A Guide to Formulating Polyurethane Dispersions for Use in Coating, Adhesive, Sealant and Elastomer Applications

SYNTEGRA

Polyurethane Dispersions

Formulating Guide

SYNTEGRA* polyurethane dispersions are high solids dispersions of polyurethane/polyurea polymers in water. They provide the performance of a polyurethane and the convenience of a waterborne latex. Polyurethane polymers have traditionally exhibited high toughness and versatility in coating, adhesive, sealant and elastomer (CASE) applications. Waterborne dispersion technology allows ease of formulation, application and cleanup as well as environmental advantages such as the elimination of monomers, odor and production of volatile organic compounds (VOC). Since the polyurethane reactive chemistry is performed at Dow, the user does not have to work with reactive materials; in addition, this product has no residual (i.e., free) isocyanate. SYNTEGRA polyurethane dispersions allow the many advantages of polyurethane polymers to be brought to CASE applications, without these conventional handling concerns. However, formulating skill is required to obtain optimum properties from SYNTEGRA polyurethane dispersions. This formulating guide is designed to help a formulator get started using polyurethane dispersions, and successfully deliver high-performance products that are environmentally and user friendly.

Shear Stability During Formulation

All aqueous dispersions are stabilized in water to maintain low viscosity during shipping, formulating and application, yet coalesce rapidly into a continuous film upon water evaporation. This is accomplished only by balancing the dispersive stability of the SYNTEGRA polyurethane dispersion with its tendency to form a film. Excess shear forces encountered during handling, formulating and pumping can destabilize these dispersions and cause coagulation. Thus, during the formulation and blending of any ingredient, care must be taken not to overshear the SYNTEGRA polyurethane dispersion, especially when hot. Mix the dispersion with formulating additives slowly under low shear conditions until well dispersed.

Plasticizers

Plasticizers can be used with SYNTEGRA polyurethane dispersions to increase formulation flexibility, and in many cases, lower costs. Plasticizers will reduce the glass transition temperature of the dried film—reducing tensile strength, hardness and modulus while increasing elongation, flexibility, coalescence and processability. In addition, because a compatible plasticizer increases the binder volume, higher pigment/binder ratios can be tolerated. Classes of plasticizers compatible with our dispersions include benzoate and citrate esters, glycols and phthalates. These may be used at 2-20%, depending upon the application.

Compatibility should be tested with each plasticizer. In general, plasticizers are not soluble in water, however, upon mixing they become a dispersed phase by the emulsifying system within the SYNTEGRA polyurethane dispersion and end up partitioning into the SYNTEGRA polyurethane dispersion polymer particles. As a plasticizer is added to a waterborne SYNTEGRA polyurethane dispersion formulation, the polymer particles swell, raising the viscosity of the dispersion. Thus, viscosity rise can be used as a measure of plasticizer compatibility.

Compatibility can also be estimated by careful examination of the dried film properties such as clarity or degree of haziness. In addition, a compatible plasticizer should not exude or bloom to the surface of the dried film over time. Incompatibility of plasticizer can cause surface tackiness, dirt pickup, adhesive bond failure and shortened shelf life.

Coalescing Solvents

During the drying of a SYNTEGRA polyurethane dispersion into a polymer film, the discreet polymer particles must combine to form a continuous film in a process called coalescence. To achieve particle coalescence, the polymer chains must be free to entangle. This requires that the glass transition temperature (Tg) of the SYNTEGRA polyurethane dispersion be the ambient temperature during film formation. In general, polyurethanes have two glass transitions: one at or below room temperature and one greater than 130°C. Due to the low temperature transition, a continuous film can be formed at ambient temperatures, however, to achieve the optimum polyurethane film properties at ambient temperatures, a coalescing solvent may be required to reduce the higher glass transition and give better chain entanglement in the final film.

The best coalescing agents are soluble in both water and the SYNTEGRA polyurethane dispersion polymer, yet will evaporate at a slower rate than water. As the water evaporates to form a SYNTEGRA polyurethane dispersion film, the concentration of coalescing solvent remaining behind increases particle coalescence. Examples of coalescing agents that can be used with SYNTEGRA polyurethane dispersions include N-Methyl-2-Pyrrolidone and DOWANOL* DM (Dow).

