

# 14

## The Manufacture of Liquid Detergents

**R.S. ROUNDS** Fluid Dynamics, Inc., Flemington, New Jersey

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### I. INTRODUCTION

Commercial liquid detergents are available to consumers as low-, moderate-, and high-viscosity Newtonian and non-Newtonian solutions, free flowing or thick, opaque dispersions, gels, and pastes. Despite the differences in composition and consistency of these diverse delivery systems, the manufacturing processes typically involve the same fundamental unit operations. Viscous non-Newtonian dental creams and low-viscosity Newtonian hard surface cleaners, for example, both require dispersive and distributive mixing, dissolution of various components, heat transfer for heating and cooling, solids and liquids conveying, pipeline transport, filtration, and filling. The primary differentiation in the processing of these various products lies in the industrial equipment that is required for each unit operation and the difficulty of each operation.

Many, if not all, transport functions and corresponding unit operations in the processing of liquid detergents are linked to rheology. This is most apparent from mathematical simulations and dimensional analyses used to describe these phenomena in manufacturing. Depending on the delivery system of a liquid detergent selected for a specific consumer application, mass transfer, heat exchange, and fluid flow or mixing characteristics can be cumbersome and, generally, manufacturing conditions are selected to minimize any obstacles created by adverse fluid dynamics.

This chapter reviews basic process requirements for both structured and unstructured liquid detergents. In addition to an overview of the process patent literature, a general review is provided for the manufacture and handling of both Newtonian and non-Newtonian fluid compositions. Also included are a limited number of practical aspects of the manufacturing process and many references that should be consulted when a production system is to be designed.

## **II. STRUCTURED AND UNSTRUCTURED LIQUID DETERGENT DELIVERY SYSTEMS**

The physicochemical state of a liquid detergent frequently determines manufacturing requirements and, for the purposes of this review, we will adopt the nomenclature of van de Pas [1], and broadly partition liquid detergents into two general material categories: structured and unstructured liquid detergents. The unstructured fluid category includes both Newtonian and marginally non-Newtonian single- and multiple-phase detergents, where the dispersed phases are not highly interactive and the volume fraction of the total dispersed phase is relatively low. These products may show minor deviation from Newtonian behavior but display neither significant elasticity nor time-dependent shear effects. Fluids of this type can generally be processed as Newtonian fluids. This broad liquid detergent classification includes many, but certainly not all, personal and household care liquid detergents, including certain shampoos, conditioners, light-duty liquid laundry detergents, hard surface cleaners, and hand dishwashing detergents. The second category, structured detergents, refers to highly non-Newtonian, viscoelastic dispersions, including physically or chemically crosslinked gels, which is an increasingly popular form of both personal and household care products. These complex fluids may exhibit yield stresses and shear effects, such as thixotropy, rheopexy, pseudoplasticity, and dilatancy, and generally will be viscoelastic products with appreciable elasticity. Dispersions and emulsions are common within this product group. For example, dental creams exemplify the “structured detergent” category, in addition to phosphate and certain nonphosphate built heavy-duty detergents, fabric softeners, and select shampoos, conditioning shampoos, conditioners, automatic dishwashing liquids, etc.

Experience has shown structured fluids to be more difficult to manufacture, due to the complexity of their rheological profiles. In addition to elasticity, dilatancy, and rheopexy, certain structured fluid compositions may exhibit solid-like properties in the quiescent state and other flow anomalies under specific flow conditions. For emulsions and solid particulate dispersions, near the maximum packing volume fraction of the dispersed phase, for example, yield stresses may be excessive, severely limiting or prohibiting flow under gravity, demanding special consideration in nearly all unit operations. Such fluids pose problems in

pumping, mixing, filling, filtration, and in storage or holding vessels, with potential for negative cumulative effects on both heat and mass transfer. In addition, impaired drainage characteristics can contribute to material loss during production, increasing operating costs substantially.

It is understood that manufacturing of liquid detergents that are unstructured in their commercial form may involve intermediate streams which are, in fact, structured fluids, such as surfactant solutions at high active concentrations, within anisotropic mesophase boundaries, or concentrated polymeric solutions and gels. Whether the source is raw material, premix, or final product, manufacturing operations for each of these classifications are discussed with a focus on any specific requirements or limitations due to the physicochemical form.

### III. LIQUID DETERGENT PROCESS PATENT TECHNOLOGY

Patent activity is very aggressive in the personal and household care detergent industry, based on the total number of worldwide patents issued annually. A review of the current patent literature highlights the complexity of liquid detergent compositions and their manufacturing requirements. In process technology, the influence of process variables on product efficacy, stability, and viscosity control is common patent subject matter, disclosed for both structured and unstructured systems.

Liquid detergent process patents frequently define both compositional and process requirements, such as raw material concentrations and specifications, order of addition of critical components, thermal history, premix or adjuvant preparation methods, product/process stabilizers, distributive and dispersive mixing requirements, and process instrumentation. These patents apply to the production of primary raw material constituents, such as surfactants, builders, conditioning agents, rheology regulators, hydrotropes, disinfectants, bleach additives, etc., in addition to the specification of fully formulated detergent systems.

One patent for the manufacture of a liquid detergent composition, containing surfactant and water insolubles, describes air injection for increased dispersion stability [2]. The preparation of admixtures is disclosed, in addition to the process for air incorporation. Also issued is a process patent for the production of a pearlescent aqueous dispersion, containing fatty acid glycol ester and a wetting agent, for use in shampoos, hair rinses, cosmetics, and other detergents [3]. The primary advantage of the process described is pearlescence achieved in the absence of crystallization. In a further example, a patent has been granted for the production of an opalescent, stable dispersion obtained through multistage emulsion polymerization of *n*-vinyl-pyrrolidone and styrene, using both anionic and nonionic emulsifiers, for use in bath foams, shampoos, and various cosmetic preparations [4].

Process requirements maximizing product stability are often disclosed in the liquid detergent patent literature. In one example, Neutrogena Corporation has been assigned a patent for a coal tar shampoo prepared with a novel, reproducible, and specific process whereby detergent clarity, color, and viscosity are maintained for extended periods of time [5]. A patent describing the process for the production of a stable liquid detergent containing surfactant, aluminosilicate, a water-soluble detergent builder, and a stabilizing agent discloses the partial gelatinization of an aqueous zeolite mixture to promote dispersion stability [6]. Dispersion stability is also the subject of a patent issued to the Colgate-Palmolive Company for stable fabric softening heavy-duty liquid detergents, including the process for their manufacture [7,8]. Further, a patent has been issued to Lever Brothers for the process of making a colorfast heavy-duty liquid detergent, whereby the sequence of addition of the builder is specified [9]. It is noted that the builder is required to be added to the batch process vessel prior to the neutralization of the anionic detergent, from acid to salt, by an alkali metal hydroxide. Advantages include rapid neutralization, with a potential for reduced batch cycle time. A process for the preparation of an aqueous liquid detergent composition formulated with clay as a fabric softener is described in a patent issued to Conoco Inc., yielding a stable finished product with no undesirable increase in viscosity following clay incorporation [10].

In structured fluid detergent delivery systems, considerable effort is directed at maintaining or enhancing product shelf life and phase stability and the patent literature contains various methods intended to increase the physical stability of surfactant-based compositions. One technology presented in the patent literature imparts an internal physicochemical microstructure within the detergent system, for the retardation of phase separation. For these detergent systems, processing requirements are frequently vital to the formation of the required internal ordering of product components. In this notable example, the use of aqueous dispersions of a multilayered lamellar liquid crystal phase to stabilize structured liquid detergent systems has been proposed and several patents issued [11–15]. In the proposed examples, which are anionic/nonionic surfactant paired compositions, both rheopexy and thixotropy are found to occur. High shear is required during detergent manufacture to obtain the appropriate lamellar liquid crystal particle size distribution and it is suggested that a high-shear device in a recirculation loop can be applied, if the shear rate is greater than  $1,000 \text{ sec}^{-1}$ , preferably within the range of  $4,000$  to  $15,000 \text{ sec}^{-1}$ . As mentioned in these patents, mixing is the strategic engineering element for the successful production of this stable, internally structured liquid detergent. Several patents have also been assigned to the Colgate-Palmolive Company for a linear viscoelastic aqueous liquid automatic dishwasher detergent composition with exceptionally good physical stability [16,17] and a process for producing the linear viscoelastic detergent [18]. This patent discloses the dispersal of a crosslinked polyacrylic acid in water, neutralization and gelation with alkali metal hydroxide, addition of builder and silicate, and emulsification of

fatty acid and detergent in an aqueous solvent. Further, air incorporation to the gel is disclosed to further promote dispersion stability.

The importance of the order of addition of detergent components throughout the mixing process as a critical process variable is demonstrated in a patent issued to Unilever, for the incorporation of perfumes in liquid detergents in laundry and personal care products via a structured emulsified liquid crystalline or vesicle delivery vehicle [19]. The selective premixing of various components is further cited as a prerequisite for the process of manufacturing structured lamellar concentrated heavy-duty liquid detergent compositions, in an additional patent issued to Lever Brothers [20]. By strict adherence to component order of addition and premix compositions, viscosity can be reduced and draining characteristics improved. Steady shear viscosity data at  $21 \text{ sec}^{-1}$  is included in the patent, defining the criteria for stability.

Lever Brothers has also been assigned a patent for the process of producing an anticorrosion aqueous liquid detergent composition containing particulate alkali metal silicate. This detergent contains 5 to 25% of a soap and/or synthetic detergent and 5 to 40% of a detergent builder [21]. A process patent has also been issued for the making of a silicone-containing shampoo, detailing the thermal requirements of various adjuvants and the final mixing process [22].

