

## *The Selection and Use of Waterbased Dispersions in Latex*

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Today, products made from latex can be found everywhere. Manufacturers of carpet, wall covering, paper, adhesives, condoms, gloves, balloons, foam pads, mattresses, tubing, non woven fabrics and asphalt all use and rely on natural or synthetic latex to build a viable and marketable product.

Commercial latexes are robust and stable. They are adequately able to resist breakdown from high shear mixing, wide swings in temperature, addition of high volumes of fillers and changes in pH.

These latexes, while having some unique and interesting physical and chemical properties are typically formulated with other chemical ingredients to improve, stabilize and protect the latex. The process of making incremental addition of ingredients to the latex in a formulation is called *compounding* and it plays a key role in the manufacture of a quality product.

Typically there are 5 categories of materials used in latex formulations:

Curatives – sulfur, zinc oxide

Accelerators – dithiocarbamates, thiurams, etc

Antioxidants – phenolic and amine type

Fillers, clays, calcium carbonate, mica etc.

Modifiers – plasticizers, extenders, etc.

These materials are added to the latex as aqueous or waterbased dispersions. Aqueous dispersions are defined as water insoluble compounding ingredients added to the latex in the form of a stable, fine

particle size, heterogeneous waterbased system. It is a key requirement that dispersions, when added to the latex must not cause harm to the latex or diminish its properties. After addition of the dispersion the stability of the latex must at least remain unchanged and preferably improved.

It is nearly impossible to produce a good latex compound with poor dispersions. Dispersions that exhibit a wide particle size distribution, show evidence of particle re-agglomeration, excessive settling and inconsistent viscosity will contribute to poor or inconsistent performance of the latex compound during the manufacturing process. It is therefore important for the dispersion manufacturer to assure consistent dispersion quality by producing a stable fine particle size dispersion that will not re-agglomerate or exhibit excessive sedimentation or settling while standing, be easy to stir, be pumpable or pourable and not affect the latex stability after addition.

A major element in the above requirement will be particle stability. The dispersion manufacturer can assure particle stability by the appropriate addition of a dispersant or surfactant (surface active agent). Chemically, surfactants are amphipathic molecules. That is, they have two distinctly different characteristics, polar and non-polar, in different parts of the same molecule. Therefore a surfactant molecule has both hydrophilic (water loving) and hydrophobic (water hating) characteristics. The organic portion (tail) of the molecule will orient itself to the particle and the polar “head” will orient itself to the water medium. The particle will be surrounded by these molecules thereby achieving a natural repulsion between particles and a degree of particle stabilization. Agents functioning as dispersants must accomplish at least 2 objectives:

- 1) Effectively cover the particle surface to minimize particle to particle interaction and

- 2) The outward directed portion of the dispersant molecule must coordinate or express similarity to that phase

The four primary processes involved in a stable dispersion are:

- 1) Displacement of adsorbed gas on the solid particle by the liquid
- 2) Formation of a protective boundary preventing particle to particle adhesion
- 3) Mechanical separation of particles to allow for complete liquid encapsulation.
- 4) Complete and homogenous redistribution of the particles into the liquid phase.

The displacement of adsorbed gas on the particle is facilitated by the addition of the dispersant into the liquid phase of the dispersion. The liquid's resulting *energy of wetting*, measured in  $\text{erg/cm}^2$ , is increased sufficiently to allow the ready displacement of adsorbed gases on the particle surface. This ability of the liquid to "wet" the particle has a direct bearing on the promotion of a stable dispersion.

Most particles in an aqueous colloidal dispersion exhibit an electric charge. The net charge on the particle affects the distribution of ions in the surrounding interfacial region resulting in an increase of ions with the opposite charge close to the surface of the particle. There exists an additional, more diffuse layer, surrounding the compact counter ion layer. This diffuse layer will have the same charge as the original particle albeit electrically weaker. The layer, in reality, represents the overall charge that the particle acquires in a medium. The "thickness" of this layer or *Zeta Potential* is an indication of the particle's ability to repel other particles in the medium. The greater the zeta potential, the greater will be the stability of the dispersion system due to mutual electrostatic repulsion. In anionic

systems, the zeta potential increases (becomes more negative) with increasing pH and can be reduced by decreasing the system pH. The pH where the zeta potential is zero will be the dispersion's isoelectric point and is the point at which the dispersion will be the least stable.

