

# Hollow Glass Microspheres for Plastics, Elastomers, and Adhesives Compounds

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## 11 Mixing and Dispersion of Hollow Glass Microsphere Products

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Hollow glass microspheres have helped to revolutionize the area of polymer fillers with an extensive variety of glass microsphere offerings. A diversity of diameters and isostatic collapse strength varieties are available for a range of mixing, processing, and end-use solutions. The advantages offered by hollow glass microspheres are many, yet due to their unique aspect ratio, density, and chemical properties, they must be handled differently than typical mineral fillers, particularly in storage, formulating, metering, mixing, pumping, and weighing. Due to their ultra-low-density, hollow glass microspheres occupy up to 20 times the space for a given weight of a traditional filler. Also, due to their thin-shelled hollow nature, they may be broken by compression at constrain points, shear under areas of tight clearance, and impact at turns in transfer equipment. As a result of the above, one must beware to minimize the compression, impact, and shear forces upon the hollow glass microspheres to ensure they are not damaged during processing and transport.

## Hollow Glass Microsphere Transport to Mixer

The first step involved in processing with hollow glass microspheres is getting them to the resin or polymer matrix. Dispensing hollow glass microspheres can be challenging, as using traditional dispensing machines can result in a significant glass microsphere breakage rate. Factors which impact the breakage rate when transporting hollow glass microspheres include material agitation methods, material viscosity, choice of pump, and temperature while incorporating hollow glass microspheres.

One must be cautious of the electrostatic forces encountered when transporting hollow glass microspheres; piping should be grounded to ensure static control. Once grounded, the main concern of transporting and mixing hollow glass microspheres is breakage. To minimize breakage a number of steps are suggested: introduce hollow glass microspheres in a pulselike flow pattern into the vortex below, as well as introduce hollow glass microspheres as late as possible in the mixing process to minimize the chance of breakage. To these ends, a high flow—low-shear mixer should be selected, and it includes anchor, bar turbine, horizontal hydrofoil, pitched blade, plow, propeller, and multishaft mixers. What these types of mixing devices have in common are low dispersive and high distributive mixing characteristics. The key is to avoid use of high shear, as this can cause damage to hollow glass microspheres. Due to the small size and low-density nature of hollow glass microspheres, one should use a dust collection system when transporting hollow glass microspheres into the mixer, as well as in other areas of potential contamination or glass microsphere escape.

When transporting hollow glass microspheres, wet or dry (i.e., before or after mixing), one should use one of the following types of pump: double diaphragm pump, non-intermeshing gear pump, or peristaltic pump. These pumps are ideal because they generally allow for high glass microsphere survival rate at the pump's maximum hydrostatic pressure. One must be sure to select a glass microsphere which has great enough strength to survive the pumps hydrostatic pressure; centrifugal, gear, lobe, progressive cavity, or close-contact intermeshing-type pumps should be avoided, as they may result in significant glass microsphere damage.

Other methods of transporting hollow glass microspheres into the product involve the use of seals, such as a diaphragm pump, or a hose with a stinger. These schemes provide an effective way of moving hollow glass microspheres to the mixer while reducing hollow glass microspheres in the atmosphere around the mixer. A proven and preferred method is to transport hollow glass microspheres into a silo above the mixer and use a rotary valve to control the rate of addition of hollow glass microspheres, such that the mixer is not overfed.

When processing, it is important to avoid pressures greater than that for which the selected hollow glass microspheres are rated. One should avoid high-shear processing with equipment such as high speed dissolvers, roll mills, and ball mills, or processes which may generate point contact shear, such as gear pumps or three-roll mills.

## **Fundamentals of Dispersion**

To have the best understanding possible for handling and mixing hollow glass microspheres, one must first grasp the fundamentals of dispersion. A complication which arises from simply vigorously mixing materials is that the very fine particles (sometimes microscopic in size) still maintain electrical and molecular attraction, and/or mechanical bonding. These fine particles tend to lump together and form agglomerates which no amount of mixing will break. An aggregate (or agglomerate) is composed of a group of particles that are strongly adherent and can be broken down only by the application of relatively strong mechanical forces. In the days before dispersers, stone mills were used to physically grind dry materials into a fine powder. Subsequently, ball or pebble mills were used; one can envision these types of mixers as a type of spray paint can, where the marble within the paint can is used to homogenize the product. The balls or pebbles fall through the product, impacting the agglomerates and breaking up lumps, and thereby coating (or "wetting") each basic crystal so that it does not stick to other particles. This process results in a smooth mixture. A further advancement was made by the introduction of roller mills, which grind the agglomerates until they are reduced to their basic particle size or smaller, and wet them to ensure they do not recombine. The ball, pebble, and roller mills break up agglomerates as well as grind pigments and other particles in the product into smaller basic sizes or crystals.

The above processing techniques were an advancement in their day, but they did take a very long time to produce a smooth product, sometimes in excess of 24 h. With the advent of the disperser, the deagglomeration process could be accomplished much more rapidly, and resulting in a smoother, more uniform end product.

The basic part of the disperser is the impeller, which is a thin disc with carefully designed teeth distributed radially about the circumference. The impeller is much more than a mixer; its hydraulic action tears particles apart and disperses them uniformly throughout the product. This work is done with two actions: firstly, particles hitting the impeller are broken apart, or deagglomerated; secondly, the intense turbulence surrounding the impeller causes particles to hit each other with great momentum and inertia. The energy of this impact physically breaks apart agglomerates. This area of immense turbulence is at the tip of the blade and extending out several inches, and is known as the zone of attrition (the location and size of this zone varies with impeller design and size). Beyond the turbulent zone, the product is processed and thoroughly mixed by the laminar flow created by the impeller. The flow separates upon impact with the tank walls, ensuring complete circulation of the batch thereby effectively homogenizing constituents. While the above processes are imperative to guarantee a homogeneous product, these forces can be damaging to fragile hollow glass microspheres, and should therefore be completed before the addition of constituents which do not require breakup, or which may be shear-sensitive.

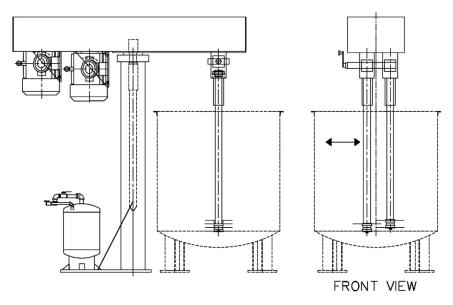
It is sometimes necessary to heat the product within the tank to facilitate a chemical reaction; this can be accomplished by increasing the rate at which the impeller rotates, or by utilizing a jacketed tank.