Numerous patents exist for the manufacture of specific surfactants and other raw materials used in the formulation of liquid detergents. For example, a patent has been granted for the design of a reactor and process of saponification [23] claimed to be applicable to the preparation of various liquid detergent cleaning agents. In this patent, saponification is described for batch processing on a semicontinuous basis. Another example is a patent describing the efficient manufacture of an amphoteric surfactant for use in shampoos by reacting amino-containing compounds with acid halide alkali salt [24]. Further, a patent has been issued for the production of a fatty acid monoglyceride monosulfate salt surfactant describing the complete sulfation of glycerol, reaction with fatty acid, hydrolysis, and neutralization [25]. Advantages of this process include reduced concentration of sulfating agent and high active concentration with low inorganic sulfate concentration. Procter & Gamble Company also holds a patent for the production of alkyl ethoxycarboxylate surfactant compounds through the reaction of an ethoxylated fatty alcohol with a hindered base and anhydrous chloroacetic acid or its salt [26]. Use of this surfactant is found in cleaning compositions such as shampoos, laundry detergents, and liquid dishwashing products. An additional Procter & Gamble patent has been assigned for the co-sulfation of ethoxylated and unsaturated fatty alcohols producing acid sulfate compounds which, upon neutralization, form mixed surfactant systems for use in heavy- and light-duty liquid detergents, shampoos, and other cleaning compositions [27].

Liquid detergents contain many product components, including surfactants, salts, soluble and insoluble builders, polymers, viscosity modifiers, fragrances,

colorants, stabilizers, hydrotropes, and other ingredients, which are often interactive and capable of affecting product efficacy and synergistically influencing rheological attributes. Throughout the process patent literature, the manufacture of liquid detergents appears to require a regimented order of addition of ingredients, with the appropriate shear and thermal history, to obtain the appropriate consistency, appearance, stability, and performance, and minimize product aging following manufacture.

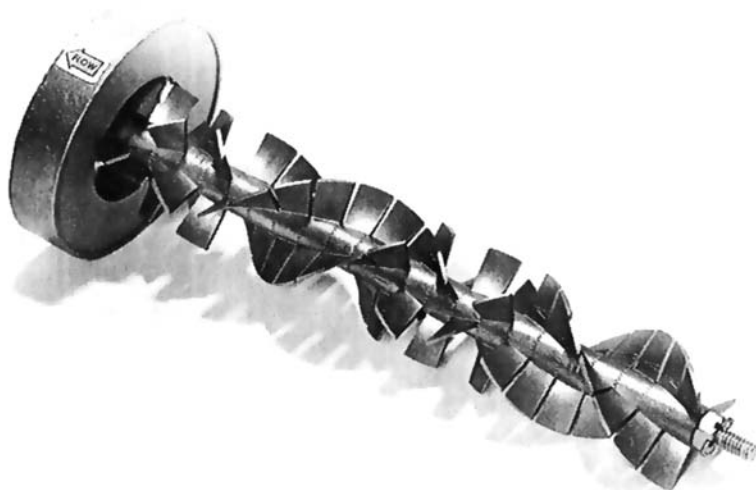
#### IV. CONTINUOUS VERSUS BATCH PROCESSES

Structured and unstructured liquid detergents can be processed in batches or continuously, depending on the specific production/volume requirements. Unstructured liquid detergents, especially those lacking significant solid components, are well suited for continuous processing. Examples of such detergents may include certain shampoos and light-duty liquids, including hand dishwashing detergents. With the development of high-precision mass flow meters, proportional metering systems, and in-line multiple stage dispersers, both dynamic and static, continuous processing is frequently the optimum process selection. If well designed, the process can be adequately controlled to ensure adherence to specifications, meeting high-volume production demands with favorable manufacturing costs.

There are various minor components in most liquid detergents, such as colorants, pH adjusters, and fragrance, and metering of these low-concentration, yet critical, components can be achieved with good accuracy in continuous operations. For pH adjustment, which frequently controls product viscosity, adequate sensors and product controls are required to ensure consistent product quality.

Continuous processes depend on various types of mixing devices, both static and dynamic, to disperse and/or blend formulation components. Several commercial examples of in-line static mixers, for both turbulent and lamellar flow, are shown in [Figure 14.1](#), exposing the internal flow elements, and an example of a commercial flow configuration containing three in-line static mixers is provided in [Figure 14.2](#). The primary advantage of such mixers, namely minimum space requirements, is clearly seen. Continuous processes are not restricted to unstructured detergents, and applications do also exist for structured systems. A dynamic in-line mixer, applicable to the blending of high-viscosity fluids, containing a helical ribbon impeller is shown in [Figure 14.3](#). In this figure, the dynamic mixing element has been removed from the in-line flanged assembly and positioned on supports in a horizontal position to show the mixer impeller. In operation, the mixer would be rotated 90° and installed in the pipeline.

Liquid-liquid dispersion in a continuous system or recycling in a batch system can be achieved by flow through an orifice. When very high energies are needed, high-pressure homogenizers are used. For lower energies, a very interesting orifice is a check valve or several valves in series. The characteristic of the check valve



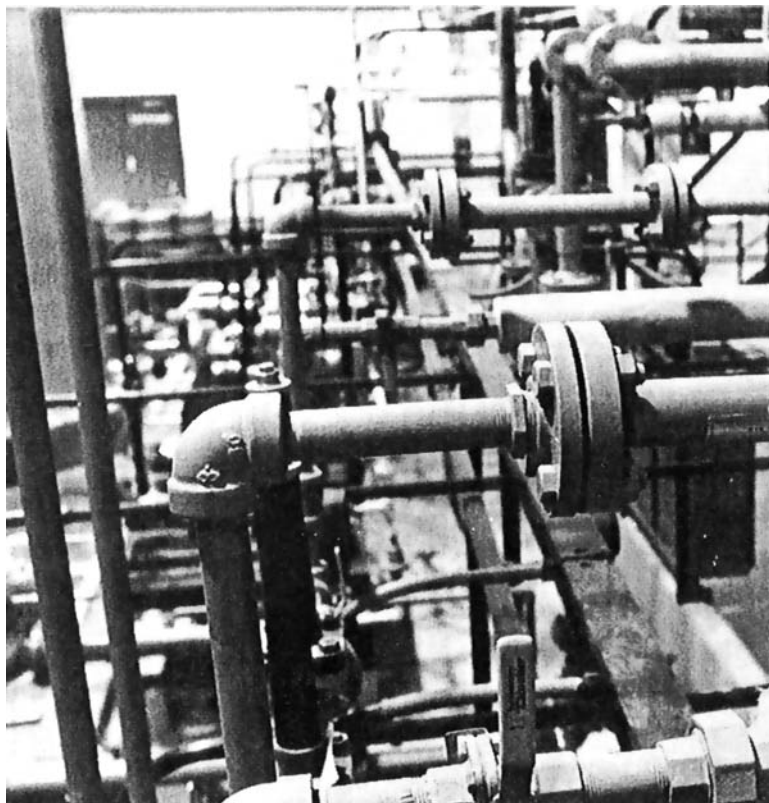
(a)



(b)

**FIG. 14.1** (a) Turbulent flow configuration in-line static mixer. (Courtesy of LIGHTNIN, a unit of General Signal Corporation.) (b) In-line static mixer with mixing elements. (Courtesy of Chemineer, Inc.)

is that it maintains a constant pressure drop independent of the liquid flow rate. It can be easily shown that the energy applied per unit of liquid volume is equal to the pressure drop. Therefore, if the pressure drop is constant, so is the energy per unit of liquid volume, or mass. This energy is what determines the size of the dispersed phase droplet, known as the Kolmogoroff theory [28].

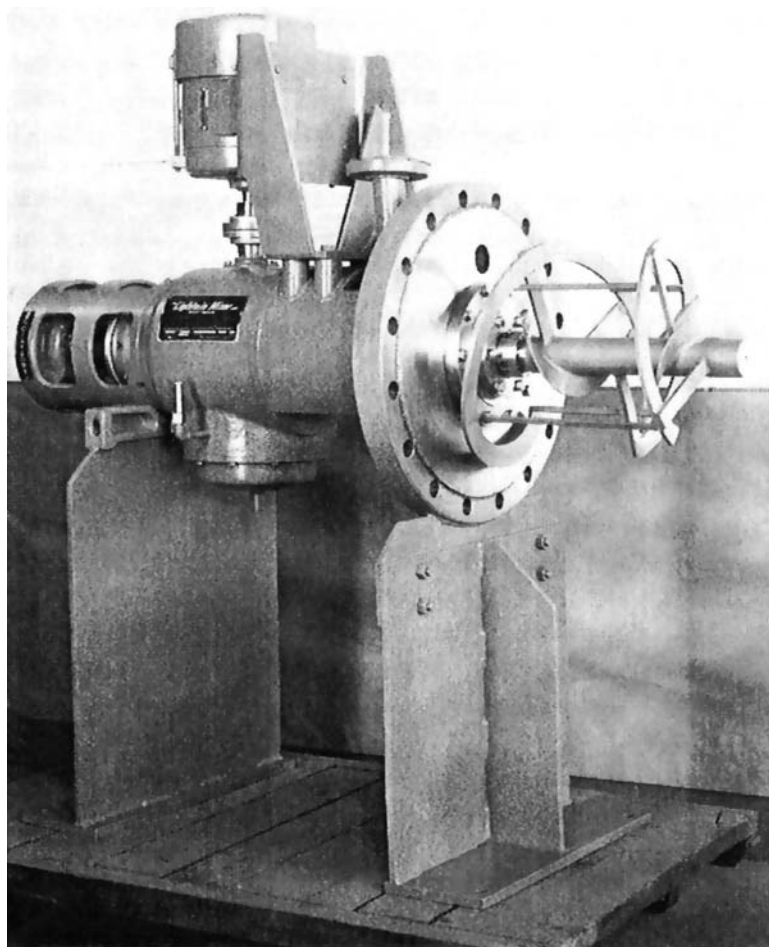


**FIG. 14.2** Commercial application of three in-line static mixers. (Courtesy of LIGHTNIN, a unit of General Signal Corporation.)