Inorganic Fillers and Pigments

Inorganic fillers, also known as extender pigments, are particles that add bulk, reduce cost, provide opacity and color, control rheology and modify specific properties of a coating, adhesive, sealant or elastomer. Typical fillers are calcium carbonate, talc, barytes, clays, silicas, titanium dioxide and carbon black. Key issues to consider when selecting fillers are rheological (thickening) properties, acidity/basicity of surface groups, particle size, reinforcing potential, density and cost. In some cases, fillers containing soluble polyvalent cations (calcium sulfates, zinc oxide) may cause coagulation of the SYNTEGRA polyurethane dispersion.

Achievement of homogeneous distribution of fillers and colloidal stability is challenging and depends on several factors: the surface of the filler particles, the dispersion medium, the type and amount of stabilizer, the compatibility of the filler and the polymer, and the amount of shear mixing. Fillers should be blended into SYNTEGRA polyurethane dispersions slowly, preventing excess shear and de-watering, and to prevent coagulation. Pre-wetting of fillers before blending may also help reduce shock to the SYNTEGRA polyurethane dispersion stabilizer system. In addition, wetting agents such as TERGITOL* 15S20 (Dow) may be used at 0.5-1% to facilitate wetting of fillers.

There is a limit to how much filler can be added while maintaining acceptable properties. Mechanical properties of filled systems are heavily dependent on critical pigment volume concentration (CPVC), which is affected by the packing and size ratio of the filler. Physical properties of filled systems that are above their CPVC tend to deteriorate.

Surfactants/Dispersants

In the production of waterborne polymers and their formulations, surfactants are used for various reasons. Dispersants are a class of surfactants that are used to disperse solid materials into water. In addition to stabilizing polyurethane polymer particles in water, surfactants improve the wetting of substrates and of filler particles formulated into the SYNTEGRA polyurethane dispersion. Dispersants can dramatically reduce the viscosity of filled systems to allow higher filler loading. Surfactants can also have negative consequences in waterborne formulations, causing foaming, reducing adhesion and diminishing water resistance.

SYNTEGRA polyurethane dispersions are stabilized by a combination of nonionic and anionic dispersants. Many formulation additives can be blended into these SYNTEGRA polyurethane dispersions and will, themselves, be dispersed in the water using the dispersant contained in the SYNTEGRA polyurethane dispersion. However, in certain situations, the amount of dispersant may not be sufficient to withstand formulation without destabilizing and coagulating the polyurethane polymer particles. In these situations, the addition of deionized water to reduce the solids may help, especially if fillers are being added.

In other situations, more dispersant can be added to help stabilize the formulation. Typically, 1-2% of a secondary alcohol ethoxylate such as TERGITOL 15S20 (Dow) or an alkylsulfonate such as DBS-60-T (Deforest Enterprises)** can be added to boost the dispersant level. Formulation materials containing cationic surfactants or highly acidic substances should be strictly avoided, as they may interfere with the stabilization system of the SYNTEGRA polyurethane dispersions.

Other Waterborne Polymers

In general, polyurethanes are moderately hard polymers that are most suited for adhesive applications between moderate to stiff substrates. For hard-surface coating applications, a harder polymer modulus will be needed and for sealants, pressure sensitive adhesives or waterproofing membranes, a softer polymer modulus may be needed. As mentioned above, inorganic fillers will increase modulus and decrease the total formulation cost. High-hardness acrylic, styrenic and vinyl acetate emulsion polymers can also be used to raise modulus and decrease costs. In addition to plasticizers discussed above, soft acrylic, styrene/butadiene, nitrile and natural rubber latexes can also be used to drop modulus and lower cost.

Test the compatibility by blending the SYNTEGRA polyurethane dispersion with a small quantity of the other latex first, watching for the formation of coagulation and the stability of viscosity over time.

Cross-Linkers

Polyurethane dispersions are polar thermoplastic polymers that, under certain conditions, may be sensitive to water, polar solvents or high temperatures. This sensitivity can be overcome with the addition of cross-linking agents.

Dow's SYNTEGRA polyurethane dispersions contain reactive groups that can be cross-linked by emulsifiable isocyanates such as DESMODUR DA (Bayer)** or epoxysilanes such as SILQUEST A-187 silane (OSI)** cross-linking agents.

*Trademark of The Dow Chemical Company
**Handle according to manufacturer's guidelines

Emulsifiable isocyanates are reactive, and, therefore, must be added just prior to application. They will limit the pot life of the system to a few hours, depending on the system. Emulsifiable isocyanates are typically used at levels of 1-5%.