Under conditions where the zeta potential is small, the particles in dispersion, are subject to agglomeration or flocculation. An agglomerated group of particles will, in effect, exhibit an outward increase in particle radius and, subsequently, based on Stokes Law, have a greater tendency to settle out of the dispersion. This effect can be overcome, often times with an increase in the system pH, with the addition of an alkali.

An increase in dispersion grind time can cause dispersion instability by reducing the particle size and thereby increasing the particle's surface area. A 50% reduction of the particle radius will double the surface to volume ratio. Since there is a finite level of dispersant in the formulation, it stands that the layer of dispersant around each particle will be reduced, thereby increasing the likelihood of particle to particle contact, increase in dispersion viscosity and particle agglomeration.

### **Characteristics of Dispersions:**

Dispersions are evaluated on a variety of characteristics or attributes assuring that the dispersions made on Friday are identical to the same dispersion formulation made the previous Monday – *consistency is the key*.

The characteristics are:

Total Solids – *Dry weight as a percent of wet weight*

Active Solids – *Weight of major ingredient (dry) as a percent of wet weight*

pH – *Nominal range 8-11*

Viscosity – *Ideal range approx 500 cps – easily stirred and poured*

Particle Size – *Target is less than 5 micron (mean)*

Particle Size Distribution – *Normal distribution, tight range*

Color – *White to off-white*

Odor – *Absence of any distinct or detectable odor*

Thixotropy – *Shear thinning – Non-Newtonian fluid*

Specific Gravity – *Normal range for materials in formulation*

Settling Rate – *Minimal settling over time*

Settling Character – *Easily re-incorporated with minimal effort*

### **Manufacturing of Dispersions:**

The simple addition of a dry chemical and a surfactant into water with subsequent stirring will not really produce an acceptable dispersion. The stirring may de-agglomerate the clumps of dry powdered chemical temporarily but will not reduce its particle size and the particles may re-agglomerate yet again. In order to effectively reduce the particle size the dry chemical, water and surfactant, along with colloidal stabilizers would need to be put into a ball mill, attritor or horizontal mill for grinding. These mills, although different in construction and design, share some common properties. They all contain *grinding media* i.e. flint pebbles, ceramic beads, high density alumina cylinders or zirconium silicate pellets that are used to grind and pulverize the dry chemical and reduce its particle size. All of the mills rely on *motion* which produces a tumbling, agitating or rotating action in the mill. The material in all of the mills will experience a *cascading effect* creating a sliding mobile mass of media and product. The media in this mass will begin to pulverize the mill contents by *point contact* at the tangent point of the media spheres. The smaller the media, the greater the number of

contacts over time and the greater the rate of particle size reduction. Grind time can be affected by:

- Choice of material
- Formulation
- Media (size and type)
- Material charge (quantity in the mill)
- Rotational speed of the mill

### **Handling Dispersions – Preparation for Compounding:**

#### **The 1<sup>st</sup> Law of Latex Compounding: *Gravity Always Wins!***

Most dispersions regardless of particle size or settling characteristics should be adequately stirred before using. This is a recommended practice with all compounding materials to assure consistency. The dispersions may show some signs of settling over time but can be readily re-dispersed in a short amount of time. During the stirring process care should be taken not to create a vortex on the material surface which will draw air into the product and create a stable bubble and a foamed product. A foamy product will have a tendency to dry quickly on the sides of the container producing flakes of agglomerated material which can be re-incorporated into the latex and may affect the latex film quality.

Typical product shelf life is 6 months but this can be affected by storage temperature and conditions.