85-90% of dispersers are used to deagglomerate formerly ground pigments or solids, and subsequently disperse these solids throughout products such as chemical compounds, inks, paint, paper coatings, plastics, and rubber compounds. These pigments or particles, as noted above, were previously ground into fine particles; however-especially when dry-the particles tend to come together in a lump and stay as such (i.e., agglomeration) until they are pulled apart again (deagglomeration). This is due to an array of attractive forces, including Van der Waals forces, adhesion, interfacial tension, etc. The intense shearing and turbulence generated by the disperser tears apart these lumps and disperses them into the coating, ink, paint, or plastic at an exceptionally rapid rate. In many cases, a product made with bulky older equipment could take upwards of 24 h; the same product could be made better in 40 min with a modern, compact disperser such as a dual-shaft quad-blade disperser with twin motors (see Figure 11.1). This type of dual-shaft mixer imparts 30% more energy into the batch due to the blades rotating in opposite directions at the point which they overlap, creating opposing flows which baffle each other. This allows for the blades to run faster while avoiding cavitatingthe formation of an air pocket which could damage the product, as well as the dispersion equipment.

A second use for dispersers is to grind off fine particles from a solid mass, such as a resin. Lacquers—made from solid resin combined with a solvent—are produced in this fashion, and can be made quickly with a disperser. Approximately 5% of dispersers are used to grind and peel away solid material which is then dispersed.

The remaining roughly 5% of dispersers are used for food cutting, mixing foodstuffs into a smooth, homogenized paste. An impeller with serrated edges and sharp angular teeth is used to create the necessary turbulence, shearing, and mixing motions—which are similar to those of a standard impeller used for manufacturing applications. This type of cutter blade is sometimes used to break up chunks of resin in the making of lacquer, as previously mentioned.

There has been a trend in the mixing and dispersing industry toward greater uniformity and consistency of products. A dispersion equipment manufacturer has developed systems that monitor, report, and track historical information to greatly aid in documenting and certifying



**Figure 11.1** A basic design for a dual-shaft disperser. Two motors allow each shaft to rotate at independent speeds. Blades can be "open" or "closed" (see front view) to change intensity of shear, size of vortex, and flow/mixing patterns. *Courtesy of Myers Engineering, Inc. (Myers 850 Series).* 

batches. Removal of the human element—and thus variability from one operator to the next—from the production process results in vastly improved product consistency from batch to batch, or from one production facility to another. By custom designing a mixer, one can better ensure repeatable results. The location and rate of additions can be more exacting with a custom machine, and is incredibly important for interbatch homogeneity.

As a case study, a mixer and disperser manufacturing company's customer, a manufacturer of mastics at five sites throughout the United States, had a corporate-level issue with batch production. The plant in Texas was requiring 45 additional minutes to produce a batch, as compared to a plant in Southern California which produced the batch in the desired time frame. The disperser company's technical team was called upon to determine the reason for this delayed mixing. The plant in Southern California was adding their calcium carbonate through a silo immediately upstream of the high speed vortex. The calcium carbonate then did not sit on the batch very long; it rotated only 90° before being pulled into the high-shear zone. It was discovered that the manufacturing

plant in Texas was adding calcium carbonate to the opposite side, downstream of the vortex, 270° from being pulled into the vortex. This forced the calcium carbonate to travel three-quarters of the way around the tank before entering the vortex, allowing the calcium carbonate to sink and settle, and leading to agglomeration. The agglomeration was the cause of the excess mixing time; to break up the agglomerates which formed in a short span of time—less than 2 min—required a significantly lengthened mix time. This demonstrates the importance of location of addition, and its effect on mix time, as well as homogeneity of final product. With the mixer and disperser manufacturer's intelligent maintenance system, one can record when additions were made, as well as noting the location of additions, a valuable tool in identifying discrepancies between batches and greatly aiding in product consistency.

A commonly used impeller type is known as an axial pumper (see Figure 11.2). This type of impeller is typically mounted higher up on the shaft and used in concert with a standard impeller design at the base of the shaft. This configuration is useful when mixing highly viscid materials which require additional force to be pushed downward toward the disperser blade, or when a tank is especially large or deep. An axial pumper can help to draw material in from the surface; there are many blade options available, and careful consideration of each will ensure maximally effective results. Holding the impeller is a finely turned and ground shaft. The shafts are commonly between 1 and 5 in in diameter, depending upon the size of the machine, the specific gravity, and the viscosity of product it will disperse.

For thorough dispersion, an impeller should be roughly one-third the diameter of the tank it is mounted in, and roughly one blade diameter from

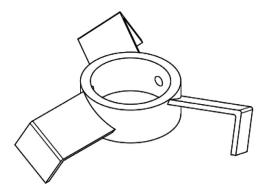


Figure 11.2 Axial pumper impeller. Courtesy of Myers Engineering, Inc.

the bottom of the tank. The impeller should not be more than three blade diameters from the top of the batch (depth once all components are charged into tank), and no less than one-half a blade diameter distanced from the top of an uncharged, premixed batch. One must note that these guidelines are generalities, and that impeller sizing and position will vary with the viscosity of the product to be dispersed.

The shape of the tank used in mixing will influence the flow characteristics of the product as it is moved by the impeller. Cylindrical tanks are preferred over square or rectangular tanks, as there are no corners which may cause the product to slow down or become entrapped. Square tanks are sometimes used in material let down, when the dispersed material is thinned with a solvent and tinted for preparation in becoming the final product.

Most dispersers are equipped with a tachometer to show the revolutions per minute (RPM) of the shaft. However, for an accurate indication of the force applied to the product, the shaft speed is typically translated into tip speed of the impeller, and denoted in feet per minute (FPM). This is calculated by multiplying the diameter, D, of the blade (in feet) by the RPM of the shaft, and multiplying by  $\pi$ . The practical relevance of this is that a 4-in diameter impeller will have a tip speed of roughly 5000 FPM when the shaft is rotating at 5000 RPM, whereas a 18-in impeller will have a tip speed of 5000 FPM for a shaft rotational rate of 1062 RPM.

**Example 1**: A process requires a blade tip speed of 5000 FPM for the desired level of dispersion and distribution of all components. What shaft RPM would be needed for a 4-in diameter blade? An 18 in diameter blade?

Tip Speed (FPM) =  $D \times \pi \times \text{RPM}$ 5000 FPM =  $(4 \text{ in})/(12 \text{ in/ft}) \times 3.14 \times \text{RPM}$ RPM = 4777 5000 FPM =  $(18 \text{ in})/(12 \text{ in/ft}) \times 3.14 \times \text{RPM}$ RPM = 1062

Because the 18-in blade is 4.5 times the diameter of a 4 in blade, the 4-in blade must have a shaft rotational rate 4.5 times greater in order to achieve the same tip speed.

As can be seen by the above example, it is critical that the FPM tip speed be used instead of RPM shaft rate to ensure that the impeller is moving at the correct speed to provide the necessary dispersion.

Another option for measuring the amount of work done by the impeller is the use of a load meter. When used with a disperser, a load meter provides a tremendous amount of data about the rheological characteristics of the product, such as thixotropy or shear thinning, dilatancy or shear thickening, and the viscosity of a product as it is being manufactured, as well as reducing the amount of time necessary to take a sample to a laboratory in order to test the viscosity. As blades age, they become worn down and thinner; a common problem—and cause—of a poorly mixed batch is the use of a worn-out dispersion blade. The blade itself is not the problem, so much as the operator assumption that a worn blade will transfer energy to the product in the same manner as a new blade.