In industrial practice, commercial liquid detergent manufacturing processes may occur on a semicontinuous basis, through a combination of batch and in-line static and/or dynamic mixers. This may be the result of special process requirements in the preparation of product intermediates, such as:

1. Inorganic solids dispersal and hydration
2. Polymer hydration/swelling
3. Surfactant neutralization
4. Thermal gelation of select components
5. Liquefaction of a component(s)
6. Emulsification
7. Thermal/temporal equilibration
8. Ion exchange





**FIG. 14.3** In-line helical ribbon blender. (Courtesy of LIGHTNIN, a unit of General Signal Corporation.)

Powder addition has to be done in an atmospheric tank. For a continuous system, powder is predominantly predispersed in an agitated tank and then the suspension is injected into the continuous system. Occasionally it is added into a continuously stirred agitated tank which is in-line in the process. Liquid flow in and out of the tank has to be rigorously controlled.

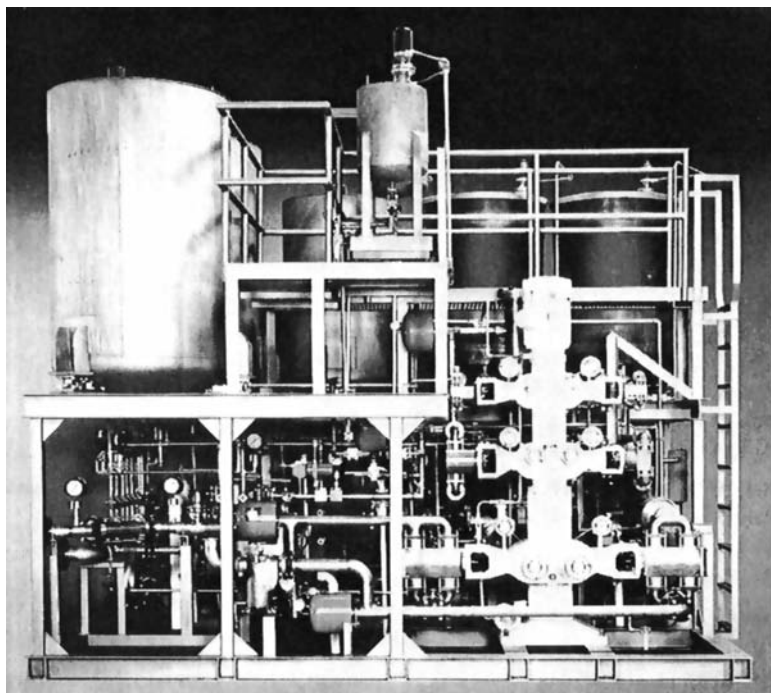
An example of a complete continuous process with a multiple head metering pump suitable for liquid detergent manufacture is provided in [Figure 14.4a](#). This

flexible and continuous manufacturing process can produce multiple product variants. Viscosity measurements, pH adjustment, level control, feedback process control to the metering pumps from the level controller at the buffer tank feeding the filling line, and an in-place water flushing cleaning system demonstrate the advantages of such production systems, in addition to the limited space requirements. These metering systems have found successful application in the production of fabric softeners, shampoos, dishwashing detergents, and other liquid detergent products [29]. Figure 14.4b shows a typical flow diagram for a continuous unit with rotary feed pumps and Coriolis mass flow meters.

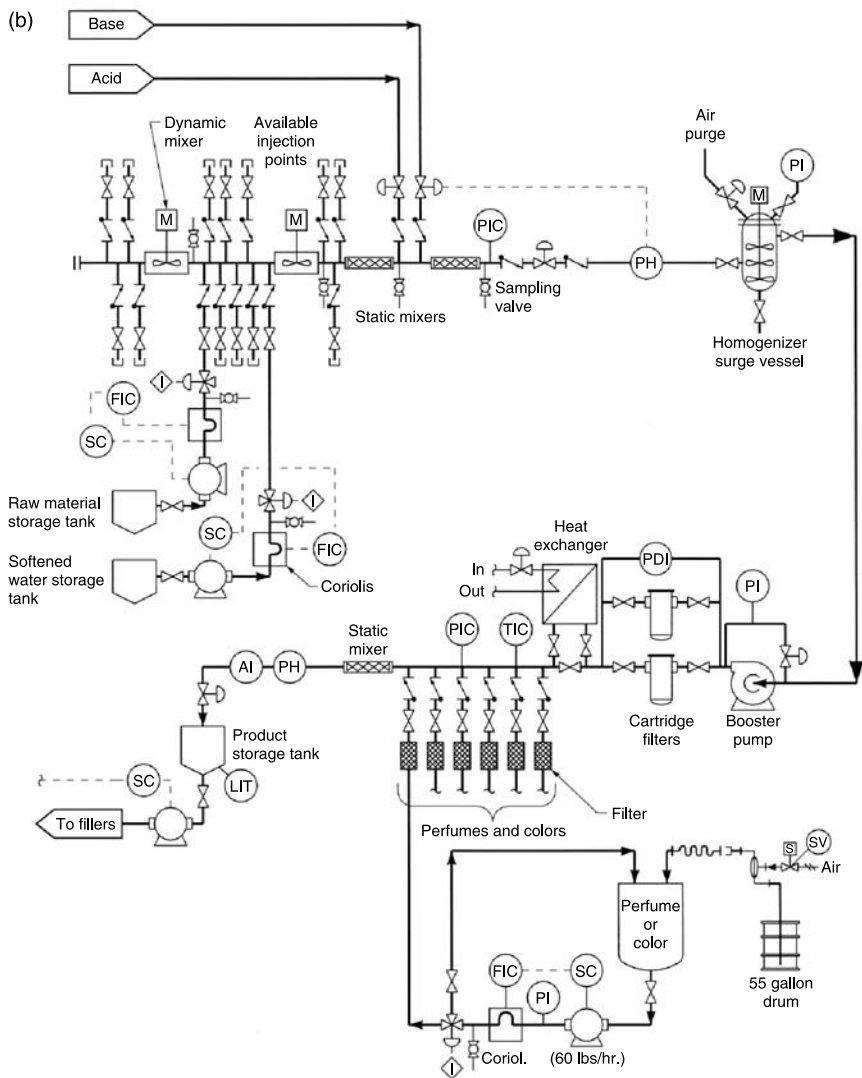
## V. UNIT OPERATIONS IN LIQUID DETERGENT MANUFACTURE

The manufacture of liquid detergents involves many of the basic engineering unit operations common throughout the chemical process industries. Depending on the specific detergent formulation, each unit operation can contribute significantly to

(a)



**FIG. 14.4** (a) Complete continuous manufacturing process. (Courtesy of Bran+Luebbe, Inc.) (b) Typical continuous unit with mass flow meters.



**FIG. 14.4** (Contd.)

the physical, mechanical, and visual properties of the finished product. For this reason, quality control and manufacturing process controls are important, particularly for structured detergents. For structured liquid detergents containing multiple dispersed phases, factors such as particle size distribution, of both solid and immiscible liquid components, particle geometry, hydration kinetics and extent of

hydration, interactions between components, kinetics governing each association under diffusion-controlled static conditions and shear environments, anisotropic surfactant phases, etc., can determine efficacy and many consumer-perceived product attributes.

Several critical unit operations are briefly reviewed with an emphasis on the process requirements of each liquid detergent classification, both structured and unstructured systems, emphasizing momentum, material, and energy transfer operations.

## A. Transport Phenomena in Agitated Vessels

Mathematical simulation of heat, mass, or momentum transfer in agitated vessels is often untenable, due to the three-dimensional components of the material and energy balances, and the large number of material and process variables. In such cases, dimensional analyses are the preferred method of correlation. Numerous references are available for a review of dimensional analysis in engineering applications [30–32].

Dimensionless groups provide an excellent overview of the critical parameters influencing heat, mass, and momentum transfer, and several are defined below:

Reynolds number ( $N_R$ ):  $DV\rho/\mu$

Froude number ( $N_{Fr}$ ):  $V^2/gD$

Brinkman number ( $N_{Br}$ ):  $\mu V^2/k\Delta T$

Nusselt number (heat):  $hD/k$

Nusselt number (mass):  $k_x D/c\mathcal{D}_{AB}$

Prandtl number ( $N_{Pr}$ ):  $C_p\mu/k$

Peclet number ( $N_{Pe}$ ):  $N_R N_{Pr}$

Schmidt number ( $N_{Sc}$ ):  $\mu/\rho\mathcal{D}_{AB}$

Using such dimensionless groups, one can easily deduce the importance of fluid properties, namely, resistance to flow, on many of the production steps in the manufacture of a liquid detergent. For example, the power needed to provide agitation in a mixing vessel, known as the power number,  $N_p$ , can be expressed as [33]:

$$N_p = f(N_R, N_{Fr}, S_i)$$

where  $S_i$  are factors relating to the design of the agitation system, e.g., agitation number, placement, and design. In mixing, fluid viscosity is clearly a significant material variable, influencing the power drawn during mixing.