### **Compounding:**

#### **The 2<sup>nd</sup> Law of Latex Compounding: *Do No Harm!***

Assuming the latex compounder has access to sufficiently stabilized, dispersions, the compounding process begins with the addition of a latex

stabilizer followed by step-wise additions of the individual dispersions until the recipe has been completed. The compounder will allow for adequate mixing of the latex between dispersion additions. The accelerator and antioxidant dispersions are typically at a 50% activity level with the curatives, zinc oxide and sulfur at a 60-68% activity. Since the densities of the various additives might range from 1 to 6 (g/cm<sup>3</sup>), one can expect that the sedimentation rates and dispersability of these materials might be varied, also. The compounder might choose to add the more dense materials first, to allow for a more thorough mixing and follow with the materials that have lower specific gravities. This would allow longer mixing for the more dense materials.

*Specific Gravity of Various Compounding Ingredients*

Zinc Oxide	5.6 g/cm <sup>3</sup>
Sulfur	2.07
Accelerators	1.2-1.7
Antioxidants	1.04-1.06

The order of addition, therefore, may contribute to a more consistent final product. In addition to specific gravity, the dispersions may differ in viscosity, thixotropy and settling rate; therefore, it would prove beneficial to assure thorough mixing of each material prior to its addition.

**Masterbatches:**

The addition of 4-5 compounding ingredients, as dispersions, represents a number of activities that qualify as *opportunities for error* that could

contribute to a variable final product. From the selection of material from inventory, the determination of the required amount of each material to the physical act of weighing and addition into the latex, all present opportunities to introduce variability into the system. The opportunities for weighing and addition errors are exacerbated if the compounding operation has multiple work shifts.

In addition, if the dispersions are purchased, then the ordering, receiving, inventory and quality evaluation of multiple stock keeping units (SKU's) represent hidden manufacturing costs, as well.

A masterbatch, a single dispersion comprising all of the various compounding additives, offers an array of advantages to the operation. There can be a five-fold reduction in the number of SKU's required for the formulation. This represents an opportunity to simplify and streamline the operation from order placement, inventory, and quality assurance to compounding.

The use of a masterbatch dispersion that simplifies the operation by reducing the number of required dispersions, minimizes the number of weighing and additions, reduces the compounding time and variability shift to shift, and simplifies operator training will, ultimately, lead to a more reliable and consistent operation.

Beyond the matter of process simplification, there are a number of other advantages to the use of masterbatches in latex compounding. There are anecdotal reports of a 25-35% reduction in downtime associated with tank cleaning because of less material "settling out" in the latex tanks. In addition, compounders have noted that they require 15-25% less additives in their latex after a conversion to a masterbatch dispersion. The observance of less settling and less additives required, go hand in hand. Less settling means

more material available in the latex. Improvement in film clarity is also an observance in compounds with masterbatches vs. single dispersions.

Typical single product dispersions are manufactured with an activity of 50% to 60%. The finished dispersions are then added to the latex at a level equivalent to the parts per hundred rubber (phr) required. As stated earlier, a latex recipe may require 5 separate additions. The single ingredient dispersion is typically produced at the high activity because it represents the lowest cost model for manufacturing. The highly concentrated single dispersion may not be the most readily miscible in the latex, when compared with a dispersion of lower concentration. The masterbatch, however, employs the high activity method but uses approximately 20% of each ingredient to make up the whole dispersion “package”. With all of the chemical components undergoing the same grinding history, in the same dispersion, there is a uniformity of morphology and isotropy of the dispersed particles.

In a masterbatch, there exists a maximum blending of the components that assure that when the dispersion is added to the latex it offers complete particle to particle (*dispersed chemical particle to rubber particle*) contact, in the correct stoichiometric proportions. Further, some dissolution and interaction of the zinc oxide and sulfur takes place during the manufacture and storage of the masterbatch dispersion, particularly in an ammoniated environment.

If a formulation requires multiple dispersions, it may be wise to consider using a masterbatch approach.

**Selection of Dispersions for Compounding Latex – what to use and when?**

It was Charles Goodyear in the early 1800's that discovered when natural rubber was mixed with sulfur and subsequently heated that it became more elastic, durable, less tacky and less affected by climate – heat or cold. He was describing the effects of vulcanization. Although there have been significant strides in the understanding of the chemistry of vulcanization over the past 170 years we still use sulfur and heat to initiate the cross linking reaction.