One can envision, for example, your hand stuck out of a moving car window. When your palm is facing the wind, you can feel the force exerted on it; when you drop your palm so it is parallel with the ground the force is reduced. A thinned blade is like your palm turned toward the ground; less force is "felt" by the blade. The force in question is the pumping or dispersing action of the impeller.

Having a load meter helps to track blade wear; when the load is noticed to be decreasing over time, one can mix longer and/or at a higher RPM to achieve the desired dispersion. The majority of individuals in the industry look only at RPM while mixing, but with the use of load cell data in conjunction with RPM, one can maintain more consistent results. In applications where blade wear happens quickly, it is more effective to maintain a consistent load while varying RPM. As the blade wears, the amount of work it does is reduced, so by holding the load constant, you better control the amount of work being applied to the product, because the amount of work being done is directly related to the load.

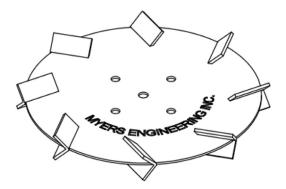
## Mixing and Dispersing Hollow Glass Microsphere Products

The incorporation of hollow glass microspheres into an epoxy system requires different mixing techniques than heavy-filled epoxies which incorporate typical fillers (such as talc, calcium carbonate, fumed silica, etc.). The dispersion of heavy fillers necessitates the use of high-shear impellers which would break the hollow glass microspheres which are intended to lighten an epoxy. In the past, microspheres did not have the crush strength that current technologies do, and were much more susceptible to breakage in traditional mixing and dispersing applications. However, hollow glass microspheres must still be incorporated with care, as they are more fragile than standard fillers, and therefore are susceptible to damage through the use of high shear. With advances in technology, dispersion equipment manufacturers and suppliers have been able to develop machines which can aggressively disperse these dense fillers as well as gently mix hollow glass microspheres—with minimal glass microsphere damage—at a variety of product viscosities.

## Radial Pumper ("Super Pumper")

Various impeller designs and configurations are used, depending on the batch viscosity and processing requirements for components within the batch. Unfortunately, despite all the technologies currently available, most companies—regardless of how big or small—do not properly apply the different types of dispersion. More than 90% of people within the industry believe that a proper tip speed for a disperser is 5000 FPM. While this speed is required for particle size reduction and deagglomeration, it is by no means necessary or efficient when used in blending applications, or in applications that contain shear-sensitive components. Blade selection is also not well understood, and there are types of blades that should be used for one type of process yet not another. For glass microsphere-filled products, it is essential to minimize shear forces, which can be damaging to the hollow glass microspheres and ultimately lead to an increase in product density from theoretical ideals.

The radial pumper impeller (see Figure 11.3) is an exemplary choice when incorporating microspheres into thixotropic and/or viscid materials. The basic principle behind the radial pumper impeller is that the angled teeth sling the material outward, continually accelerating the perpetual batch movement; the teeth do not shear the product.



**Figure 11.3** Radial pumper impeller design. Forward facing teeth accelerate product with minimal impact shear. *Courtesty of Myers Engineering, Inc.* 

By creating perpetual batch movement, viscid material (from 10,000 to 150,000 cP and above) can be thoroughly mixed while maintaining a lowshear environment. Forward facing teeth provide longer contact between the impeller and product captured in the flute; this results in a higher velocity or product energy each time the hollow glass microspheres are in contact with the impeller surface. The hollow glass microspheres remain in contact with the impeller surface longer, developing a higher velocity and energy transfer, which enables the mixer to run slower, resulting in less initial impact force upon the hollow glass microspheres. This blade configuration allows for a rolling vortex to be achieved without the damaging forces of traditional high speed dispersion.

The radial pumper physically pushes the product outward, creating an area of low pressure underneath the shaft, as product rushes back to fill in the void in an attempt to equalize pressure and product distribution. This low-pressure void is a good place to add hollow glass microspheres into the batch, especially when the mixing tank being utilized does not have a good seal. When hollow glass microspheres are incorporated subsurface in this manner, they are thoroughly assimilated into the liquid product. This enables rapid blending without exposing hollow glass microspheres to the atmosphere, a potential health and safety hazard. The material within the tank acts as a filter, by wetting out the hollow glass microspheres so they cannot become airborne.

A common complication caused by addition of hollow glass microspheres atop the batch is that the initial charge of hollow glass microspheres become wetted (i.e., are absorbed into the surface), while subsequent amounts of hollow glass microspheres "flour" the surface of the batch. Once the surface becomes fully saturated with a dry substance such as hollow glass microspheres, it can no longer draw in new material. This is why one should add hollow glass microspheres at the vortex, so they are quickly drawn into the product and do not sit on the top of the batch, preventing incorporation of later additions of hollow glass microspheres, or leading to agglomeration.

Their microscopic size, along with their low aspect ratio, leads to the hollow glass microspheres behaving as ball bearings upon the top of the batch, effectively rubbing against one another while doing little in the vein of incorporation and assimilation. Due to their low density, the hollow glass microspheres are not readily pulled downward into the batch by their own mass; and due to their sensitivity to shear, one cannot utilize mixing speeds which would easily incorporate denser fillers such as talc, calcium carbonate, or glass fibers. To combat this dilemma, one should integrate hollow glass microspheres in the vortex created by the dispersion blade atop the product; or if subsurface addition is preferential, incorporate hollow glass microspheres at the low-pressure void created directly under the blade and shaft assembly. Wherever one chooses to incorporate hollow glass microspheres, it should be at a location such that the hollow glass microspheres can be directly injected into the region of laminar flow (i.e., not an area of low or no velocity).

### High-Shear Disperser Blade

High-shear dispersion blades (Figure 11.4) can be used when good dispersion and deagglomeration of dense fillers and pigments is needed, with a variety of product viscosities, and when shearing of the product is required. A typical periphery speed for a high-shear dispersion impeller is 5000 FPM; this speed causes damage to hollow glass microspheres, but is required to properly break down other fillers within the batch. The high-shear dispersion blade utilizes the principles of point shear and pumping to mix higher viscosity products.

Pumping is the physical act of the impeller moving product aside as the impeller rotates. This process centrifuges the product outward in a radial direction until it reaches the wall of the tank, at which point the flow is split horizontally into two; this forces the flow of material up and down the side wall of the tank. The upward flow of material "wells" up the side of the tank to the surface where it loses velocity, and then rolls back to the center of the vortex where it then falls to the disperser blade to begin the process all over again. The downward flow continues until it hits the bottom of the tank, where it then changes flow direction—picking up any undispersed solids that have settled or stuck to the bottom of the

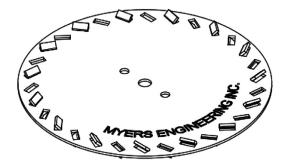


Figure 11.4 An illustrative high-shear dispersing blade. Various mixing, dispersing, and flow characteristics can be obtained by augmenting the number, size, and location of "teeth." *Courtesy of Myers Engineering, Inc.* 

vessel—while moving to the low-pressure zone underneath the dispersion blade. The material is then drawn upward where it is reintroduced to shear, thus continuing this recursive process. The key to this configuration is perpetual batch turnover, which continually reintroduces the particles to the high-shear zone.

