DETERGENCY AND DETERGENTS

1. Introduction

The cleaning of a solid object, ie, the removal of unwanted foreign matter from its surface, is done by methods ranging from simple mechanical separation such as blotting or abrasion to removal by solution or selective chemical action. The term detergency is limited to systems in which a liquid bath is present and is the main cleaning component of the system. The action of the bath involves more than simple solution or simple hydraulic dislodging of soil, although both will occur and contribute to the cleaning. The cleaning is enhanced primarily by the presence in the bath of a special solute, the surfactant, which alters interfacial effects at the various phase boundaries within the system. Thus, a typical detersive system consists of a solid object to be cleaned, called the substrate; soil or dirt attached to it which is to be removed in the washing process; and a liquid bath that is applied to the soiled substrate. In turn, each of these elements can vary widely in properties and composition. The final cleaning benefit results from interaction of these elements and the conditions used, ie, temperature, time, mechanical energy input (agitation) and, in the case of aqueous baths, the presence of hardness ions in the water.

In the cleaning or washing process in a typical detersive system the soiled substrate is immersed in or brought into contact with a large excess of the bath liquor. Enough bath is used to provide a thick layer over the whole surface of the substrate. During this stage, air is displaced from soil and substrate surfaces, ie, they are wetted by the bath. The system is subjected to mechanical agitation, either rubbing or shaking, which provides the necessary shearing action to separate the soil from substrate and disperse it in the bath. Agitation also promotes mass-transfer in the system, just as in a heterogeneous chemical reaction. The bath carrying the removed soil is drained, wiped, squeezed, or otherwise removed from the substrate. The substrate is rinsed free of the remaining soiled bath. This rinsing step determines the final cleanliness of the substrate. The cleaned substrate is dried or otherwise finished.

A meaningful discussion of detergency requires a definition of clean. In the physiochemical sense, a surface is clean if it contains no molecular species other than those in the interior of the two adjoining phases. It is difficult to achieve such a state even under the most exacting laboratory conditions. Practically, a surface is clean if it has been brought to a desired state with regard to foreign matter present upon it, as judged by agreed upon criteria. Household linen, for example, is considered clean when it is free of visible soil even though it may carry a starch and a softening finish. In the dyehouse of a textile mill, a piece of goods such as this would be rejected as dirty and returned for scouring because these finishes interfere with dyeing. Most standards for cleanness involve a visual or optical judgment for the presence of foreign matter. In some systems, for example, the desizing of cotton, the degree of cleanness may be specified by weight percentage of soil on the substrate. In other systems, such as the degreasing of metal, it is the weight of soil per unit area of substrate surface that specifies cleanness. In washing dishes or glassware, cleanness is often specified by complete water wettability or freedom from water break, as well as by appearance (see also METAL SURFACE TREATMENT; TEXTILES).

Although it is impossible to list all the practical detersive systems that might be encountered, a large proportion fall in a small number of classes. This classification disregards surfactant structure and type of substrate (fibrous or hard surface) and is restricted to a consideration of the soil present on the substrate, the mechanical action employed, the bath ratio, and the detergent used. Some of the more commonly encountered detersive systems are classified on this basis in Table 1.

2. Components of Detersive Systems

2.1. Substrates. Solid objects to be cleaned vary widely in chemical composition and surface configuration. With few exceptions, however, they can be divided into fabrics and fibrous materials, and hard surfaces. Fabrics present a highly complex configuration and can entrap soil even though it may be physicochemically removed from the surface. Most fabrics are organic polymeric materials that may be swellable by water or permeable to small molecules and ions dissolved in the bath. Many common polymeric fabrics, cotton, polyester, rayon, nylon, wool and cellulose esters, contain ionogenic or polar centers capable of localizing (generally anionic) electric charges. Hard surfaces, on the other hand, are relatively flat and smooth. They cannot entrap soil that has been detached by physicochemical action. In general, they are impermeable to water and water-soluble materials although they vary widely in their wettability and polarity. The most important types are glass, metal, and organic polymeric materials including painted surfaces, linoleum, and plastic tile.

