitwood, General Dynamics, "Enhanced Bonding of Fiber Reinforcements to Thermoset Resins", 33rd International SAMPE Symposium, Anaheim, CA, March 7-10, 1988.

[3]. Monte, S.J. and Sugerman, "Heavy Metal Free, High Solids Anticorrosive Baked Coatings", 33rd Int'l SAMPE Symp., Anaheim, CA, March 7-10, 1988 (SAMPE II).

[4]. Monte, S.J. and G. Sugerman, G., "High Temperature Inorganic Anti-corrosive Coatings Using Organometallic Titanate and Zirconate Quat Blends (QB)," Corrosion '90, Las Vegas, NV, April 23-27, 1990, Paper No. 432.

[5]. Monte, S.J. and Sugerman, G., "Corrosion Resistant One Hundred Percent Solids, Environ-mentally Sound Coatings", Water-Borne & Higher Solids Coatings Symposium, New Orleans, LA Feb. 3-5, 1988.

[6]. Monte, S.J. and Sugerman, G., "Alkoxy Titanates and Zirconates as Corrosion Inhibitors in Clear Coats and Unfilled Polymers", Corrosion/88, NACE, St. Louis, MO, March 21-25, 1988.

[7]. Monte, S. J. and Sugerman, G., "Very High Solids and Waterborne Anticorrosive Coatings", Western Coatings Societies' 19th Biennial Sympo-sium and Show, Anaheim, CA. March 14-16, 1989.

[8]. Monte, S.J. and Sugerman, G., "The Usage of Organometallic Reagents as Catalysts and Adhesion Promoters in Reinforced Composites", Second International Conference on Composite Interfaces (ICCI-II), Case Western Reserve University, Cleveland, Ohio, June 13-17, 1988.

[9]. Monte, S.J. and Sugerman, G., KPI; A. Damusis and P. Patel, Polymer Institute, University of Detroit, Application of Titanate Coupling Agent in Mineral and Glass Fiber Filled RIM Urethane Systems," SPI Urethane Division 26th Annual Technical Conference, November 1981.

[10]. Monte, S.J. and Sugerman, G., KPI, "Titanate Coupling Agents - 1985 Urethane Applications", SPI Urethane Division 29th Annual Technical / Marketing Conference, October 1985.

[11]. Monte, S.J. "Injection Molding with Neoalkoxy Titanates and Zirconates', SPE RETEC, White Haven, PA, USA October 19, 1995.

[12]. Monte, S.J., "Titanium and Zirconium Esters vs. Couplers and Single Site Catalysts for In-Situ Repolymerization and Copolymerization Useful for Recycled Polymeric Compositions," ACS Rubber Div., Louisville, KY, Oct. 8-11, 1996, Paper No. 57.

[13]. Monte, S.J., "Better Bonding and Metallocene-like Catalysis Benefits for Elastomers", *Rubber Technology International '96, UK & Int'l Press*, a Div. of Auto Intermediates Ltd (1996).

[14]. Monte, S.J. "Compounding and Molding with Neoalkoxy Titanates and Zirconates", Polyblends '97 SPE Div./Sect. Conference, NRCC, Montreal, Canada, Oct. 9, 1997.

[15]. Monte, S.J., "Increased Productivity of Thermoplastics Using Organometallic Titanate and Zirconate Coupling Agents", SPE ANTEC, May 1-3, 1989.

[16]. Monte, S.J., "Coupling Agents Increase PVC Productivity", *Plastics Compounding Magazine,* November/December 1989.

[17]. Glaysher, W.A., Haff, D.R., Schlaubitz, H.H., and Monte, S. J., "The Use of Organometallic Coupling Agents as Process Aids in Blow Molded HDPE"' SSPE RETEC, High Performance Blow Molding Conference, Oct. 9-10. 1990.

[18]. Monte, S.J., "New Opportunities in Recycled Plastics With Neoalkoxy, Titanate and Zirconate Coupling Agents"' SPE Recycle RETEC, October 31, 1989.