Similarly, under nonisothermal conditions, as might be experienced in heat exchange by forced and free convection in an agitated vessel, the equations of change for the energy function can be expressed as:

$$DT^*/Dt^* = (N_R N_{Pr})^{-1} \Delta^{*2} T^* + N_{Br} (N_R N_{Pr})^{-1} \varphi_v^*$$

The time rate of temperature will be a function of the dimensionless groups which include resistance to flow, or viscosity,  $\mu$ , as one of the physical properties governing the heat exchange process.

In mass transfer, the primary variables to be considered include all physical properties, including density of relevant phases, viscosity, and diffusivity. Where liquid–solid mass transfer in agitated vessels is the interest, factors related to particle geometry, such as shape and size, need to be considered, as well as process design, including vessel geometry, agitator configurations, and speed [34]. Since fluid viscosity function is the distinguishing feature between structured and unstructured fluids, it is clear that rheology is a major factor in the processing of liquid detergents.

## 1. Momentum Transfer

Momentum transfer involves all unit operations where fluid motion occurs. The most common examples of this operation include pipeline transport, mixing, and the filling operation. In liquid detergent manufacture, mixing is undoubtedly the most important momentum transfer unit operation, occurring in-line or in agitated batch vessels [35]. While mixing appears to be a very simple and straightforward procedure, it can be extremely complex [36–40] and perhaps the most difficult of the unit operations used in liquid detergent manufacture.

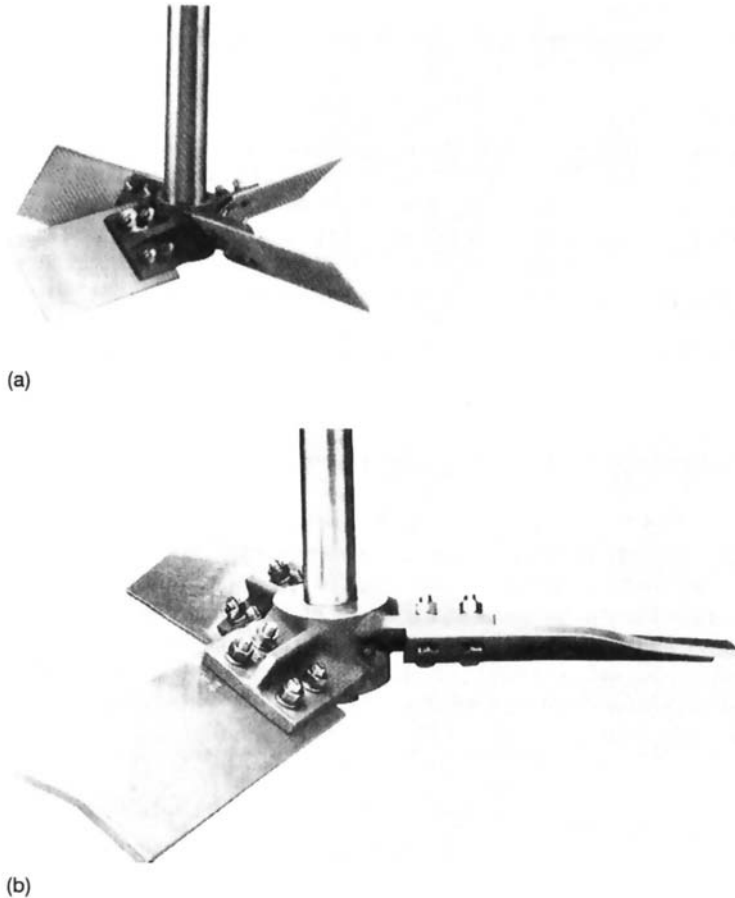
Each mixer configuration imposes a strain distribution to the fluid being processed, which may influence the overall characteristics of the final product. As such, mixing can be the critical production step determining the physical and mechanical characteristics of the finished product. The physical stability of the product, immediate and long-term aging effects, efficacy, texture, appearance, and rheology are some of the important product characteristics that can be significantly altered by the total shear or strain history a product experiences during mixing. Scale-up from laboratory to pilot plant through to production volumes becomes a significant challenge, as it is difficult to reproduce exactly the fluid velocity profiles and residence times, or total strain, that a fluid experiences during its process history.

Equally important is the influence of fluid properties on the efficiency and power requirements of the mixing operation. This is especially true for structured liquid detergents with appreciable elasticity shear sensitivity. For these structured systems, there is a strong interdependence between rheology and mixing efficiencies. A basic understanding of the flow characteristics of the finished liquid detergent product and all intermediate streams or product components is a key to the selection and optimization of the mixing process.

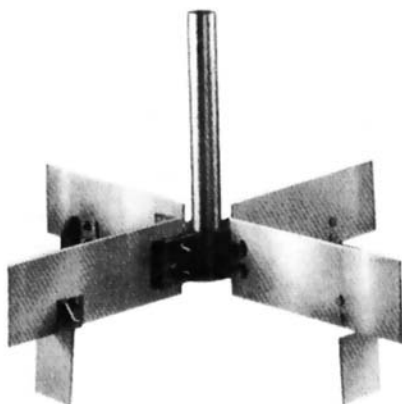
Research devoted to the processing and mixing of complex non-Newtonian fluids has not been extensive. This is unfortunate since many commercial fluids, including structured liquid detergents, can be non-Newtonian fluids, with appreciable normal stresses, and guidelines or process design criteria for viscoelastic fluids are generally unavailable. Most dispersions at high solids content and gels

fall within this category, creating significant challenges in the design of an efficient batch, continuous, or semicontinuous manufacturing process.

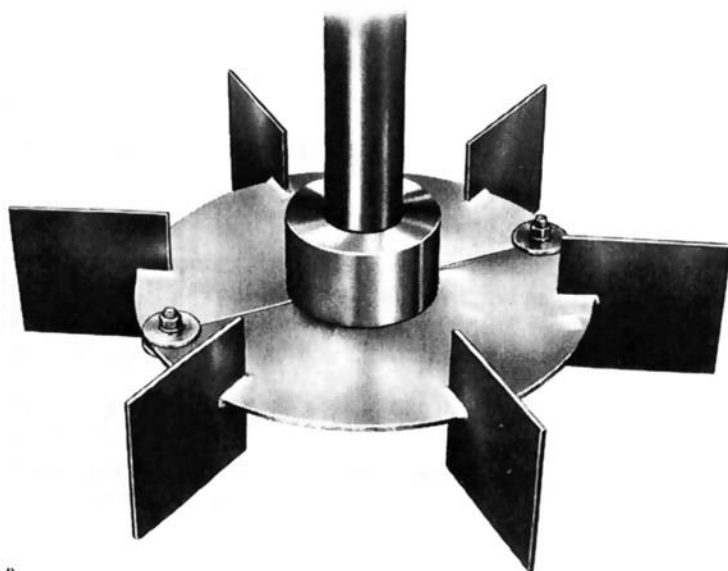
(a) *Mixing of Structured Versus Unstructured Liquid Detergents.* Several common radial and axial flow open impellers used in batch mixing of low- to medium-viscosity, unstructured or weakly structured liquid detergents are shown in Figure 14.5. In addition to the type of impeller, impeller diameter, vessel height and diameter, impeller locations, and baffles are design variables to be specified for a particular application. Placement of baffles to minimize vortexing and facilitate mixing, and the type and location of impellers will depend on the specific



**FIG. 14.5** (a) Pitch blade impeller, (b) high-efficiency impeller, (c) straight blade turbine impeller with stabilizer, (d) welded disc impeller. (Courtesy of Chemineer, Inc.)



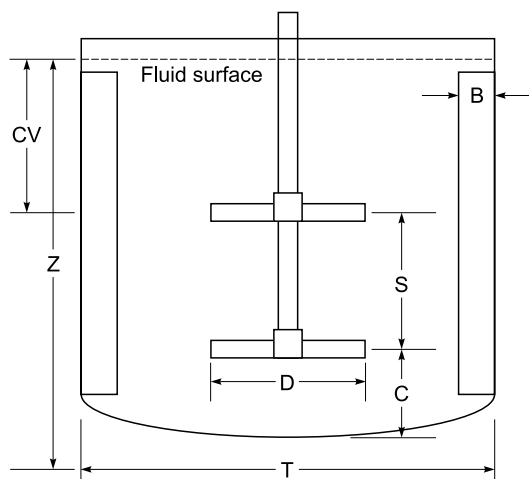
(c)



(d)

**FIG. 14.5** (Contd.)

mixing needs. Due to the size and scale of most industrial mixing vessels, multiple impellers are generally needed to obtain an adequate degree of mixing. A simple schematic of a batch mixer is provided in [Figure 14.6](#), showing all relevant engineering dimensions.



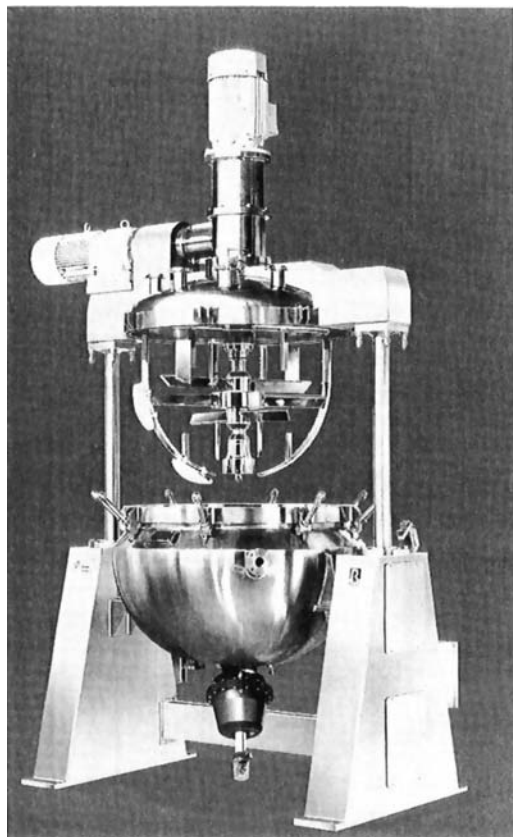
**FIG. 14.6** Schematic of batch mixing vessel with baffles and dual impellers with indicated engineering dimensions.

