# How to use Organometallic Coupling Agents?

Two Application Principles for Thermoplastics Melt Mixing

The physics of mixing is as important as the chemistry of coupling. Two principles govern the applications art of coupling agents: uniform distribution before the polymer melt phase for uniform coupling/catalysis and high specific energy input during the polymer melt phase for maximum shear/work energy for dispersion so that coupling at the filler interface and catalysis in the polymer interphase are made complete.
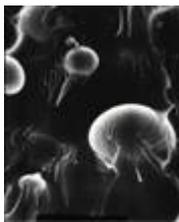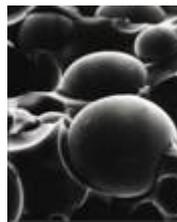
Titanates coated   **Without titanates**

Often times, poor mixing methodology can defeat the best polymer filler reinforcement additive compound design.

Uniform Distribution – Before the Polymer Melt Phase or Before Filler Contact for Uniform Coupling and Catalysis

Subject organometallics work on a catalytic principle at stoichiometric levels of 0.1 to 2.0 parts additive per thousand parts polymer and 0.5 to 0.7% by weight of most fillers.

As stated, in room temperature liquid waterbased or high solids polymer systems, it is best practice to add the coupling agent into the liquid phase just prior to addition of the filler or particulate to be coupled. The titanate must be soluble directly into the organic or water phase or able to be cosolvated or emulsified.

Coupling in atomic monolayers may take place on the surface of a particulate in both the organic and water phase. In order to effect atomic monomolecular level coupling, the titanate or zirconate must be solubilized in the organic (solvent, plasticizer, polymer) phase or finely emulsified into the water followed by addition of the particulate or reinforcing fiber. If the organic phase has a high molecular weight, then sufficient shear and high mixing torque is needed to assure titanate distribution.

Since titanates are transesterification catalysts and are used as catalysts in the synthesis of esters such as DOP, it is best practice to dissolve them into an ester plasticizer just prior to use so as to keep residence time minimized to avoid side reactions that diminish effectiveness.

In thermoplastic and thermoset melt systems, the coupling agent must be dispersed as thoroughly as possible throughout the unmelted polymer or polymer composite materials before the onset of melting. During melting, catalysis is initiated as the titanate or zirconate solvates into the polymer organic phase for reaction with polymer ligands and coupling to the filler/fiber interface.

The concern with localization and physiabsorption of the coupling agent on the filler or fiber which results in whole segments of uncoupled particulate surfaces, as well as over and under catalysis of the polymer, is largely overcome by using masterbatches of the coupling agent. A simple rule is to use like coupling agent form to like polymer physical form, i.e. liquid to liquid, powder to powder and pellet to pellet. Therefore, an organosoluble liquid coupling agent should be used for solvent or high solids liquid polymers, a quaternized or emulsifiable grade of coupling agent for water based emulsion polymers, a 65% active coupling agent masterbatch   for powder polymer systems such as thermoset epoxy powder coatings, rigid PVC composites and elastomers, and a 20% active coupling agent masterbatch for pelleted polymer systems.

Titanate TCA-L12 with its powder masterbatch DLC-L12 and its pellet masterbatch MB-L12.

The pellet form is the simplest and best for the typical thermoplastic injection, blow molding or extrusion-processing set-up. Powder forms of the coupling agent work best in high shear dry blend mixers such as a Henschel and batch mixers such as double sigma blade or internal mixers or 2-roll mills because they are easier to weigh out and avoid localization caused by poor mixing techniques, sticking to the ram or mixer walls. The powder form can also be fed gravimetrically to the throat of an extruder.

Specific Energy Input During the Polymer Melt Phase

Once the polymer begins to melt, work energy through mechanical shear creates the required intimate polymer/catalyst (coupling agent) mixing. The area under the power curve formed by a plot of torque vs. time is a measurement of the work energy or shear on the polymer/catalyst matrix. The most efficient polymer mix cycles generate peak torque (AMPS) in a short time. Torque is controlled by temperature, rpm's and backpressure or plasticizer/solvent/water letdown. High torque creates high polymer shear rates. Polymers are non-Newtonian in flow and their melt viscosity decreases asymptotically with increasing shear. Under high shear rates, polymers exhibit the lowest viscosity with the least amount of rheological variation as compared to greater polymer viscosity variation at lower shear rates - i.e. high shear rates give reproducible results. Most polymers (except for heat sensitive PVC) are not damaged by higher shear. Low shear rate melt indexers are not the way to measure the effect of subject additives. Use torque readout instrumentation that plots rheological effects over a wide shear rate range.