[19]. Monte, S.J., "More Efficient Manufacture of Better Foamed, Filled and Unfilled Polymer Compounds With Titanate and Zirconate Coupling Agents", Northeast Regional Rubber & Plastics Exposition, September 21-22, 1994, Mahwah, NJ.

[20]. Monte, S.J., Sugerman, G. "The Use of Organometallic Titanates & Zirconates as Reactants and Compatabilizers in Polymers", Compalloy '90, Mar. 9, 1990, New Orleans, LA.

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

[22] JP 2001288440 Yamazaki, Akira, Kyoritsu Chemical Industry Co., Ltd., Japan

[23] Kataoka, Mitsumune, Tokin Corp., Japan, JP 2002025806 A2 20020125, "PTC resistors (PTCR) with good adhesion to foil electrodes, their manufacture, and compositions therefore"

[24] Voelkel, A. and Grzeskowiak, T., Poznan University of Technology, Institute of Chemical Technology and Engineering, “The Use of Solubility Parameters in Characterization of Titanate Modified Silica Gel by Inverse Gas Chromatography”, Chromatographia Vol. 51, No. 9/10, May 2000.

[25] Wang, Yeh and Huang, Jiang-Shen, Dept. of Chem. Eng’g, Tunghai University, “Single Screw Extrusion Compounding of Particulate Filled Thermoplastics: State of Dispersion and Its Influence on Impact Properties”, Journal of Applied Polymer Science, Vol. 60, 1779-1791 (1996).

[26] Krysztafkiewicz, A.; Rager, B.; Jesionowski, T., Institute of Technology and Chemical Engineering, Poznań University of Technology, “The Effect of Surface Modification on Physiochemical Properties of Precipitated Silica”, Journal of Materials Science 32 (1997) 1333-1339.

[27] Kajiyama, Aklhisa; Nakamura, Tatsuya, Toda Kogyo Corp., EP 1 041 041 A1 dated 04.10.2000, “Layered rock salt-type oxide particle powder and process for producing same”.

[28] Kijima, Yasunori, Sony Corp., Japan , US 6312837 dated 20011106, “Organic electroluminescent device with high luminance and its manufacture”.

[29] Chen, Mei; Ao, Ning-Jian; Chen, Ying; Yu, He-Ping; Qian, Hong-Lian; Wang, Chen; Zhou, Hui-Ling; Qu, Ju-Lan; Guo, Chen-Kun, Key Laboratory of Rubber Processing of Agriculture Ministry, Guangdong, 524001, Peop. Rep. China, “Study on aging of clay-rubber masterbatch from modified clay”.*J. Appl. Polym. Sci.* (2001), 82(2), 338-342 CODEN: JAPNAB; ISSN: 0021-8995, John Wiley & Sons, Inc.

[30] Imaoka, Nobuyoshi; Iriyama, Yasuhiko; Kobayashi, Kurimasa, Asahi Chemical Industry Co., Ltd., Japan, JP 3217057 dated 20011009, “Magnetic powder-resin composite materials for bonded magnets”.

[31 Ichazo, M.N.; González, J.; Albano; C.; Diaz, B.; Departmento De Mecánica, Grupo De Polimeros, Universidad Simon Bolivar, ANTEC 1999, “Study of the $CaCO_3$ Filled PP/HDPE Composites Using Different Surface Modifiers”.

[32] Liu, Z. H.; Kwok, K. W.; Li, R. K. Y.; Choy, C. L., The Hong Kong Polytechnic University, Department of Applied Physics and Materials Research Centre, Hong Kong, Kowloon, Hung Hom, Peop. Rep. China, “Effects of coupling agent and morphology on the impact strength of high density polyethylene/CaCO3 composites”, *Polymer (2002), 43(8), 2501-2506* CODEN: POLMAG; ISSN: 0032-3861.