For high-viscosity structured and unstructured surfactant systems, one example of an alternative mixer design, consisting of three top-entering coaxial agitators, surface-sweeping anchor, counter-rotational blades, and rotor/stator homogenizer, is provided in Figure 14.7. Details of this turboemulsifier are shown in Figure 14.8, showing the presence of a powder inductor through the vessel bottom near the high-speed homogenizer turbine, variable-speed drive, jacketing for heating and cooling, and provisions for vacuum or pressurized operation. For high-viscosity systems, common marine propellers and turbines are generally unsuitable, providing limited bulk flow to the process fluid under normal operating conditions. The efficiency of the mixing operation and the effectiveness of the flow field that is generated in the bulk of the fluid will have a significant impact on blending times and the kinetics of these operations that are governed by effective mass, heat, and momentum transfer. Figure 14.9 broadly summarizes the viscosity limitations of most commonly used industrial agitators [41,42].

Large, jacketed 316 stainless steel construction mixing vessels with variable drive agitators are expensive. Due to the high capital cost, space requirements, and high operating costs associated with such vessels in batch operations, they are typically required to be multifunctional and capable of performing many of the manufacturing elements of a liquid detergent. At large production batch volumes of 10 to 20 metric tons or larger, this puts a great demand on the impeller/drive selections and placement of these impellers and baffles within the mixing vessel.

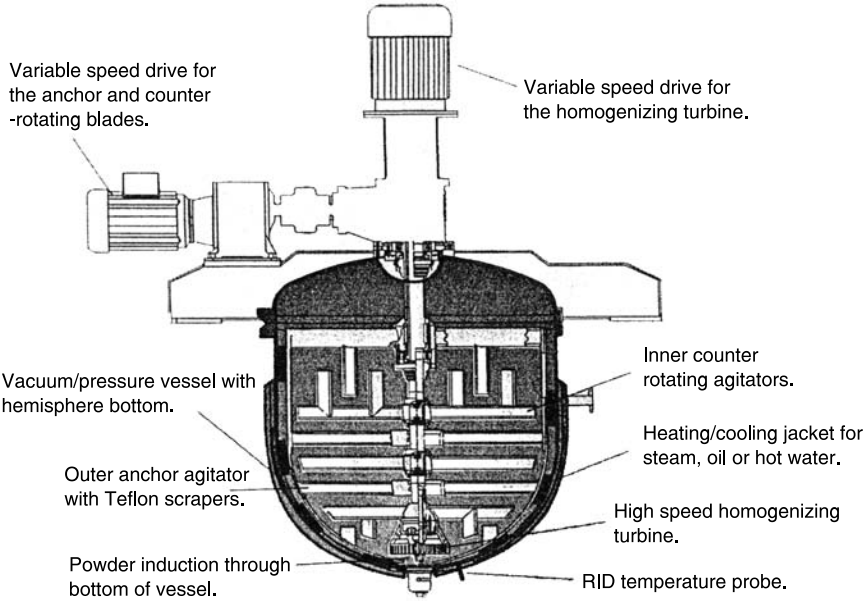
For liquids with viscosities less than 200 cP, jet mixing is a very economical option [43].



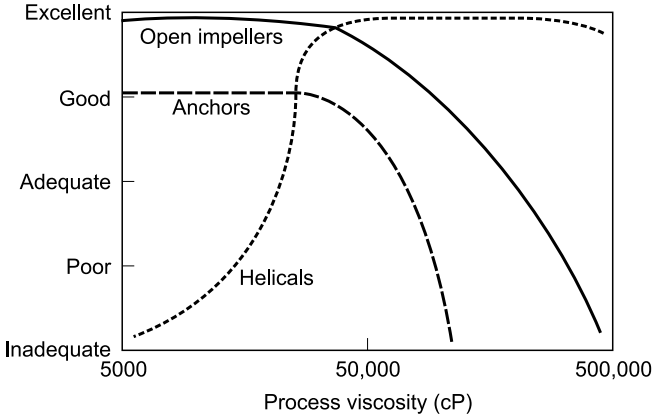


**FIG. 14.7** Ross turboemulsifier. (Photo courtesy of Charles Ross and Son Company, Hauppauge, New York.)

Most industrial batch operations do not utilize single vessels for the manufacture of a liquid detergent; multiple vessels of various sizes and specifications are used to perform discrete functions. Vessels with and without temperature control may be selected to prepare polymeric solutions, or surfactant premixes, or dissolve various solid components uniformly prior to the final blending operation. Further, intermediate product components may be prepared in sufficient bulk to support multiple production batches. This is generally desirable when production of intermediates is time consuming, excessively increasing individual batch cycle times. In continuous operations, this approach may also be applied to various product intermediate streams metered through a final multistage in-line disperser. This may be achieved with static in-line mixers or dynamic multiple-stage dispersers, depending on the specific product requirements. Use of multiple supporting vessels, frequently of



**FIG. 14.8** Detailed schematic of turboemulsifier. (Photo courtesy of Charles Ross and Son Company, Hauppage, New York.)



**FIG. 14.9** Viscosity limitations of various impeller configurations. (From Klinkenberg, A. and Mooy, H.H., *Chem. Eng. Proc.*, 44, 17, 1948.)

smaller size, can reduce cost by application of special requirements such as heat transfer or high shear only where needed.

In batch mixers, impellers impose flow, or momentum transfer, to the fluid mass contained within the vessel. The power consumption during mixing for a given fluid viscosity and density is proportional to the rotational speed of the impeller and the impeller diameter and flow is achieved by the momentum transferred to the fluid by the motion of the impellers. Placement of the agitator will be determined by the mixing requirements when the vessel is fully charged and also by requirements during batch filling and discharge. Agitator placement is coordinated with ingredient order of addition to limit, for example, excessive foaming in the presence of surfactants. The order of addition of formulation components can also be balanced to limit undesirable rheological properties and promote the formation of the desired microstructural state.

For unstructured liquid detergents, standard methods can generally be used to size and specify mixing equipment. Pseudoplastic behavior with low order of magnitude normal stresses would most likely not present serious mixing problems. Structured detergents, however, and intermediates, may require special consideration. Significant deviation from Newtonian behavior cannot be ignored in the specification of a production agitation system, as this can produce significant errors in the estimation of power requirements for a particular application. This is especially true for fluids capable of developing solid-like mechanical properties in the quiescent state.

The influence of elasticity on the mixing unit operation is well illustrated by Prud'homme and Shaqfeh [44]. A correlation of dimensionless mixing torque vs. Reynolds number is provided for three Newtonian fluids, two of which exhibit significant elasticity, as determined by the magnitude of the primary normal stress differences. For Rushton turbines, the results indicate a fourfold increase in torque during mixing, for the fluids exhibiting high normal stress differences, indicating the fluid rheology must be considered in the assessment of torque and power requirements for various agitation systems.

Power consumption is an important mixing design parameter, dependent upon impeller diameter ( $D$ ), rotational speed ( $N$ ), and fluid properties including viscosity ( $\mu$ ) and density ( $\rho$ ), and power consumption of impellers is usually provided as correlations of power number,  $N_p$ , to Reynolds number,  $N_r$ . For fluids exhibiting time-independent power law viscosity functions,  $\tau = K\dot{\gamma}^n$ , the generalized Reynolds number in agitation can be expressed as:

$$N_r = [\{D^2 N \rho (8N)^{1-n} / K\} \{4n / (3n + 1)\}]^n \quad (1)$$

Power characteristics for the mixing of non-Newtonian fluids have been determined for various impellers and other critical mixer design variables, using pseudoplastic, dilatant, and Bingham slurries, and polymeric solutions frequently

encountered in the manufacture of liquid detergents, such as clay dispersions and cellulosic and carbomer solutions [45,46]. This research has also provided correlations of the mean fluid shear rate and impeller speeds, for various impeller geometries and fluid viscosity functions. Typical agitators used in these investigations include anchors, paddles, fan paddles, and turbines in agitated vessels with and without baffling. Results clearly indicate that power requirements for mixing of non-Newtonian fluids can be much greater than for Newtonian systems.

Power consumption and blend times in the mixing and agitation of Newtonian and non-Newtonian fluids are not equivalent and, in fact, blend times can be much longer for non-Newtonian fluids when comparing fluids with comparable apparent viscosity values. Through dimensional analysis, the dimensionless blend or mix time,  $\theta_m$ , is expressed as:

$$\theta_m = f(N_R, N_{Fr}, S_i) \quad (2)$$

Su and Holland report power input per unit volume and mixing time are substantially higher for pseudoplastic fluids than for their Newtonian counterparts [47]. Godleski and Smith [48] report blend times nearly 10 to 50 times longer for non-Newtonian aqueous dispersions of hydroxyethyl cellulose when compared to equivalent viscosity Newtonian fluids, using flat-blade turbine agitators. Blending times for the pseudoplastic, time-independent cellulosic fluid are also noted to increase even further in baffled vessels. This study suggests a strong dependence of mixing efficiencies on fluid rheology.