Successful use of titanates and zirconates, or any very active additive used at low levels, therefore requires the optimum specific energy input. Lower temperatures, increased back pressure, higher rpm's and other changes in the compounding conditions are necessary to compensate for the rheological changes the coupling agent induces into the compound. Remember, the compounding device – whether it's a single or twin screw, intensive or continuous mixer, a two-roll mill, a Cowles dissolver or high shear mixer – becomes in effect a Reactor for coupling and catalysis mechanisms. It's the interfacial shear that is controlled by the system's viscosity that does the work -- and the geometry of the compounding machine just facilitates achieving the necessary work energy. You can't just let the Banbury or twin screw compound without monitoring torque or amps. If you are run control compounds and titanate containing compounds at the same conditions – you are not practicing good science, but simply comparing "apples to oranges" as it relates to specific energy input. Mixing the control and titanate containing compounds to equivalent work energy is good science.

Most qualified polymer compounders know that the best formulation can produce poor results because of poor mixing. PVC, thermoplastic and rubber custom compounders – and also coatings, inks adhesives and sealants chemists – are alert to mixing art techniques such as two passes, solvent let downs, solubility parameters, upside down mixing, predispersion of critical ingredients, ram pressures, back pressures, increased rpms, blade and screw designs, mixing element inserts and all other manner of approaches that seek to impart the optimum amount of mechanical shear work energy to the interface of all the ingredients in the matrix.

Some common compounding mistakes are: add the liquid titanate with other compound ingredients in a plastic bag; dump the liquid coupling agent on top of the other ingredients in a static bowl; add the liquid coupling agent in a ribbon blender or a Banbury. Good practice is to: before the melt phase –spray apply the liquid titanate (diluted) or dropwise add the liquid titanate to a fluidized bed of the powder ingredients in a high shear mixer such as a Henschel, Papenmeier, Littleford Lodige, Patterson Kelley V Blender with intensifier bar and other such blenders typically used by PVC compounders, to practice the first principle of uniform distribution. It is good practice to add the coupling agent into the other ingredients in a plastic bag and shake vigorously if the coupling agent is in a masterbatch DLC powder form or MB pellet form. Again, a simple rule of thumb is: "liquid additives into liquid polymer systems, powdered additives into powdered systems and pelleted additives into pellet systems."

Dosage Determination Principles

Optimum dosage is determined by the materials used in the compound. An obvious statement, but, then why do so many investigators choose 1.0% or 1 phr coupling agent dosage as a single data point to determine efficacy? In addition, unlike silanes, titanate or zirconate dosage is often determined by the Function 2 catalysis effect rather than the Function 1 coupling effect. Most of the titanate literature points to 0.2 to 0.6% as an optimum dosage for most unfilled formulations? A 3-data point ladder study is much more useful for all unfilled and filled polymer formulations.

For example, one test shows how a high pigment to binder ratio of 80% Ferrite in Mineral Oil shows 0.5% by weight of Ferrite to be the optimal loading.

Amount Based on Organic Polymer

A simple test devised to demonstrate the repolymerization effect on low molecular polyethylene wax (AC 617A – Allied Signal) was to dilute one part of the PE wax with three parts of mineral oil. Mineral oil is a convenient C20 aliphatic low molecular weight room temperature model for polyethylene. The resultant 1:3 blend had a viscosity of 22,400 cps. The addition of 0.1 wt. % to the blend of zirconate ZCA-12 increased the viscosity to 5,000,000 cps, 0.2 wt. % to 7,000,000 cps, and 0.4 wt. % to 1,800,000 cps thereby indicating 0.2 wt. % was optimum for this system. Most polymers give balanced property effects at 0.2 to 0.6% titanate dosages.

Amount Based on Inorganic Pigment

The amount needed to form an atomic monolayer of coupling agent is pigment surface area dependent and generally lies between 0.2 to 0.5 to 0.7% by weight of pigment. Even nanoclays and fine surface area silicas and blacks show some significant dispersion improvement at 0.5% dosage.

Consistent with the concept of coupling and catalysis, although 6% titanate may appear to be a large dosage from a coupling viewpoint, the low levels of nanoparticulate used result in often ideal catalytic levels of titanate dosage in the 0.1 to 0.4% by weight of polymer range.

Although surface area is an obvious dosage determinant, the way a pigment or filler is produced can also determine dosage. For example, an ultramarine blue pigment with a surface area of $3m^2/g$ required 0.35% titanate, while the same pigment having a surface area of $1m^2/g$ required 3.2% titanate. The different dosage requirement was not all surface area dependent, but mostly caused by the different surfactant chemistries used in the water slurries of the pigment before drying.