## Mixing Dynamics and Dispersion Blade Placement

Proper blade placement is critical to obtaining good dispersion and a homogenized mixture of ingredients. The ideal distance from the bottom of the mixing tank to the blade is typically between 1/2 and 1 times the blade diameter, depending on the substance being mixed, its viscosity, and the tank diameter to liquid height ratio.

The further down the blade is within the tank, the more work the blade must do to move product at the top of the batch. This will lead to destruction of hollow glass microspheres, as they are being ground at the bottom of the batch—where the rapidly rotating dispersion blade is creating high shear—and not fully being incorporated at the top of the batch. A limited-lift style mixer can remedy this issue; as the shaft can be raised or lowered, the position of the impeller—and hence the location of the vortex—can be altered. The lack of mixing at the top of the batch can be due to many things, such as a viscous fluid which does not readily transmit energy and/or movement, or due to the lightweight nature of hollow glass microspheres not sinking into the batch by their own gravity.

In utilizing a lift style mixer, the dispersion blade can be raised closer to the surface of the batch; this maintains a vortex for efficient addition of hollow glass microspheres while putting less energy into the product, and thereby minimizing glass microsphere damage. Once a certain volume percentage (approximately 30% by volume) of hollow glass microspheres is added, the specific gravity of the product is reduced to a point where the vortex is reduced or completely eliminated. Placing the dispersion blade at the proper location and depth for a specific application will minimize mix time, glass microsphere damage, and energy consumption. See Figure 11.5 for an example of a standard tank and blade configuration.

Mixing of viscous systems includes two main mechanisms: dispersive and distributive mixing. The goal of dispersive mixing is deagglomeration, or attrition of particle size. The purpose of distributive mixing is to produce a homogeneous compound, where particles are evenly distributed

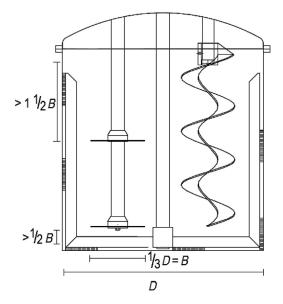
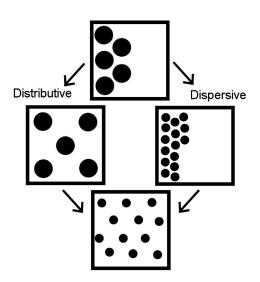


Figure 11.5 Standard ratios used in sizing a disperser.

in the resin matrix, as the nomenclature implies. Dispersive mixing is an intensive process, aimed at reduction in agglomerates. Distributive mixing is an extensive process focused on spatial uniformity. When one thinks of mixing and dispersing equipment, generally both distributive and dispersive mixing are required to achieve the desired output. Figure 11.6 illustrates each type of mixing, and the end result when the two processes are combined.

Dispersive and distributive mixing are the main means by which complex solutions of solids and viscous liquids are formed. Dispersion is the process of breaking down aggregates and/or agglomerates down to their elementary particles. Aggregates are clumps of particles which are primarily joined at their faces, forming a mass which has significantly less surface area per volume than the base particles. Agglomerates, on the other hand, are joined at their edges and corners, resulting in a volume that has nearly the same surface area as the combined surface area of constituent particles. Based on this geometrical difference in structure, aggregates are much more difficult to break up than agglomerates; aggregates are much stronger due to the decreased surface area of the solid, in conjunction with greater intermolecular forces.

For hollow glass microspheres, a blade with higher product displacement than product dispersion is ideal. For example, a radial pumper impeller will displace the product while reducing shear, as compared to



**Figure 11.6** Schematic representation of distributive and dispersive mixing processes. The two modes combined result in a homogenized product with agglomerates reduced to primary particle size.

a high-shear dispersion blade. Product displacement is related to tip speed of the blade; however different impeller configurations will transmit energy differently, and necessitate varying shaft rotational rates and tip speeds. For example, aluminum paints should be mixed at a tip speed of 1200–1800 FPM; this ensures thorough mixing, while minimizing destruction of aluminum flakes. An analogy can be drawn between aluminum paints and glass microsphere-filled liquids and pastes; in that a homogeneous mixture is desired yet there are materials in the product that may be damaged if a high tip speed is used during mixing. For such an application, a radial pumper impeller is desirable, as it moves the batch and provides adequate homogenization while reducing shear forces, in comparison to a high-shear disperser blade.

## **Mixer Design Options**

A variety of single, dual, tri, and quad shaft mixers are available for a multitude of applications and product viscosities. Single shaft radial pumper impeller mixers are best suited to low-viscosity glass microsphere products, such as paints and coatings. High viscosity mixtures (such as caulking compounds and putties) are thoroughly mixed with minimal glass microsphere damage, utilizing dual- or tri-shaft styles of mixers.

## Single Shaft Dispersers

Single shaft mixers and dispersers utilize one of a variety of dispersion and mixing blades to quickly and efficiently combine materials for a uniformly dispersed product. A standard disc impeller blade (see Figure 11.4) creates laminar flow to disperse material beyond the edge of the blade tip for particle size reduction. The alternating teeth create high shear radially about the impeller; this is where dispersive mixing takes place.

## **Dual- and Tri-Shaft Dispersers**

Multishaft dispersers combine multiple blades, augers, and/or sweepers within the confines of a single tank to maximize usefulness, productivity, and reduce multiple handlings of a batch to obtain a homogenized end product. Dual- and tri-shaft mixer designs typically include one impeller blade, with the other shaft(s) comprised of a helical auger, a helical (ribbon) sweeper, and/or sweepers with fixed or articulated wipers.

Multishaft dispersers incorporate multiple blades, using different speeds and flow patterns so that each can develop maximum results at each phase of the batch. A mixer and disperser manufacturer produces mixers which use two to four different speed ranges with an appropriate blade to maximize mixer performance, minimize batch time, cleanup, and waste. As discussed in the basics of dispersion, most products start with a high speed dispersion impeller to disperse on a fine level, much like a blender.

As the complexity of the product increases through variations in viscosity, temperature requirements, specific gravity, evacuation of air, pressurization, and the sensitivity of the raw material being added, the following additional shafts may be incorporated in the design of a mixer.

The low-speed shaft is a typical secondary shaft that is added to the representative disperser. In bygone days this was done to help material flow as the viscosity and specific gravity became too great for a single shaft. In subsequent years, the tanks became jacketed for heating and cooling. When this was done there was a problem in that the material that was stuck to the side of the tank would become an insulator, thus preventing the remainder of the batch from necessary changes in temperature. At this point in time, risers and wipers have been added to the sweep blade of the low-speed shaft. Functioning much like a spatula, the wiper removes the material from the wall of the tank, allowing fresh material to contact the wall of the tank for adequate heat exchange and thorough distributive mixing.