There have been contradictory results reported in the literature, however, regarding the influence of fluid elasticity on the mixing unit operation [49–52]. Further research is apparently required to define adequately the influence of viscoelasticity on mixing in agitated vessels, for a broad range of fluid properties and mixer configurations.

Carreau *et al.* [53] have investigated the behavior of Newtonian, inelastic, and elastic non-Newtonian high-viscosity paste-like fluids in helical ribbon agitators, showing that the efficiency of mixing both pseudoplastic and viscoelastic fluids is lower than for Newtonian fluids, decreasing significantly with increasing fluid elasticity. Ranking the three fluid systems, the efficiency rating is such that viscoelastic < pseudoplastic < Newtonian.

As with open impellers, elastic fluids are apparently more difficult to process in helical ribbon mixers. To quantify this effect, the mixing efficiency of a highly elastic Separan solution is only 20 to 40% that of glycerol, which is Newtonian.

The effect of fluid rheology on the power consumption of helical ribbon agitators has also been evaluated [54] and power consumption as a function of generalized Reynolds number for shear thinning but inelastic fluids defined. When shear thinning effects are small, and elasticity is negligible, deviations from the Newtonian

power curve are slight. At low Reynolds numbers, this is also true for viscoelastic fluids. At higher fluid velocities, fluid elasticity begins to dominate the power curve. Further, it appears that shear thinning delays the effect of elasticity on mixing efficiency for structured fluids. The transient and extensional nature of the flow field is stressed as a key factor in the increased energy required to obtain a required degree of mixing. Fluids that exhibit both shear thinning and elasticity show deviations from the Newtonian power curves at higher Reynolds numbers than viscoelastic fluids with minimal shear effects.

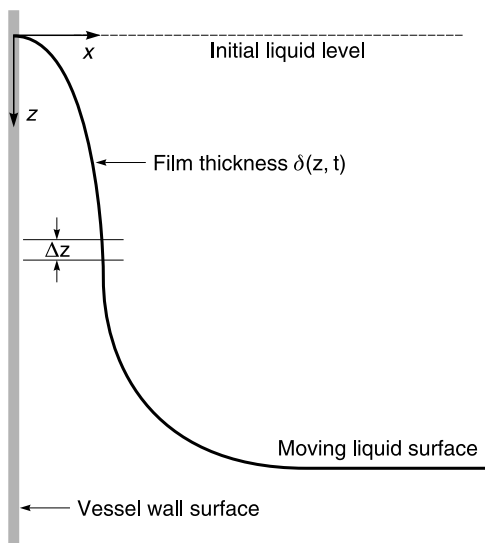
Power needed to maintain mixing may not be the same as the power needed at the inception of flow when processing structured liquid detergents. An interruption in the process sequence can introduce a transient power requirement quite different from the steady-state design criteria. The rheology of structured liquid detergents systems is quite complex and can introduce many variables not applicable to unstructured systems. When yield stresses are significant, and delays are expected at any part of the mixing process, slip drive couplings to the motor drive may be required. This may prevent damage to agitator motors and shaft assemblies when agitation is restarted. For pumping, mixing, and any fluid transport operation, fluids with yield stresses require shear stresses in excess of the yield stress to initiate and maintain flow. Depending on the magnitude of the yield stress, this can be problematic.

In a batch mixer, a sufficient shear stress exceeding the yield stress may occur only near the impeller, producing flow in the immediate vicinity of the impeller, but with stagnation zones throughout the remaining fluid bulk. This has an overwhelming impact on the efficiency of the mixing operation and can be further complicated in the presence of baffles. One solution is to utilize large surface sweeping agitators such as gate, anchor, or pattern mixers to minimize regions experiencing stagnation. Discharging vessels containing these types of fluids can also be difficult, resulting in residual material on the vessel surfaces which cannot be fully evacuated. For example, in discharging a vessel under gravity, a film thickness,  $\delta(z, t)$ , remaining on the vessel wall can be calculated as a function of draining time ( $t$ ) and distance from the initial fluid height ( $z$ ), as shown in [Figure 14.10](#). For Newtonian fluids, from the unsteady state mass balance, the film thickness can be expressed as [55,56]:

$$\delta(z, t) = \{(\mu/\rho g)(z/t)\}^{1/2}$$

where  $\mu$  = viscosity,  $\rho$  = density, and  $g$  = gravitational constant. As we would expect, film thickness is directly proportional to fluid viscosity, and inversely related to density.

For a comprehensive overview of the mixing unit operation, for both structured and unstructured fluids, various references are available describing the specific requirements for the design and specification of complete mixing systems [57–79].



**FIG. 14.10** Film thickness on vessel wall during drainage.

(b) *Dispersive Mixing.* There are liquid detergents that require specific particle size distributions of certain components to maximize efficacy and substantivity, for both solid–liquid and liquid–liquid dispersions. Examples of such products include hair conditioners, shampoos, conditioning shampoos, body cleansing bath gels, and fabric softeners. In conditioning shampoos containing silicone oils, substantivity and effective deposition on hair is a function of particle size, ionic charge of the particles, and silicone oil viscosity [80]. Formulation and processing of these systems can be extremely demanding.

Emulsions are difficult to process batchwise if a strict control on particle size distribution is required. Processing may also be hindered by the complex rheological properties these emulsions can exhibit. Very strict mixing controls are therefore not unusual to ensure that product during manufacture, at the filling line, and on the market shelf is within specification.

Fundamental mixing studies on simple two-component systems have provided insight into the effect of mixing parameters on critical emulsion properties such as particle size distribution. For example, Nagata [81] has shown the distribution of sizes of the dispersed liquid phase as a function of agitator speeds. As we might expect, a normal distribution occurs at higher speeds. In a similar study, the effect of surface tension was determined for several liquid dispersed phases from benzene to paraffin oil [82].

Due to the very broad distribution of shear rates that fluids experience in batch mixers, control of particle size distributions may not be possible. There are, however, alternative agitation systems that can be used in tandem to achieve a more controlled distribution of emulsion droplets or particulate solids. These include colloid mills, in-line dynamic dispersers in recirculating lines, and other high shear flow-through devices. These devices can be very successful in tailoring emulsion and dispersion characteristics. An example of a colloid mill with optional rotor/stator options is provided in [Figure 14.11](#), capable of producing stable emulsions to the submicrometer range. This rotor/stator design provides four-stage shearing action for effective dispersion and de-agglomeration. [Figure 14.12](#) details a two-stage tandem shear pipeline in-line mixer with two turbines and mating stators on a single shaft to provide greater high shear dispersal. Use of external in-line mixers positioned in batch mixer recirculation loops is an effective process method for achieving a high degree of dispersive mixing [83].

(c) *Pumping of Newtonian and Non-Newtonian Fluids.* For liquid detergent products known to be shear sensitive or containing particulates, pump selection is an important process variable. Whether driven by centrifugal force, volumetric displacement, mechanical impulse, or electromagnetic force, an understanding of fluid exposure to high shear in close clearances is required. An internal schematic of a rotary gear pump is shown in [Figure 14.13](#), showing the close clearances between impeller surfaces and pump casing, with two alternative rotary screw pumps illustrated in [Figure 14.14](#) and [Figure 14.15](#).

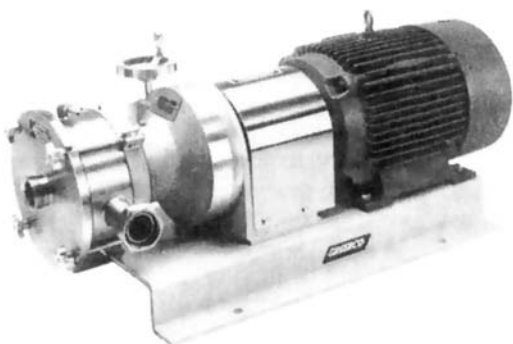
## 2. Aeration Avoidance

Aeration and foaming are serious problems in liquid detergent manufacturing. Bottles cannot be filled with aerated liquid to a specified volume or mass. Most often aeration and foaming are produced by the process, and not by air contained in raw materials or water.

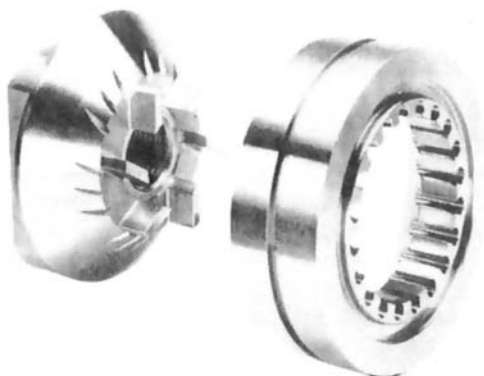
In agitated vessels, air is incorporated during improper liquid feed, splashing, through the vortex, or during powder addition. Agitation further disperses the air, making it more difficult to separate, producing foam as the air rises to the liquid–air interface. Avoiding incorporation of air rather than separation once it is incorporated should be pursued. To avoid air entrapment while feeding liquid, several process configurations are possible, including:

1. Deep tube feeding.
2. Bottom tank feeding.
3. Feed entering from the top of the tank, discharging against the tank wall tangentially and downwards in such a manner that the liquid spirals along the tank wall.