[33] Gonzalez, J.; Albano, C.; Ichazo, M.; Hernandez, M.; Sciamanna, R., Departamento de Mecanica, Universidad Simon Bolivar, Caracas, 1080A, Venez., “Analysis of thermogravimetric data of blends of polyolefins with calcium carbonate treated with Lica 12”, Polym. Degrad. Stab. (2001), 73(2), 211-224 CODEN: PDSTDW; ISSN: 0141-3910, Elsevier Science Ltd.

[34] Doufnoune, R.; Haddaoui, Univerité FERHAT-Abbas, Institut de Chimie-Industrielle, Département de Génie des Polymères Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Sétif 19000-Algére, Private Communication, February 1999, “Correlation of the Mechanical Properties of Various Polypropylene/$CaCO_3$ Compounds and the Effects of Coupling Agents on the Surface of $CaCO_3$ Particles”.

[35] The Instit. Sc. & Ind. Res., Osaka University, "Effects of coupling agents on the mechanical properties improvement of the TiO_2 reinforced epoxy system", *Mater. Lett.(1996)*, 26(6), 299-303 Coden:MLETDJ;ISSN:0167-577X.

[36] Murakata, Tadahiro; Yamamoto, Ryoich; Yoshida, Yuichi; Hinohara, Masanobu; Ogata, Tateaki; and Sato, Shimo, Dept. of Materials Science and Eng’g, Yamagata University, “Preparation of Ultra Fine TiO_2 Particles Dispersible in Organic Solvents and Their Photocatalytic Properties”, Journal of Chem. Eng. of Japan, Vol. 31, No.1, pp. 21-28, 1998.

[37] Koike, Yukizumi; Mano, Shizuko, Tsuyakku K. K., Japan, JP 10315247 dated 1998-12-02, “Surface treatment of titanium flake colorants and decorating plastic moldings using the same”.

[38] Bodelin-Lecomte, Sophie; Le Gars, Guenola, L'oreal, Fr., EP 864322 dated 1998-09-16, “Method of preparation of a solid cosmetic composition containing plaster”.

[39] Ren, Z.; Shanks, R. A.; Rook, T. J., Department of Applied Chemistry, RMIT, University, Melbourne, 3001, Australia, Polymers & Polymer Composites (2002), 10(2), 173-181, CODEN: PPOCEC; ISSN: 0967-3911, Rapra Technology Ltd., “Processing and properties of polypropylene composites with high filler content”.

[40] Young, Eugene F.; O’Keefe, Dennis J., Xerox Corp., US Patent 5,489,497 dated Feb. 6, 1996, “Magnetic Toner Compositions with Surface Additives”.

[41] Uchida, Naoki; Kouzawa, Minoru; Misawa, Hiromitsu; Aoki, Koso; Miura, Suehiko, Toda Kogyo Corporation, Japan, Eur. Pat. Appl., 61 pp., EP 1225600 dated 2002-07-24, “Black magnetic iron oxide