Sweep blades come in several types. The "low profile" blade is primarily used for the sole purpose of wiping the walls of the tank. Due to this blade's low profile design, it does not move much material and therefore does not require a great deal of horsepower, keeping the capital cost—as well as operating cost—of the equipment down. Conventional peripheral speed for a blade of this type is on the order of 400 FPM.

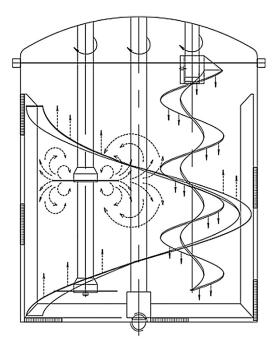
The next step up is a "pitched angle" blade. This blade is slightly stiffer than the previous. The pitch of the riser gives this blade the ability to provide a greater displacement, thus moving more products forward. As the product becomes more viscous, this forward movement of the mixture ensures that the high-shear zone is perpetually fed with new material. Tip speed range of this blade is 400–600 FPM.

Next we have the "box angle" blade. Shaped like a triangle, this blade is extremely strong and is used when the considerable viscosity could cause a typical sweep blade to twist. This blade also has a large displacement and will move product more aggressively than a low profile design.

The final low-speed blade is a helical sweep. This blade has the strength of a box angle blade, while incorporating a helical flight which runs the perimeter of the tank. The purpose of this blade is to assist in lifting the material up the side of the tank and bringing it to the surface of the batch. As the material moves to the surface, it creates a void at the bottom of the batch, while simultaneously causing the material from the center of the mixer to be moved out to the wall of the tank, where it will be exposed to heat transfer and be lifted to the surface, completing one iteration of the this cyclical process. This blade is a superlative component in adding lowviscosity-or low density-materials. In the case of hollow glass microspheres, the gentile folding action will work the hollow glass microspheres into the batch and mix them evenly from top to bottom. When mixing hollow glass microspheres, mixers can utilize a dualdirection blade to engage the wipers only when wiping is absolutely essential, as the close tolerances essential to effective wiper action will grind the hollow glass microspheres, thereby destroying them.

A helical—or ribbon—sweeper (see Figure 11.7) functions similarly to a sweeper with wipers, as described above, yet with the added benefit of overturning the product as it rotates. The ribbon sweeper lifts the product upwards as it rotates, which thereby causes the material to fall back down upon itself in the center of the batch. This is a useful shaft to incorporate into the design of a glass microsphere-product mixer, as it works the hollow glass microspheres into the solution without the damaging effects of high energy.

Wiper blades are typically made of nylon, micarta, or teflon. Wipers are effective for homogenizing a mixture, as well as efficiently transferring heat away from the shaft and outward toward the outer wall of the mixing tank. However, wiper blades, by their intent and nature, have extremely



**Figure 11.7** Typical blade configuration of a multishaft mixer. Flow lines illustrate the various functions served by each blade. Blade type, front left-to-right shaft: twin high speed disperser blades, low-speed sweep with articulated wipers, and intermediate speed helical auger.

close contact with the sides of the tank, and may cause hollow glass microspheres to be crushed or damaged as they move product away from the wall of the tank. To minimize glass microsphere casualty, an articulating wiper blade sweeper should be utilized. As an illustrative case, the sweeper can rotate clockwise (employing the sweeper wipers) when hollow glass microspheres are not yet incorporated, and good heat transfer is desired. Once hollow glass microspheres are added to the product, the sweeper is then made to rotate counterclockwise, disengaging the wiping action of the articulated wipers; this allows for good mixing while ensuring that hollow glass microspheres are not damaged in the process of their addition to, and incorporation within, the batch. The sweep blade still rotates to provide distribution, but without the wipers engaged there is ample clearance so as to not damage the hollow glass microspheres.

The selection of intermediate speed blades comes in two ways: first, a reduced speed disperser, known as a blender. Running between 3000 and 4200 FPM, this range will provide good homogeneity during mixing. As

a result of the reduced speed range, one can get more work done with a lower horsepower, saving limited energy resources.

The bulk of the intermediate speed impellers are in the 800–1400 FPM range. One example of this is a gate blade, which functions similarly to an egg beater. This blade will work the material by stretching it much like a taffy mixer. This blade is not effective when the product becomes high in viscosity or when the specific gravity falls below 0.8. When this happens, the gate traps a ball of material in the center of the blade which will not be subjected to any vertical movement. By itself, the gate only works the material, and does not offer any vertical benefit.

Turbine blades will offer some vertical movement, as well as some working of the material in the impact zone. A turbine blade offers better mixing than a gate blade, while being less aggressive than a dispersion impeller. For this reason, in the last couple of decades, this has been a common method for incorporation of hollow glass microspheres.

Next is an auger, which typically has a pipe in the center of the flight for support. While this is a preferred design for some products with high viscosity—due to the design which provides extra strength—it is hard to clean and will "pack" with material. To understand the packing concept, visualize the accumulation of mud or snow in the tread of a tire. The auger can become filled with a ball of material, inhibiting proper function.

A helical auger is similar to the auger, but does not have the pipe in the center (see right-hand side of Figure 11.7). Strength lost by the removal of the pipe in the center is made up for by building the flights out of heavier material. With an open center, this blade is much easier to clean. As the blade surface comes in contact with the material, it presses the material down into the batch. As this happens, some material slips to the outside diameter (OD) and inside diameter (ID) of the flight. Unlike the full auger, the material that slips to the ID hits the center of the auger where it is trapped and cannot get out without being pressed to the bottom of the tank. The cavity that is created in the center of the helical auger will rapidly fill with hollow glass microspheres; because the hollow glass microspheres cannot escape the center of the blade without mixing material, this blade is the absolute best option for highly-filled or higher viscosity material that contains hollow glass microspheres. This blade also offers a great advantage for de-gassing of material. When the blade is run in reverse, it pulls the material up from the bottom of the mixer and allows it to fold out on the surface. This action of folding out (as opposed to "folding in") reduces the surface tension of the material and makes it easier to release the micro-sized air bubbles. Application of vacuum expedites this process, as larger bubbles of air can be transmitted to the top of the batch and air removed more rapidly.

#### 11: MIXING AND DISPERSION OF HOLLOW GLASS

Aside from the upward drive of the ribbon sweep, dual- and tri-shaft mixers can be equipped with an auger which delicately drives the hollow glass microspheres downward. The helical auger gently opens a void at the top of the product batch which hollow glass microspheres can fall into, being deeply incorporated into the mix, and minimizing the problem of the hollow glass microspheres "flouring" the top of the batch. The hollow glass microspheres cannot escape, thus they are folded and worked into the mixture; this creates good glass microsphere integration with the rest of the material. Figure 11.7 shows a multishaft mixer which incorporates dual high-shear dispersion blades on a single shaft, a ribbon sweep, a helical auger, and scrapers. The advantage of a multishaft disperser is the generation of a variety of streamline and flow patterns within a single tank. For this reason, improved homogenization can be achieved in a shorter time frame, with less equipment, and less product handling.