The amount of coupling agent will even vary with time with vast differences in viscosities depending on whether the viscosity was measured at room temperature immediately after mixing, or 1-hour, or 1-day or 28-days later. This variability is due to the pore velocity (the speed or time it takes for a fluid to penetrate and wet the additional internal inorganic surface area created by its capillary pores as determined by the geometric three-dimensional nature of the pigment) and other long-term interactions with the polymer interphase.

Generally, 1 to 5 micron mineral fillers require 0.35% to 0.70% titanate by weight of the filler.

Amount Based on Combined Inorganic and Organic

A good dosage/data evaluation point would be that which is obtained by the calculation of the combined amount of coupling agent needed to form an atomic monolayer on the filler/reinforcement surface and the amount needed for optimum repolymerization effects on the polymer interphase. For example, the optimum dosage for a CaCO3 filled PVC may well be that obtained by the combined weight of 0.5 wt% of the filler portion and 0.2 wt% of the PVC portion. If Henschel pretreatment is employed, dilution of 1 part coupling agent in three parts plasticizer will enhance significantly the uniformity of coupling agent distribution. Since titanates are transesterification catalysts, they should not be added to the ester until just before mixing is started. Airless spray gun application to a dry fluidized bed of compound ingredients will minimize diluent requirements. A discussion follows on the necessity to dilute titanate when pretreating Mg(OH)2. Similar tests with ATH, CaCO3 and other fillers showed that dilution with plasticizer or mineral oil was not necessary.

Mixers for pretreatment
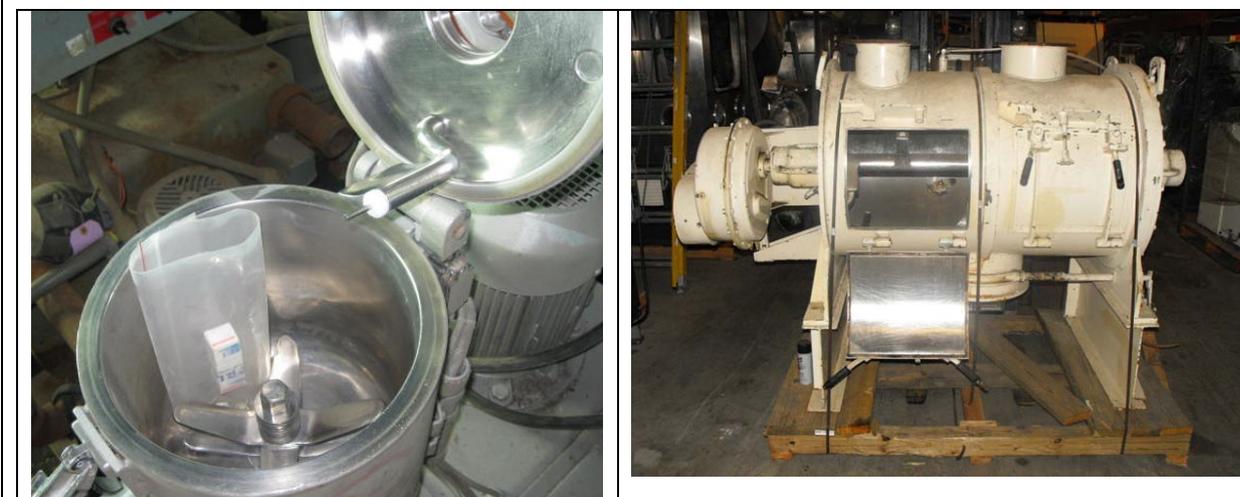
Henschel mixer	Littleford Lodige mixer
Patterson Kelly V mixer	**Sigma mixer**
Vertical mixer	**Airless Spray Gun**
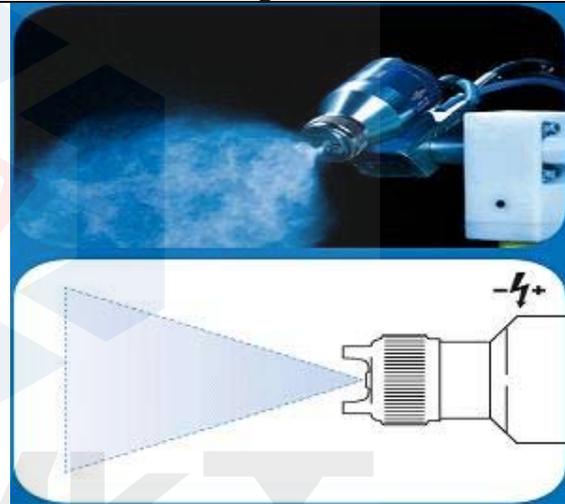
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