particles for magnetic toner".
[42] Kozawa, Minoru; Aoki, Koso; Misawa, Hiromitsu; Miyazaki, Sigenori; Uchida, Naoki; Fujioka, Kazuo, Toda Kogyo Corporation, Japan, EP 794154 dated 1997-09-10, "Magnetite particles, magnetic iron oxide particles, process for the production of the same and magnetic toner using the same".
[43] Sousa, Rui A.; Reis, Rui L.; Cunha, Antonio M.; Bevis, Michael J., Department of Polymer Engineering, University of Minho, Guimaraes, 4800-058, Port., Annual Technical Conference - Society of Plastics Engineers (2001), 59th (Vol. 3), 2550-2554 CODEN: ACPED4; ISSN: 0272-5223, "Interfacial interactions and structure development in injection molded HDPE/hydroxyl-apatite composites".
[44] Vaz, C. M.; Reis, R. L.; Cunha, A. M., CS Department of Polymer Engineering, University of Minho, Guimaraes, 4800-058, Portugal, Biomaterials (2001), Volume Date 2002, 23(2), 629-635, CODEN: BIMADU; ISSN: 0142-9612, Elsevier Science Ltd., "Use of coupling agents to enhance the interfacial interactions in starch-EVOH/hydroxylapatite composites"
[45] Horibe, Hideo; Nishiyama, Itsuo; Hiroi, Osamu; Mori, Teijiro; Hayashi, Tatsuya; Takahashi, Chie; Murata, Shiro; Nishina, Kenichi; Sogabe, Manabu; Ishikawa, Masahiro, US 2002137831 dated 2002-09-26, "Polymeric PTC composition and circuit protection device made therefrom".
[46] Kataoka, Mitsumune, NEC Tokin Corp., Japan, JP 2002226601 dated 2002-08-14 "Preparation of electrically conductive composition for fabrication of positive-temperature-coefficient (PTC) devices."
[47] Yang, Huaming, Department of Mineral Engineering, Zhongnan University, Changsha, 410083, Peop. Rep. China, Feijinshukuang (2001), 24(2), 24, 36, CODEN: FEIJDJ; ISSN: 0253-2298, Feijinshukuang Bianjibu Journal, "Preparation of activated saponite powder and its use in PP plastic".
[48] Ahmad, Sahrim; Abdullah, Ibrahim; Abdullah, Mustfa; and Wai, Wong Chuan, Faculty of Applied and Physical Sciences, Universiti Kebangsaan Malaysia, "Electrical and Magnetic Properties of Barium Ferrite Thermoplastic Natural Rubber (TPNR) Composites", Sci. Int. (Lahore), 10(4), 375-377, 1998, ISSN 1023-5316; CODEN; INTE 8.
[49] Monte, S. J.; Sugerman, G; Kenrich Petrochemicals, Inc., U.S. 6,197,135 dated March 6, 2001, "Enhanced Energetic Composites".
[50] Monte, S.J.; Sugerman, Kenrich Petrochemicals, Inc.; G; Dixon, Scott J. USAF Contractor, U.S. 5,753,853 dated May 19, 1998, "Solid Propellant with Titanate Bonding Agent".
[51]. Mitsubishi Cable Ind., US 4,769,179 - 9/6/88. 'Magnesium Hydroxide flame retardant composites'.
[52] Eichler, Hans-Jürgen; Palmer Michael; Herbiet, René, ALUSUISSE MARTINSWERK GMBH, WO 00015710 dated 14. September 1999, "Surface-Modified Filling Material Composition".
[53] Jiang, Pingkai; Wang, Genlin; Zhu, Zikang; Wu, Haifeng; School of Chemistry and Chemical Engineering, Shanghai Jiaotong Univ., 200240, Peop. Rep. China; Hecheng Shuzhi Ji Suliao (2001), 18(5), 35-38; CODEN: HSSUEJ; ISSN: 1002-1396; Hecheng Shuzhi Ji Suliao Bianjibu; "Interfacial and mechanical properties of aluminum hydroxide highly filled polyethylene composite".
[54] Wang, Genlin; Jiang, Pingkai; Zhu, Zikang; Yin, Jie, School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai, 200240, Peop. Rep. China, Journal of Applied Polymer Science (2002), 85(12), 2485-2490, CODEN: JAPNAB; ISSN: 0021-8995, John Wiley & Sons, Inc., "Structure-property relationships of LLDPE-highly filled with aluminum hydroxide".
[55] Wang, Gen-Lin; Jiang, Ping-Kai; Zhu, Zi-Kang; Yin, Jie, School of Chemistry and Chemical Engineering, Shanghai Jiaotong, University, Shanghai, 200240, Peop. Rep. China, Chinese Journal of Polymer Science (2002), 20(3), 253-259, CODEN: CJPSEG; ISSN: 0256-7679, Springer-Verlag, "Morphology and properties of linear low-density polyethylene highly loaded with aluminum hydroxide".
[56] Braga, Vittorio; Goberti, Paolo; Zucchelli, Ugo; Marchini, Roberta, Basell Technology Company Bv, Neth., WO 2001048075, EP 1155080 dated 2001-11-21, "Flame-proof polyolefin compositions".
[57] Imahashi, Takeshi; Kazuki, Keiko, Kyowa Kagaku Kogyo K. K., Japan, JP 2001312925 dated 2001-11-09, "Heat deterioration-, water-, and fire-resistant electrically insulated electric wires and cables, and moldings".
[58] Imahashi, Takeshi; Yoshii, Makoto; Sawa, Yoshiharu, Kyowa Chemical Industry Co., Ltd., Japan, EP 1008445 dated 2000-06-1, "Flame-retardant laminated resin molded articles with easy coloring property".
[59] Chiang, Wen-Yen; Hu, Chia-Hao, Department of Chemical Engineering, Tatung University, Taipei, 104, Taiwan, Composites, Part A (2001), 32A(3-4), 517-524,CODEN: CASMFJ; ISSN: 1359-835X, Elsevier Science Ltd., "Approaches of interfacial modification for flame retardant polymeric materials".