In the first two cases, no air slug should be in the pipe, lest it be dispersed into bubbles by the agitation. If air slugs are present, there should be no agitation at



(a)



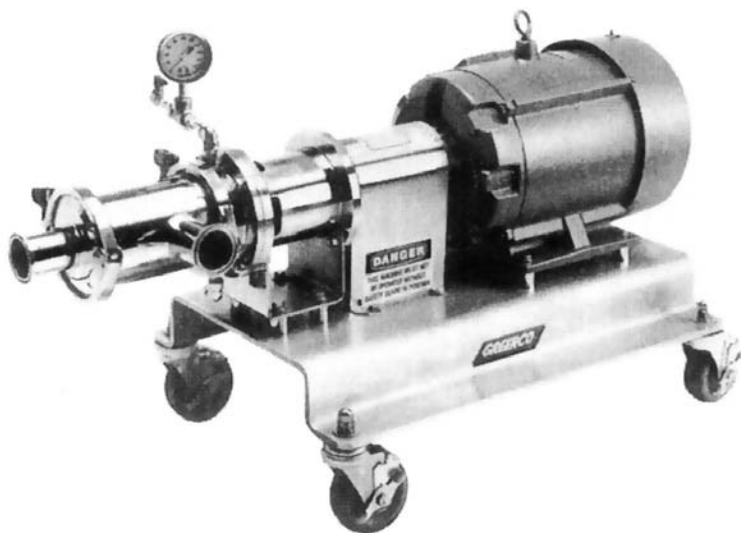
(b)



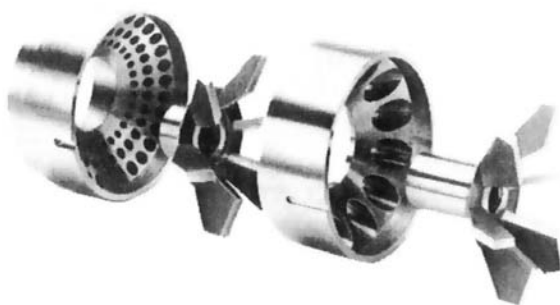
(c)

**FIG. 14.11** (a) Greerco colloid mill. (b) Standard colloid mill rotor/stator combination with plain, smooth milling surfaces for most emulsions and dispersions. (c) Specialty rotor/stator that has grooved milling surfaces for viscous emulsions. (Courtesy of Greerco Corp., Hudson, NH.)





(a)

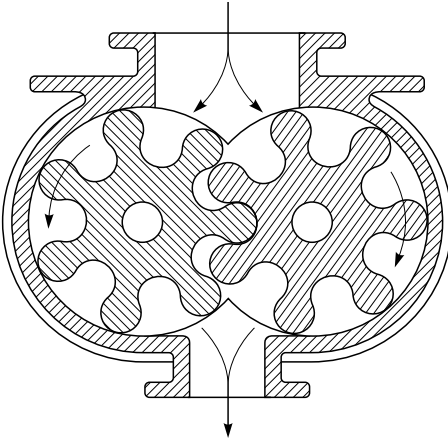


(b)

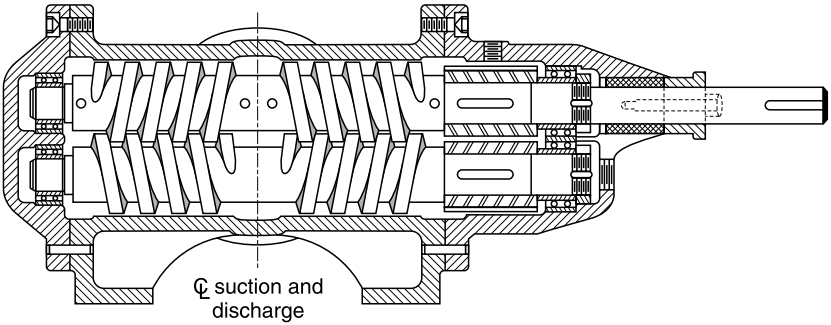
**FIG. 14.12** (a) Greerco 4" two-stage sanitary tandem shear pipeline mixer. (b) Exploded view of tandem shear turbine/stator assembly. (Courtesy of Greerco Corp., Hudson, NH.)

the time of addition since the slug will become a large bubble that rises quickly to the surface.

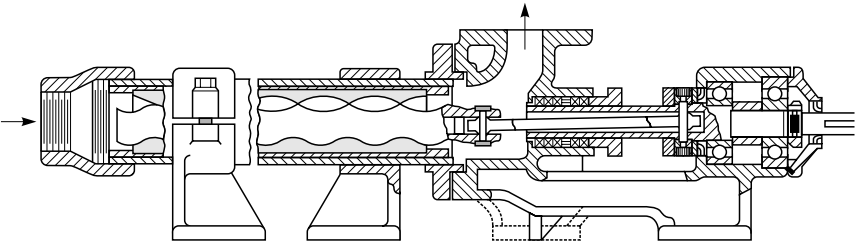
If aeration has occurred, the common way to de-aerate is to stop agitation and wait until the air rises and separates. More efficient than this is to design the tanks for de-aeration. This is done by laminar agitation at a Reynolds number of 45 using an eccentric shaft at one third the tank diameter and one half the turbine diameter from the bottom. This accelerates de-aeration while still mixing [84].



**FIG. 14.13** Schematic of gear pump. (From Perry, R.H., Chilton, C.H., and Kirkpatrick, S.D., *Chemical Engineers' Handbook*, 4th ed., McGraw-Hill, New York, 1963.)



**FIG. 14.14** Two-rotor screw pump. (From Perry, R.H., Chilton, C.H., and Kirkpatrick, S.D., *Chemical Engineers' Handbook*, 4th ed., McGraw-Hill, New York, 1963.)



**FIG. 14.15** Single-rotor screw pump with elastomeric lining. (From Perry, R.H., Chilton, C.H., and Kirkpatrick, S.D., *Chemical Engineers' Handbook*, 4th ed., McGraw-Hill, New York, 1963.)

Producing low pressures in the tank also accelerates de-aeration but the foam formed on the interface may be quite stable. Usually large tanks used for mixing liquids are not built to withstand vacuum. There are commercially available continuous de-aerators based on the formation of a film on a vessel wall and subjecting it to vacuum and/or centrifugal force. They tend to fail when the foam produced is well stabilized.

High-density foam floating on the interface can be destroyed mechanically or with hot air, or by spraying water (ethanol or other solvent, if possible). High-density foams are more difficult to break and frequently impossible. Again, de-aeration is much more difficult than aeration avoidance.

Continuous systems are mostly pressurized and normally no aeration occurs. A well-designed system will not incorporate air in the suction of the centrifugal pumps and will have no accidental venturi effect.

### 3. Heat Transfer

Forced-convection heat transfer is a common unit operation in the production of liquid detergents. Whether experienced in jacketed process vessels, agitated vessels with immersion coils, or other forms of heat exchange, there are multiple causes for thermal regulation during detergent manufacture. Temperature may be controlled to increase the dissolution rates of various components, facilitate mixing, accelerate hydration, moderate phase behavior of the product intermediates, regulate viscosity, reduce yield stresses, etc.

Many liquid detergent products contain components that serve as product viscosity modifiers, added to achieve the desired consistency of the commercial product. Cellulosic polymers, for instance, are an excellent example of such an additive and various polysaccharides are capable of gelation under specific thermal conditions. In such cases, heat transfer during manufacture may be required to complete hydration and effect the necessary conformational change in the select polymer system [85], in the appropriate aqueous environment. Products requiring controlled heat transfer processes may include various dental creams, shampoos, built liquid detergents, and hard surface cleaners.

Heat transfer may also be required to maintain isothermal or adiabatic conditions in the presence of endothermic and/or exothermic reactions, as the result of mixing product components, surfactant neutralization, and other chemical reactions. In these cases, heat transfer requirements may be severe to minimize exposure of the bulk fluid to high temperatures for extended time periods, resulting in irreversible thermal degradation.

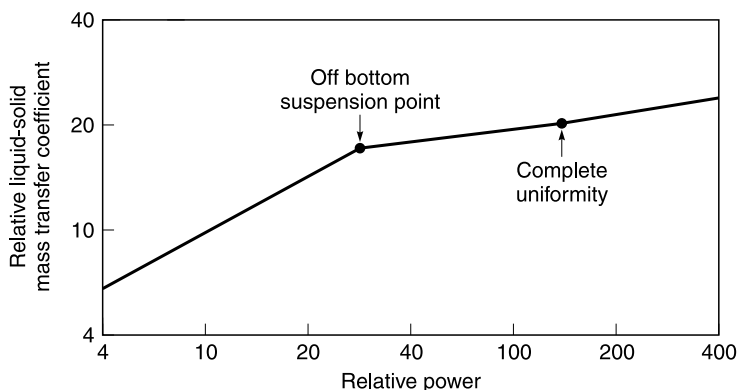
### 4. Mass Transfer

Liquid–solid and liquid–liquid mass transfer is highly dependent upon surface area, or particle size. Mass transfer is involved in simple wetting, dissolution, hydration, swelling of product components, ion exchange, electric double layer formation,

dispersion stabilization through adsorption or absorption, and surfactant phase equilibration, among others. Both momentum and heat transfer are frequently concurrent in the effectiveness and efficiency of most mass transfer operations.

(a) *Solids Hydration: Builders and Polymers.* Solid-liquid suspensions are frequently encountered in the production of liquid detergents. For example, the chelating agent sodium tripolyphosphate, in anhydrous form, is a common builder in both laundry and automatic dishwasher detergents, forming a hexahydrate when exposed to an aqueous environment. It is known that material and process variables can influence phosphate hydration kinetics [86–89]. The shear exerted on the slurry during hydration, rate of phosphate addition, order of addition of various components, electrolytic solution environment, temperature, tripolyphosphate characteristics including Phase I/Phase II crystalline form, particle size distribution, and pH, for example, can influence the rate and extent of sodium tripolyphosphate dissolution. Formation of the hexahydrate may result in an increase in consistency of the phosphate slurry, limiting the solids concentration during processing. The rheology of phosphate liquid detergents is critically dependent upon the characteristics of the anhydrous phosphate, Phase I/II ratio, which influence degree of hydration. Modification of the hydrating characteristics of Form II phosphate to minimize undesirable processing effects is the subject of a patent issued to Lever Brothers [90].