2.2. Soils. Soils vary greatly. They may be a single solid or liquid phase but usually are two or more phases, intimately and randomly mixed and irregularly disposed over the substrate. In a large number of important detersive systems, the nature of soil and the quantity present are well known. This is the case, for example, in most textile mill operations such as raw wool scouring, the boil-off and scouring of loom-state woven goods, and the soaping of printed cottons. In the cleaning of fabricated metal parts to remove forming and drawing lubricants, buffing compounds, etc, the nature of the soil is well known. The behavior of soils encountered in dishwashing is well characterized.

As a result of many painstaking investigations, the soils on apparel encountered in laundering have been shown to be complex mixtures containing both oily and finely divided solid material (1,2). The oily material consists largely of fatty acids and polar fatty material but a considerable proportion of neutral nonpolar oil is also present. The solid components vary widely with the locale in which samples are taken, and resemble local street dust in composition.

Particle size is one of the most important factors in determining the ease with which solid soil can be removed from a substrate. Particles of >5 μm dia are generally easily removed. Particles of <10 nm dia cannot be removed by ordinary detersive processes once they are attached to a typical textile fabric. Such particles are responsible for the gradual irreversible graying of white goods with continued wear and laundering. Particles in this size range tend to

Table 1. **Detersive Systems**

System	Soil	Mechanical action	Bath ratio	Detergent
		Fabric and fibrous		
textile and allied manufacturing				
raw wool scouring	liquid at operating temperature	very gentle	high	organic surfactant
wool yarn and piece goods	liquid	gentle	moderately high	organic surfactant
scouring gray cottons	mostly solid; waxy and starchy	vigorous	low	built surfactant
scouring syntheticfabrics	mixed; oily lubricant and sizing residues	moderate	medium	built surfactant
de-inking paper	mixed; oily and pigment	vigorous	high	heavily built surfactant
laundering				
household	mixed and variable	moderate	high	unbuilt or built surfactant
commercial and industrial	mixed and variable; heavier than household soil	vigorous	high	built surfactant
rug cleaning inplant	heavy solid	moderate gentle	medium to low	organic surfactant, may be built
on location	heavy solid	vigorous; superficial brushing	very low; foam bath	organic surfactant foam
		Hard surfaces		
glass and ceramics				
hand dishwashing	mixed oily and solid organic	moderate to vigorous	high	organic surfactant
machine dishwashing	mixed oily and solid	vigorous hydraulic	high	inorganic[a]
commercial bottle washing	light solid organic	vigorous hydraulic	high	inorganic[a]
metals				
prefinishing cleaning	oily	moderate to gentle hydraulic	high	inorganic[a]
postforming emulsion cleaning	oily and mixed	gentle hydraulic	high	mixed inorganic and surfactant
cleaning metal structures and equipment, tanks, dairy equipment, etc	variable; mostly oily or organic solid	usually vigorous rubbing, sometimes hydraulic	usually low in wash cycle; may be high in rinse cycle	inorganic[a], built surfactant
organic surfaces, paint, linoleum, plastic tile	mixed solid, organic solid, and oily	usually vigorous low rubbing	low	lightly to moderately built surfactant
		Cosmetic and personal cleaning		
shampooing	oily	vigorous rubbing in rinse cycle	low in wash cycle; high	organic surfactant
bathing and washing	mixed, mostly oily	mild to vigorous rubbing	high; sometimes low in wash cycle	organic surfactant

[a] Organic surfactant frequently added to aid wetting and draining.

form clumps and clusters before they reach the fiber surface. These clusters behave like individual large particles. Particles or clusters in the range of 100 nm dia resist removal by simple agitation in liquids that are not surface active, but these particles are removable by normal detersive processes. This is the size range of greatest interest.

Soil may include material that is soluble in the bath, such as encrusted sugar residues and molecularly dispersed material such as fruit juice stains. Removal of these soils is an important aspect of cleaning but is not generally considered in discussions of detergency.