The required time and temperature for vulcanization to take place can be reduced by the addition of a variety of *accelerators*. These materials are in turn, activated by the presence of zinc oxide. Sulfur and zinc oxide are collectively known as *curatives* and together with an appropriate accelerator and antioxidant they can initiate, vulcanize and stabilize a polymer to produce the desired commercial properties.

Sulfur is inherently difficult to grind and usually requires a longer grind time than other materials. In addition, it is nearly twice as heavy as most other materials, except zinc oxide and can lead to settling of the material when mixed with thin latex. It is usually added to the latex formulation at a 0.5 – 2.0 parts per hundred rubber (phr). Care should be taken to not add more than is necessary to minimize settling and improve the aging characteristics of the rubber. Using a fine particle size dispersion may allow you to reduce the quantity of sulfur required.

Zinc oxide can be added at 0.5 to 3.0 parts in a formulation depending on type of polymer with more added into synthetic (SBR, CR and NBR) latex than with natural latex. Typically a higher surface area material is selected (9-11 M<sup>2</sup>/gram) vs 2-5 M<sup>2</sup>/gram. The higher surface area material is more reactive with less required by comparison.

There are approximately 50 chemicals that are used as accelerators and the selection is usually based on the desired speed of reaction as well as the intended shelf life of the product, the vulcanization method used, whether a liquid or powdered chemical (sodium or zinc salt) will be required and the resistance to over cure processing heat history.

The choice of accelerators is extensive with 4 major classes of materials used:

Dithiocarbamates

Thiurams

Thiazoles

Sulphenamides

Dithiocarbamates or ultra accelerators are typically chosen for their speed of reaction. They usually require zinc oxide in the formulation for processing efficiency. The zinc dialkyl dithiocarbamates will tend to pre-cure natural latex but will have little effect with synthetics. These materials may also cause some light colored goods made from natural latex to turn slightly brown when in the presence of copper. It is therefore recommended that process wash water be piped with plastic or stainless materials rather than copper piping to eliminate this effect.

These materials are typically added at a 1 phr level and may be used in combination with thiazoles i.e. zinc mercaptobenzothiazole (ZMBT) as a secondary accelerator to provide a flatter cure and greater heat resistance to the polymer.

Thiuram accelerators are very fast accelerators with a later onset of cure that can provide some processing safety and reduced pre-cure to latex compounds. They are widely used as secondary accelerators with

dithiocarbamates as well as sulphenamides. They are often used in “sulfurless” cure systems where long term aging is a consideration.

Thiazole accelerators are medium fast accelerators that show good processing safety, minimal procuring and are relatively flat curing. They can be retarded slightly by incorporating a thiurams accelerator in combination.

Sulphenamide accelerators are often used as delayed action accelerators and can be improved with the addition of DPG. These materials should be stored in a cool dry environment.

### **Antioxidants:**

These materials are used in latex to reduce or eliminate polymer deterioration due to heat (thermal oxidation), light (photo-oxidation) and flexing.

For rubber products to be commercially viable their useful life had to be extended to meet environmental and mechanical demands.

There are a wide variety of antioxidants used for latex products manufacture. The characteristic that separates these materials will be whether they are staining (phenolic) or non-staining (amine type). Antioxidants used to produce white or light colored goods are predominantly phenolic.

The selection of an antioxidant will depend on a variety of factors i.e. life cycle environment for the rubber product and its target manufacturing cost, product packaging , the requirement for minimal taste and odor, the requirement for a non-staining, non-discoloring antioxidant? How will the antioxidant affect the latex chemical stability? Will antioxidant volatility be important? Will the antioxidant be required to meet certain FDA considerations such as CFR Title 21 designations?

The correct interpretation of these factors and their effect on the final product should lead to a successful application of an antioxidant dispersion.

**Summary:**

- Latex materials are used in the manufacture of a wide variety of products
- Latex must be compounded with chemical ingredients to improve its properties – these chemicals are in the form of waterbased dispersions
- Typical materials to be found in a latex compound are curatives, accelerators and antioxidants.
- Masterbatches are combinations of materials in a single dispersion - they offer advantage to the compounder.
- Excellent products from latex depend on excellent dispersions