The agitation rate and solids suspension should be sufficient to maximize available surface area, especially where mass transfer is occurring. The dependence of the mass transfer coefficients on relative power is shown in Figure 14.16 [91]. The mass transfer coefficient is much higher when complete off-bottom solids

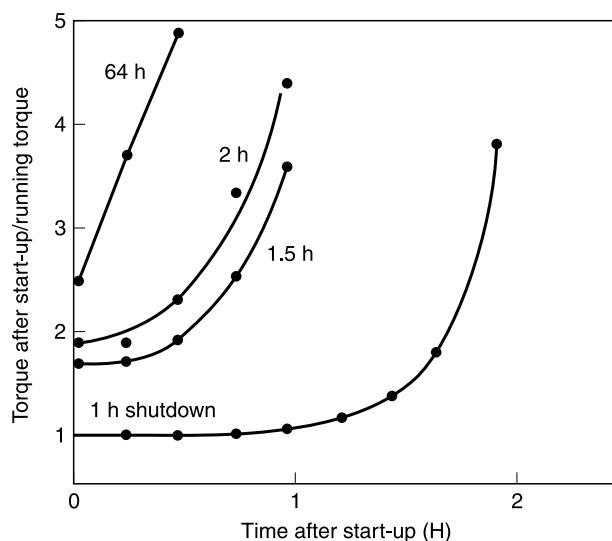


**FIG. 14.16** Dependence of mass transfer coefficients on solids suspension. (Adapted from Oldshue, J.Y., *Fluid Mixing Technology*, McGraw-Hill, New York, 1983, p. 234. With permission.)

suspension is achieved. Even in cases where suspension of solids is the process objective, as in phosphate hydration, for example, it is necessary to determine if complete solids suspension and uniformity throughout the continuous phase is required or if off-bottom suspension with a solids gradient throughout the vessel is adequate. A general review of mass transfer in mechanically agitated vessels involving particulate suspensions is provided by Upadhyay and Kumar [92].

Phosphate hydration in the primary detergent mixing vessel represents a good example of the challenges facing a process development or manufacturing engineer in the specification of a multifunctional mixing vessel. If we assume that the phosphate hydration or other solids dispersal will occur early in the manufacturing process, the immediate requirements of the mixing vessel is that an agitator is adequately positioned to keep all solids suspended during the hydration process. If this occurs as a highly concentrated dispersion with a minimum of solvent, solids suspension may be difficult to achieve and the extent of hydration limited, placing constraints on the impeller selection and location within the mixing vessel.

A major difficulty associated with solids dispersion and hydration is settling in the event of a process interruption. Depending on the duration of the interruption, redispersal of solids may be difficult to achieve. An excellent example of this is provided in Figure 14.17, showing the agitation times required to redisperse solids after settling [93]. Depending on the nature of the solid being processing, particle



**FIG. 14.17** Agitation requirements to redisperse settled solids. (From Oldshue, J.Y., *Fluid Mixing Technology*, McGraw-Hill, New York, 1983, p. 234.)

size and shape, degree of compaction, and impeller location, redispersal may not be possible. Adequate characterization of the slurry during process development is needed to anticipate such difficulties. Depending on the impeller location relative to the compacted solids region, precautions may be necessary to protect the agitator motor drive. In certain instances, compaction may occur when agitator motion is reintroduced due to the forces exerted on the settled solids by the surrounding flow field.

Polymer processing during the manufacture of a liquid detergent represents another difficult processing step since certain polymers may undergo rapid hydration when introduced to an aqueous solvent. This complicates the mixing operation and may require a predispersion of the polymer with a second inert powdered ingredient, predispersion of the polymer solid in a nonaqueous solvent, or high-shear dispersion. This can also be achieved in a dynamic in-line mixer through a transfer or recirculating line attached to a mixing vessel, as previously discussed, or a powder inductor, as shown in [Figure 14.8](#). High-shear dispersion reactors, or mechanical dry powder dispersers, are known to reduce favorably blending times, while increasing the concentration of polymer that can be dispersed, even for certain hydrophilic carbomer polymers [94].

When mixing hydrating species, the order of addition of components can again be significant. Polymer hydration, for example, can be significantly hindered in the presence of specific salts. In general, with liquid detergents of limited shelf life, the order of addition of ingredients can be critical in finished product attributes. This is especially true for structured high solids dispersions. The order of addition can influence phase stability, rheology, and many other product properties.

## **B. Microbial Contamination**

As more restrictions on product preservatives have been set in the last 10 years, more instances of microbial contamination have appeared and liquid detergent process equipment and operations have approached those used in the food and pharmaceutical industries. Process equipment is being installed to a more sanitary level, which means easier to clean and disinfect. Predominantly the equipment is designed for “cleaning in place” (CIP) without the need to disassemble. This chiefly means that surfaces are polished, circulation dead spaces are avoided, and drainage is virtually perfect. Usually the equipment is washed with alkaline and acid solutions, and then with a disinfectant solution. Additional equipment to handle and recirculate disinfectant solutions becomes part of the system design.

The predominant material of construction is 316 and 304 stainless steel or variations of both, but plastics such as polyolefins and fluorinated hydrocarbons are also used. Extensive literature in this area is available even if directed more toward foods and pharmaceuticals processing [95–97].

### C. Product Shelf Life

Liquid detergents can be dynamic systems in a metastable thermodynamic state during and following manufacture. Depending on the complexity of the formulation and concentration of surfactants, polymers, and other additives, changes in consistency, texture, appearance, color, etc., can be experienced following manufacture and this is not unusual for many detergent systems. Controlling this effect, however, is necessary to ensure consistent product throughout the shelf life and represents the underlying necessity of effective heat, mass, and momentum transfer during product manufacture.

For example, a product may exhibit a Brookfield viscosity of several thousand centipoises at the filling line, yet viscosity may continue to increase or decrease following production, for a period of time. Most undesirable is progressive thinning or thickening for extended time periods. Depending on the mechanism responsible for the thickening or thinning behavior, this may be accelerated through effective heat and mass transfer at the relevant manufacturing step. Possible causes of such phenomena include continuing hydration of polymeric and solid species, occlusion of solvent in porous solids, surfactant phase equilibration, etc. Heat transfer may well be used to increase the rate of each of these effects during manufacture, thereby moderating any changes in consistency following production, driving the product to a more stable pseudoequilibrium or steady state.

Heat transfer can occur in either batch or continuous configurations. Both types of processes require fluid motion to obtain an effective heat transfer to the bulk of the fluid. In batch processing using jacketed vessels, helical coils, or coils in a baffle configuration, for example, sufficient agitation is required for heat transfer through the medium while continuous systems rely on flow rate to achieve effective heat transfer to satisfy process requirements. Effective heat transfer in batch operations for structured liquid detergents may require scrapers or anchor-type impellers to increase heat transfer coefficients in jacketed vessels.

Effective mass transfer is as important since product stability can be seriously compromised in colloids and suspensions, both liquid–solid and liquid–liquid phases, if the morphology of the interface is not properly formed, and interactions sufficiently developed. Phase separation is the major consideration in such complex systems, and is easily affected by poor process history.

## VI. SUMMARY

Liquid detergents are seldom in equilibrium during processing or throughout their shelf life. Few of the reactions are driven to completion during manufacture; they continue throughout product shelf life. Ion exchange, crystallization, phase equilibration, adsorption, absorption, diffusion, etc., may continue to occur from the point of manufacture to the point of use. If these proceed without significant

change in physical properties, there may be little reason for concern, unless efficacy is impaired. Unfortunately, however, these can result in viscosity increases with product age, induce physical phase separation, shift particle size distributions, alter color and fragrance, etc., leading to product changes that are consumer perceptible. With a rigorous statistical experimental design during process development, many of these characteristics can be understood and successfully controlled.

Both structured and unstructured liquid detergents have process requirements and limitations. The order of addition of ingredients and the shear history experienced during processing can determine the physical state of the detergent and ultimate stability. Any additional unit operations such as pumping, pipeline transfer, and filling need to be defined in a manner that does not irreversibly alter the structured phase. The objective throughout manufacturing is to deliver a consistent product to the consumer with minimal variability encountered during production.

Specification of raw materials used in the manufacture of liquid detergents is critical to controlling process effects. Although some detergents are relatively insensitive to broad fluctuations in raw material characteristics, others are extremely sensitive to minor variability. Apparent in the patent literature, surfactant chemistry can be a critical component. For example, when manufacturing with a surfactant/solvent composition near a phase boundary, a minor change in electrolyte concentration, surfactant composition, and concentration can significantly alter product characteristics.

Mixing is an important unit operation in the production of a liquid detergent. Effective mixing of liquid detergents requires a basic understanding of the rheology of the system being manufactured. A preliminary investigation of the fluid properties such as viscosity behavior, normal stress differences, time dependence or shear effects, yield stresses, and structural kinetics including deformation and recovery are relevant and necessary in anticipation of specific agitation requirements. As we have seen, the elastic effects are particularly important to identify and monitor during processing of liquid detergents, depending on the physical form of the product, and can be a significant engineering challenge.

## ACKNOWLEDGMENTS

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