In the case of epoxysilanes, the pot life is pH dependent. For one-pack stability, the pH of the system must be between 6 and 8.5. Epoxysilanes will usually be used in levels of 0.5-3%, based on the resin solids of the system. It is necessary to allow the formulation to stand for a minimum of two days after the silane is added.

Biocides

Many water-based formulations can support the growth of microorganisms such as fungi and bacteria. Bacteria can continue to grow even without oxygen resulting in poor formulation performance. Fungi can grow in the end-use product to cause discoloration and odor. Biocides are materials added to prevent microorganisms before they damage the product in the can or end product. Dow's SYNTEGRA polyurethane dispersions are treated for microorganisms by using a biocide. Formulation additives that are derived from proteins, carbohydrates or fatty acids are particularly susceptible to biological attack. Any formulations using these additives can be further protected with additional biocide to provide package stability and stability in use.

Defoamers

During formulation or application of SYNTEGRA polyurethane dispersion coatings, adhesives, sealants and elastomers, foaming may cause concerns. Bubbles may form craters or pinholes in films, or weaken the strength of adhesives, sealants or elastomers. Small amounts (0.005-1.0%) of commercial defoamers such as FOAM BLAST 163 (Ross Chemical)** will reduce this problem. Coalescing agents can also have defoaming properties.

Rheological Additives

Rheological additives are used at levels of 0.5-2% in waterborne systems to control the flow of the formulation during application, and sometimes the adhesive properties of dispersion-based films. Most of these thickeners are polymeric in nature, which allows them to act within the aqueous phase to produce a high viscosity network based upon polar hydrogen bonds such as hydroxyl groups. This rheology is thixotropic. The resultant high viscosity can be reduced upon shearing, such as when the formulation is pumped, sprayed or roller coated. ACRYSOL 6030 and ACUSOL 810 (Rohm & Haas)** are examples of polyacrylate polymer thickeners. In addition to hydrophilic acrylic polymers, hydrolyzed polyvinyl alcohol, hydrolyzed polyvinylpyrrolidone, polyurethane associative thickeners, natural polymers such as starch, casein and alginates and inorganic materials such as fumed silica can also be used to control rheology of waterborne systems.

Other Additives

Ethylene or propylene glycol (Dow) is typically added to waterborne formulations to reduce their freezing point. UV stabilizers in combinations with antioxidants (Ciba-Geigy)** will reduce weathering and yellowing. Wax emulsions (Michelman)** may be used to improve slip and mar resistance of coatings. Silane adhesion promoters (OSI, Dow Corning)** may be used to improve adhesion, especially to glass or ceramic surfaces under wet conditions.

Safety Considerations for Polyurethane Dispersions

Polyurethane dispersions can be safely handled when simple precautions are understood and followed. Material Safety Data Sheets (MSDS or SDS) for polyurethane dispersions are available from The Dow Chemical Company. MSDS are provided to help customers satisfy their own handling, safety and disposal needs, and those that may be required by locally applicable health and safety regulations. MSDS are updated regularly. Therefore, please request and review the most current MSDS before handling or using any product. Copies of MSDS are available on request through your nearest Dow Sales office.

Customer Notice

Dow encourages its customers to review their applications of Dow products from the standpoint of human health and environmental quality. To help ensure that Dow products are not used in ways for which they were not intended or tested, Dow personnel are willing to assist in dealing with ecological and product safety considerations. Your Dow representative can arrange the proper contacts.

The Dow Chemical Company
Polyurethanes
9008 Dow Center, Midland, MI 48674
United States & Canada: 1-800-447-4369
Europe: +32-3-450-2240
Pacific: +60-3-7958-3392
China: +800-600-0015
LAA: +989-832-1426
www.dow.com • www.PUR-CASE.com

Dow Polyurethanes, a leading supplier of polyurethane raw materials, offers one of the broadest lines of polyurethane products and systems in the industry. Dow's raw materials are used in rigid foams, flexible foams, adhesives, sealants, coatings, elastomers and agrifibers, as well as in many other applications. Applications for these products cover a wide range of end uses, including cushioning for furniture and bedding, carpet backing, automotive seating and instrument panels, office furniture, flooring, and insulation for appliances, sheathing and roofing.

Living.
Improved daily.

Printed in U.S.A.
Published June 2003

Form No. 109-01632-0603XCRCG
CH 381-258-E-0603