2.3. Baths. The baths discussed here are aqueous solutions. Most nonaqueous cleaning systems, such as metal degreasing operations, depend entirely on solvent action and therefore cannot be considered examples of detersive systems. Some nonaqueous systems, however, are true detersive systems. Modern dry cleaning baths, for example, contain solutes that are surface active in the conventional hydrocarbon or chlorinated hydrocarbon medium and aid soil removal. The physical chemistry of such systems differs considerably from that of aqueous systems. Among bath components the solute that is effective in cleaning, usually a mixture of several components, is called the detergent. The term detergent is also used frequently in the restricted sense of a surfactant of high detersive power. In many hard-surface systems, however, nonsurfactants such as alkaline silicates and phosphates exert a true detersive effect. They are, in fact, the principal detergents in these systems even in the complete absence of any surfactants. In the cleaning of fabric systems, the most important detersive component in the bath is the surfactant. Nonsurfactant components that augment the cleaning effect of surfactants are called builders. Many materials that act as builders in fabric systems, eg, phosphates and silicates, are the primary detergents in hard-surface systems, although their primary contribution to the cleaning process may differ in the two cases.

3. Formulation

Detergents are formulated to clean a defined set of soiled substrates under an expected range of washing conditions. Some detergents, the familiar bar or toilet soap, for example, consist essentially of only one component. There are few systems, however, in which a suitably formulated detergent consisting of several components does not outperform the best single-component system. Although detergents for hand dishwashing rarely contain builders, those currently used in the U.S. contain at least three surfactants, and may contain up to six. Ingredients of laundering detergent formulations for fabrics may be divided into the following groups: surfactants (qv), including soap and various others; the inorganic salts, acids, and bases, including builders, and other compounds that do not contribute to detergency but provide other functions, such as regulating density and assuring crispness of powdered formulations; organic additives that enhance detergency, foaming power, emulsifying power, or soil-suspending effect of the composition; and special purpose additives, such as bleaching agents (qv), fluorescent whitening agents (qv), antimicrobial agents, blueing agents, or starch, which provide desirable performance functions but have no direct effect on soil removal (see also INDUSTRIAL ANTIMICROBIAL AGENTS).

Fabric detergent formulations for special applications, such as the various specific operations within the textile mill, are frequently much simpler. They tend to contain little if any builder or special-purpose additive. The indispensable ingredient in fabric detergency is the organic surfactant. Formulations for hard-surface detergency such as those used in automatic machine dishwashing, are simpler than fabric-washing compositions. An organic surfactant is frequently not needed and inorganic salts are the detersive ingredients.

3.1. Surfactants. The most important components of detersive systems are, of course, the surfactants described elsewhere in the *Encyclopedia*.

3.2. Builders. Builders are substances that augment the detersive effects of surfactants (3). Most important is the ability to remove hardness ions from the wash liquor (ie, soften the water) and thus to prevent them from interacting with the surfactant. Such interaction reduces detersive effectiveness. Hardness ions can also interact with the negative charges present on soil and fabric surfaces (formed, eg, by ionization of −OH or −COOH groups) reducing electric repulsion between them, thus hindering the detersive process. Hardness ions are best removed by sequestration to form soluble chelates (see CHELATING AGENTS). Less desirable is the formation of insoluble precipitates that may deposit on fabrics and machines and can, over many wash-and-wear cycles, lead to incrustation on machine parts and harshening of fabric. A third mechanism for removing hardness ions from wash liquors is through ion exchange in which calcium in solution displaces sodium ions in the ion exchanger, thus effectively removing the hardness from solution. The ion exchanger, in general, is a solid. Unlike precipitated calcium carbonate, however, the particle size of the ion exchanger can be controlled and the problem of the presence of insoluble particles in the wash liquor can be reduced.

In general, builders supply alkalinity to the wash liquor and thus function also as alkalies. In addition, they can exert a suspending (antiredeposition) effect and keep detached soil from depositing on the fabric; builder ions with multiple charges are especially effective in this area.