The versatility of a tri-shaft design allows one to accomplish thorough dispersion of polymers and additives, and then shut down the high-shear impeller when ready to add hollow glass microspheres. For high viscosity applications, this system is many times more efficient and effective than any other mixer; other systems may require moving a batch one or more times to obtain a homogeneous mix of all components of the product. Henceforth, a dual- or tri-shaft mixer can eliminate the need for double handling of the material. For example, in the past, products have been compounded by creating the dispersion base on a dissolver, then transferred over to a sigma (or paddle) style mixer. This reduction in handling and number of steps to create a batch has lead to an increase in output and a decrease in square footage demand on a mixing plant, increasing the efficiency, productivity, and profitability of a compounding facility.

Another mixing option which can improve disperser safety is to use a sealed—or enclosed— mixer, thereby reducing operator exposure to glass microsphere inhalation. All mixers can be either atmospheric (i.e., without a lid, or, with a lid that does not change the pressure within the vessel), or sealed, and thus capable of having vacuum applied. A sealed tank allows for inerting the atmosphere within the tank (e.g., with nitrogen or other nonreactive gases) and reducing the pressure within the tank to facilitate batch production. Pulling vacuum on a sealed tank is an efficient means of transporting hollow glass microspheres into a product, either subsurface or at the top of the batch. With hollow glass microspheres especially, it is important to direct their flow into the vortex or void created at the top of the tank; this minimizes "floating" and potential agglomeration. A sealed tank can also be used to raise the pressure, which can be useful in aiding the feeding of pumps. It is important to pump the glass microspheres in at a rate which they can be incorporated into the batch, otherwise overfeeding of the batch may result. Overfeeding the mixer can lead to the necessity of longer mix time, and consequently, the damaging effects of mixing action on hollow glass microspheres. To this end, it is very important to add hollow glass microspheres quickly and efficiently to minimize shear forces they experience. In general, a good practice is to add hollow glass microspheres toward the end of batch agitation to prevent prolonged exposure to the mixing process. In summary, add hollow glass microspheres once dispersion is complete, obtain a homogeneous mixture with the hollow glass microspheres as quickly as possible, and discharge the batch.

Certain styles of mixers and dispersers should be avoided when hollow glass microspheres are to be incorporated into a product. These include, but are not limited to, planetary, double planetary, and horizontal mixers. Planetary and double planetary mixer designs rely on close contact between disperser blades to thoroughly mix the product by shearing it. This can be problematic, as it may result in significant glass microsphere damage due to the tight clearance of blades rotating opposite of one another, which creates high shear. Planetary and double planetary mixers tend to mix the product in a horizontal fashion, meaning that there is primarily mixing and dispersion in the lateral direction. This depth-striated mode of mixing does not quickly incorporate hollow glass microspheres, contributing to a longer mix time, and an increased risk of glass microsphere damage. Horizontal mixers use a more gentle folding over of the product, but this style of mixer can be difficult to clean, and the product can leak out of wearing seals at the ends of the mixer.

## Difficulty in Mixing of Hollow Glass Microsphere-Filled Products

When mixing liquids of vastly differing viscosity a problem arises, in that the mixing will take longer than with liquids of similar viscosity, as well as the necessity of more energy being applied to achieve a homogenized dispersion. An analogy can be drawn between a viscous solution of resins and hollow glass microspheres. Hollow glass microspheres, although a solid, exhibit flow characteristics similar to inviscid liquids, particularly when fluidized, as during transport to a mixing vessel. If one considers the fluidized hollow glass microspheres the "thin" liquid, and the resin or composite matrix as the "thick" liquid, it can be seen that mixing will not readily take place. In addition to this correlation, it is noted that the mixing of floating solids (i.e., lower in density than the liquid they are added to) requires greater energy input than the mixing of neutrally buoyant or sinking solids [1].

Current literature and research is lacking in the area of dispersion of floating solids, especially solids of small size. For a more thorough understanding of mixing of hollow glass microspheres, additional advances in the area of their specific viscosity, rheology, and flow and dispersion characteristics in matrices of moderate to high viscosity must be investigated.

As stated by Atiemo-Obeng et al. [2], "solids that float without agitation include solids that are less dense that the liquid, dense solids with trapped gas, and solids that are difficult to wet." [2]. hollow glass microspheres exhibit all three of these dispersion difficulties: they are composed of soda-lime borosilicate glass which is more dense than the matrix they are combined with, yet due to their "shell thickness" and entrapped gases, are actually less dense than the matrix; being made of glass, which is a highly non-porous substance, they do not truly "wet" in the same sense that a clay, talc, or calcium carbonate would wet; and are therefore difficult to wet and incorporate into a product.

In the incorporation of solids, more than just the chemical and physical properties of a material is of importance. Atiemo-Obeng et al. [2] state that "both average size and the particle size distribution are important properties." Hollow glass microspheres come in a multitude of different average sizes and size range variance. This ensures that the size of an average glass microsphere, as well as the complete scope of diameters encompassed, will be suitably incorporated in the dispersion process, with minimal breakage. The greater the size distribution, the more difficult it can be to homogenize a mixture. This is due to the smaller particles filling voids between larger particles, effectively creating agglomerates and regions which entrap air and do not allow the matrix material to fully penetrate.

## Effect of Particle Shape and Size on Dispersibility

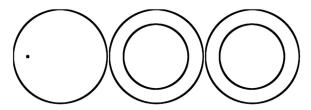
A multitude of factors can impact the ease or difficulty with which one material may be combined with another. Research by Atiemo-Obeng et al. [2] shows that large, dense particles are harder to suspend in solution than light particles; spherical particles—due to their aspect ratio of unity—are harder to suspend than particles of high aspect ratio, such as platey talcs or glass fibers. One must weigh what factors contribute more or less to

a particle's incorporation into the continuous matrix. It can be assumed that a small, non-dense, spherical particle will also be difficult to incorporate, yet for nearly opposite reasons than a large, dense particle of virtually any shape or aspect ratio. This need to hypothesize or draw conclusions based on an inference from dissimilar fillers reinforces the necessity for additional research to be performed on the rheological properties of, and dispersion of, hollow glass microspheres in solution.

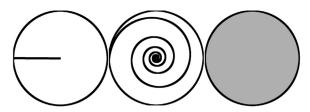
## Location of Additions

Dispersional studies by Weetman [3] confirmed the importance of location of additions to a batch: "typical low velocity regions occur near the top of the tank (where feeds are often introduced) and underneath a large pitched blade impeller (if used) at the bottom of the tank." [3] This suggests that additions of hollow glass microspheres at the top of the batch may not be fully incorporated, evenly dispersed, or may require a longer duration of mixing than anticipated to become thoroughly incorporated. To expedite the process, it is recommended that hollow glass microspheres be charged into the batch as close to the vortex as possible. This ensures that—due to their low density, as well as flow characteristics—they do not "flour" the top of the batch, which would lead to agglomeration and/or prolonged mix time (which may result in extensive glass microsphere breakage).