[60] Kato, Masaharu; Omoto, Masanobu; Ishimatsu, Hirofumi; Madalle, James; Kratzer, Jeff A.; EP 0 708 143 A1 dated 24.04.1996, “Polyvinyl Chloride Based Resin Composition and Products Derived Therefrom”.

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

[62] Galanti, Andrea; Laus, Michele; Fiorini, Maurizio, CS Mixer S.r.l., Ravenna, Italy, “Reinforcement of SBS by organophilic clay fillers”, *Kautsch. Gummi Kunstst.* (1999), 52(1), 21-25, CODEN: KGUKAC; ISSN: 0022-9520, PB Huethig GmbH, cc 39-9 (Synthetic Elastomers and Natural Rubber).

[63] Monte, S.J., Kenrich Petrochemicals, Inc., “Titanate and Zirconate Coupling Agents in Foamed Polymers”, RAPRA Foams Conference, March 13, 2001, Frankfurt, Germany.

[64] Hilborn, Bradley L.; Harrison, Bruce L., Henkel Corporation, USA, WO 2000012571 dated 2000-03-09, “Corrosion inhibitors and corrosion-resistant structural foam”.

[65] Peng, Jiahui; Chen, Mingfeng; Peng, Zhihui; Lin, Changqing; Zhang, Jianxin, Chongqing University, Peop. Rep. China, Faming Zhuanli Shenqing Gongkai Shuomingshu, 11 pp., CN 1305972 dated 2001-08-01, “Preparation of thermal insulating mortar for building external wall”.

[66] Miller, N. A.; Jones, M.S.; and Stirling, C.D., Industrial Research Limited, “Waste Plastics/Cellulose Fibre Composites”, Polymers & Polymer Composites, Vol.6, No. 2, 1998.

[67]. Monte, S.J., U.S. Patent 5,659,058 dated August 19, 1997, “Thermally Stable Antistatic Agents” – Monte, S.J.

[68] Monte, S.J., “Permanent, Transparent, Non-Blooming and Non-Hygroscopic Antistatic Agents Based On Combined Neoalkoxy Organometallics”, Addcon World 2001 Conference, 9 October 2001, Berlin, Germany.

[69] Katz, Harry S.; Milewski, John V, “Handbook of Fillers and Plastics”, Van Nostrand Reinhold, New York, 1987.

[70] Alaka, R.; Maddison, J., Kobe Steel Europe Ltd., WO 97/27993 dated 30 January 1997, “LIQUID COMPOSITE MOULDING PROCESS”.

KENRICH
PETROCHEMICALS, INC.
140 East 22nd Street
Bayonne, NJ 07002-0032 USA
Tel: 201-823-9000
Toll Free: 866-KENRICH
Fax: 201-823-0691
Email: kenreact@4kenrich.com
Web: www.4kenrich.com