The effect of orientation of additions into the matrix is apparent in solutions which are viscous, non-Newtonian, and exhibit laminar flow [4]. An initial orientation of concentric addition will result in a concentric distribution after many rotations, that is, the hollow glass microspheres will not be evenly distributed throughout the batch, but striated within a fix radius about the tank. This is akin to additions which are "point focused" (see Figure 11.8). Conversely, additions which are made in a radial manner will more quickly disperse throughout the entire batch (Figure 11.9), and may be thought of as a "line" addition, as opposed to a "point" addition. By the simple nature of the geometrical terms used to describe these two methods of additions in a laminar flow regime, one can readily grasp that concentric addition is essentially one dimensional, whereas radial addition exemplifies a two dimensional means of incorporation. From this simple analogy one can easily infer that a two dimensional addition will result in homogenization more expediently than a one dimensional addition. The radial addition has the added benefit of hollow glass microspheres immediately being pulled into the vortex, by broadcasting the addition across the batch, toward the center of the vortex.



**Figure 11.8** Concentric addition at instant of addition, after one rotation, and after many rotations.



**Figure 11.9** Radial addition at instant of addition, after a few rotations, and after many rotations.

## The Science of Mixing and Dispersing

## Surface Tension

The ease with which a solid may be dispersed within a liquid is a function of adhesion tension, which is often considered to be an indication of the degree of wetting. Adhesion tension is a function of contact angle (between a solid and a liquid), surface tension, and the interfacial tension between the solid and liquid [5]. The Young–Dupre equation exemplifies this relation.

$$\gamma_{SA} - \gamma_{SL} = A_{SL} = \gamma_{LA} \cos \theta \qquad (11.1)$$

where

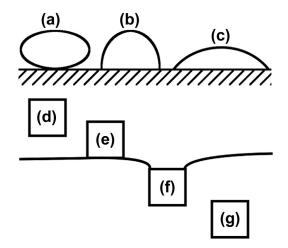
$$\begin{split} \gamma_{SA} &= \text{``surface tension'' of the solid} \\ \gamma_{SL} &= \text{interfacial tension of the solid and liquid} \\ \gamma_{LA} &= \text{surface tension of the liquid} \\ A_{SL} &= \gamma_{SA} - \gamma_{SL} = \text{adhesional tension} \\ \theta &= \text{contact angle} \end{split}$$

The above equation conveys the interplay between these physical phenomena.

## Wetting Phenomena

Wetting phenomena are directly related to the surface tension of the liquid,  $\gamma_{LA}$ , and the liquid—solid contact angle,  $\theta$ . As a general rule, when  $\gamma_{LA}$  is greater and/or  $\theta$  is smaller, wetting, and hence mixing, occurs more rapidly.

Figure 11.10 shows various important contact angles for a liquid—solid system. When the contact angle,  $\theta$ , is between 90° and 180°, adhesional wetting takes place and is spontaneous. When the angle of contact is less than 90°, immersional wetting (i.e., immersion of the solid phase into the liquid phase) takes place (conversely, when  $\theta > 90^\circ$ , immersional wetting is not spontaneous, and the solid can be considered to be emerging out of the liquid phase). Spreading wetting occurs only when  $\theta = 0^\circ$ , and the solid is preferentially transferred into the liquid. When  $\theta = 0^\circ$ , a substance is considered to be hydrophilic; for substances or solids which do not experience a 0° contact angle, varying degrees of hydrophobicity are considered to exist.



**Figure 11.10** Important contact angles in the mixing process: (a) adhesional wetting, contact angle  $90^{\circ} < \theta < 180^{\circ}$ ; (b) immersional wetting, contact angle  $\theta = 90^{\circ}$ ; (c) spreading wetting, contact angle  $\theta < 90^{\circ}$ ; (d–e) adhesional wetting; (e–f) immersional wetting; and (f–g) spreading wetting.

## Estimating Effects on Viscosity

As solids are added to a liquid, or preexisting solution of solids and liquids, the viscosity changes—the new solution tends to be more viscous. The viscosity of a slurry can be determined from the viscosity of the liquid (or liquids, or solution), and a dimensionless parameter known as the relative viscosity, which takes into account the volume fraction of solid particles contained in the slurry, as follows:

$$\mu_{\rm s} = \mu_{\rm r} \mu_{\rm l} \tag{11.2}$$

where

 $\mu_{s} = slurry viscosity$   $\mu_{r} = relative viscosity$  $\mu_{l} = liquid viscosity$ 

The slurry viscosity is proportional to the liquid viscosity, with the constant of proportionality being the relative viscosity, which is dependent upon many factors, that is, filler loading, filler shape (aspect ratio), and smoothness.

Einstein developed an equation to determine the relative viscosity, however, the equation is only valid at low loading concentrations, and for very fine particles:

$$\mu_{\rm r} = 1 + 2.5\phi \tag{11.3}$$

where  $\phi =$  volume fraction of solid particles.

Guth and Simha [6] modified this equation to consider particleparticle interactions at higher filler loadings:

$$\mu_{\rm r} = 1 + 2.5\phi + 14.1\phi^2 \tag{11.4}$$

Thomas [7] modified this equation further by fitting with empirical data:

$$\mu_{\rm r} = 1 + 2.5\phi + 10.05\phi^2 + Ae^{B\phi} \tag{11.5}$$

where

A = 0.00273B = 16.6 The above equations are for use with any filler shape (and within a wide range of filler size distributions). Further work by Kitano et al. [8] modeled the basic Einstein equation for use with very high loading concentrations of particles:

$$\mu_{\rm r} = (1 - \phi/A)^{-2} \tag{11.6}$$

where A = 0.68, for smooth, spherical particles.

The Kitano et al. equation is based on their work done with glass microspheres, glass balloons, and silas balloons in viscous particle-filled polymer melts [9]. Modified forms of this equation are:

$$\mu_{\rm r} = (1 - \phi/\phi_0)^{-2} \tag{11.7}$$

$$\mu_{\rm r} = \exp[(2.5\phi)/(1-k\phi)]$$
(11.8)

where

$$\phi_0 = 0.68$$
$$k = 1.25$$

are constants relating to the packing factor of spherical particles with a Gaussian size distribution within less than one standard deviation. Kitano et al. [9] found that these equations are useful in predicting  $\mu_r$ versus  $\phi$  for  $\phi \leq 0.4$ , and are better fitted for high volume loadings than the equation derived by Thomas. The reason for this better fit is due to their simplicity, and the inclusion of only one constant, which is a function of packing factor of the filler, as opposed to empirically derived constants.

To illustrate how the modifications to the Einstein equation impact the value of the slurry viscosity, let us use an example.

**Example 2**: Assume a liquid has an arbitrary viscosity equal to 1.0. Using Eqns (11.2)–(11.8) to determine the relative viscosity ratio, what would the slurry viscosity be if 30% by volume ( $\phi = 0.3$ ) microspheres is added to the liquid?

$$\mu_{\rm s} = \mu_{\rm r} \mu_{\rm l} = 1 \tag{11.2}$$

$$\mu_{\rm r} = 1 + 2.5 \phi = 1.75 \tag{11.3}$$

$$\mu_{\rm r} = 1 + 2.5\phi + 14.1\phi^2 = 3.019 \tag{11.4}$$

$$\mu_{\rm r} = 1 + 2.5\phi + 10.05\phi^2 + Ae^{B\phi} = 3.0516$$
(11.5)

$$\mu_{\rm r} = (1 - \phi/A)^{-2} = 3.2022 \tag{11.6}$$

#### 11: MIXING AND DISPERSION OF HOLLOW GLASS

$$\mu_{\rm r} = (1 - \phi/\phi_0)^{-2} = 3.2022 \tag{11.7}$$

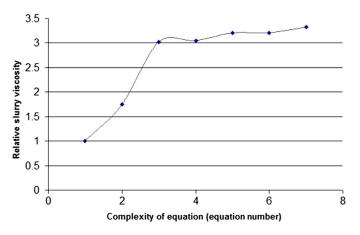
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$$\mu_{\rm r} = \exp[(2.5\phi)/(1-k\phi)] = 3.3201 \tag{11.8}$$

This is clearly a vast range in values, from 175% to 332% of the liquid's viscosity. We can see through this that as these equations introduce constants related to particle—particle interactions, observations based on empirical data, filler shape, surface roughness, and packing factor that the results seem to converge. The wide array of values indicates that many physical phenomena are at play here, and must be carefully considered in order to predict rheological characteristics essential for accurate sizing of dispersion equipment.

See Figure 11.11 for a schematic representation of how the introduction of various physical phenomena alter (and improve) the prediction of slurry viscosity based on volumetric loading.

Kitano et al. [9] also found that highly filled materials tend to exhibit a yield stress,  $\sigma_y$ , and that yield stress increases with increased filler concentration. The concentration of filler (by volume) and yield stress are related and—when plotted on a log–log scale—produce a linear plot. Kitano concludes that the only appreciable influence a filler has on relative viscosity—at a given concentration—is the size distribution of particles. Hollow glass microspheres are manufactured in an array of sizes, with each class of bubbles being of a narrow size range; this limits variability in product quality and provides optimally measurable and predictable rheological data.



**Figure 11.11** Graphical representation of Example 2 showing logarithmic progression in accuracy of slurry viscosity equations.

## **Rheological Effects on Dispersion**

Deagglomeration in viscous solutions is primarily achieved by means of extensional (elongational) flow and (laminar) shear flow. Shear flow is defined as the fluid velocity gradient being at right angles to the direction of flow; this can be thought of as flow through a pipe (see Figure 11.12). Extensional or elongational flow occurs when the velocity gradient is parallel to the direction of flow, as in a contraction, or narrowing region, which the flow must pass through. See Figure 11.13 for visual of these types of flow. Laminar shear flow deforms fluid elements due to the relative motion (velocity) between streamlines. Elongational flow causes the material to be stretched, therefore accelerating it at different rates. Both of these processes result in increased interfacial area between the solids and the liquid(s), and therefore result in reduced striation thickness of additions, a key requirement in providing homogeneous mixture quality. Laminar shear flow "tears apart" the liquid (and any agglomerates within), resulting in a mono dispersed product. These mixing phenomena are primarily responsible for reduction of agglomerates when the solution is viscid, and molecular diffusion is negligible.

When shearing rates are equal, elongational (extensional) shear does more to disperse solids than rotational shear. This is true for a wide variety of viscosity ratios, as well as when the viscosity ratio is near unity.

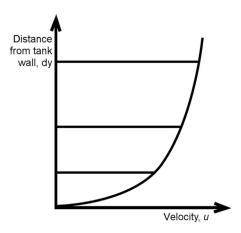


Figure 11.12 Flow rate generated by shear stress. Flow velocity is greater farther from vessel walls.

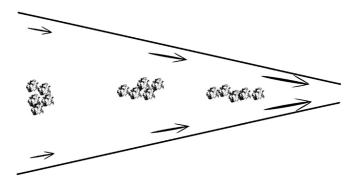


Figure 11.13 Elongational (extensional) flow. Arrows indicate flow velocity.

Compare Figures 11.8 and 11.3, elongational flow and concentric additions (which is evocative of rotational shear forces), respectively. One can envision elongational flow being akin to radial additions; the addition is "stretched" thinner and thinner (i.e., elongated). By this simple analogy it can be more clearly seen that elongational shear is critical to batch, and therefore product, homogeneity.

The rheological characteristics of hollow glass microsphere dispersions tends to be complex, due to the physical attributes of the components involved. The main physical properties to consider are Brownian (dispersive) motion, viscosity, density, buoyancy forces, Stokes (frictional) forces, and the gravitational force acting on the materials. As summarized by Walter, "high viscosities, low differences in density between dispersed particle and dispersant and, especially, small particle sizes favor rheological stabilisation. Rheological stabilisation is mostly employed for (viscous) [materials]" [10]. The majority of hollow glass microsphere applications are viscous, leading to rheological stabilization through hindrance of Brownian motion, buoyancy, and frictional forces. The buoyancy force is simply the weight of liquid (or semi-solid) displaced, as shown in Eqn (11.9):

$$F_{\rm B} = V_{\rm s} \rho_{\rm l} g \tag{11.9}$$

where

 $V_{\rm s}$  = the volume of a hollow glass microsphere

 $\rho_l = density$  of the liquid phase

g = acceleration due to gravity

The frictional (Stokes) force, also known as the drag force, was first derived to quantitatively explain frictional forces on very small spherical objects (i.e., very small Reynolds number) within viscid media, and is given as

$$F_{\rm d} = 6\pi\mu rv \tag{11.10}$$

where

 $\mu = matrix viscosity$ 

r = radius of the hollow glass microsphere

v = settling or flotation velocity, depending on density/buoyancy

The gravitational force is simply the mass of an object multiplied by the acceleration due to gravity, and can be rewritten as

$$F_{\rm G} = V_{\rm s} \rho_{\rm s} g \tag{11.11}$$

where  $\rho_s$  = density of hollow glass microsphere

Since the gravitational force is equal to the sum of the buoyancy and friction forces, we can rearrange Eqns (11.9)-(11.11) to solve for *v*, the settling (or flotation) velocity, as follows:

$$F_{\rm d} = F_{\rm G} - F_{\rm B}$$
 (11.12)

$$6\pi\mu rv = V_{\rm s}\rho_{\rm s}g - V_{\rm s}\rho_{\rm l}g \qquad (11.13)$$

Given the volume of a sphere, Eqn (11.13) reduces to

$$v = (2/(9\mu))r^2(\rho_s - \rho_l)$$
(11.14)

The negative sign of  $(\rho_s - \rho_l)$  signifies the natural floatation of glass microspheres; the dispersion difficulties associated with which were detailed in earlier sections. The viscosity in the denominator shows that the greater the viscosity of the matrix, the more inhibited the floating of hollow glass microspheres will be. The square of the radius (with units of meters or feet) indicates that the smaller a particle is—even if it is suspended in a product of low viscosity, or the density difference between materials is very large—the particle will be less likely to settle or float (depending on sign of density difference). Overall, what this equation expresses is, despite initially being technically challenging to incorporate in a homogeneous manner, hollow glass microspheres will tend to stay within the matrix, given ample viscosity and/or density of the matrix.

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