Phosphates. Pentasodium triphosphate [7758-29-4], sodium tripolyphosphate, STPP, $Na_5P_3O_{10}$, is the most widely used and most effective builder in heavy-duty fabric washing compositions (see also PHOSPHORIC ACID AND PHOSPHATES). It is a strong sequestrant for calcium and magnesium, with a pK^{Ca} of ca 6, and provides excellent suspending action for soils. Because of its high sequestration power, it also finds extensive application in automatic-dishwashing detergents. Sodium tripolyphosphate forms stable hydrates and thus aids in the manufacture of crisp spray-dried laundry powders.

Tetrasodium pyrophosphate [7722-88-5], $Na_4P_2O_7$, is another important primary builder and detergent. In sequestration, it is not quite as effective as sodium tripolyphosphate and its usage in heavy-duty laundry powders has declined in recent years. Functionally, tetrasodium pyrophosphate is both a builder for surfactants (ie, water softener) and alkali.

Where hardness is present in excess of the sequestering capacity of sodium tripolyphosphate and pyrophosphate, both can function as precipitant builders.

Trisodium phosphate [7601-54-9], trisodium orthophosphate, Na_3PO_4, is an important constituent of hard-surface cleaners including those for ceramic, metal, or painted surfaces. It may be used with soaps, surfactants, or other alkalies. It precipitates many heavy-metal ions but does not sequester to form soluble chelates. It is thus a precipitant builder and additionally an alkali.

Glassy phosphates (sodium polymetaphosphate [50813-16-6], sodium hexametaphosphate [10124-56-8]) vary in composition, depending upon the manufacturing process. They exert a powerful sequestering and suspending effect combined with a low solution pH, about 6 or 7, and tend to hydrolyze or revert in aqueous solution and heat to pyrophosphates and orthophosphates.

Potassium phosphates, particularly tetrapotassium pyrophosphate [7320-34-5], $K_4P_2O_7$, are considerably more soluble than their sodium analogues. They have been used as builders in liquid detergents.

In the early 1970s, a number of U.S. jurisdictions banned the use of phosphates as detergent builders. The trend has continued to the point today that phosphates are banned in a sizeable proportion of the U.S. (about 45%). Consequently, several alternatives to phosphates have been introduced into heavy-duty U.S. laundry detergents. No entirely satisfactory single substitute for sodium tripolyphosphate has been found that is as cost effective. Sodium tripolyphosphate aids detergency not only via water softening (calcium/magnesium sequestration) but also via soil suspension, soil removal, and antiredeposition benefits, all of which are closely related mechanistically. Additionally, STPP provides excellent spray-dried powder properties. However, it has been found that use of a water softener such as 4A Zeolite, in combination with a mixed active system, buffer such as carbonate, and soil suspension antiredeposition agents such as NaCMC, poly(ethylene glycol), polacrylate, polyacrylate/maleate copolymers, plus other cobuilders such as citrate, can provide general cleaning at least as good as the old high P formulations. Indeed current products containing enzymes and effective low temperature bleach are superior. It seems likely that all principal U.S. detergent manufacturers will remove phosphate from their products in the near future.

Sodium Carbonate. Sodium carbonate softens water by forming insoluble calcium carbonate with calcium ions in hard water. Carbonate can also reduce calcium levels by ion pairing, although the benefit to detergency is questionable. Buildup of calcium carbonate on machine and fabrics, which can occur with time, is undesirable. Sodium carbonate [497-19-8] does not provide any suspending action. It does, however, provide alkalinity to the wash liquor and is an effective alkali.

Silicates. Sodium silicates have been used extensively as soap builders in laundering formulations since well before the advent of synthetic surfactants. Silicates are more effective in removing magnesium than calcium hardness. Again, they function primarily as alkalies. In addition, they act as anticorrosive agents and prevent deterioration of washing machines, specifically metal pump parts. However, in recent years, many of these machine parts have been replaced by engineering plastics and the anticorrosion function has lost some of its importance. Alkaline silicates act as primary detergents in machine-dishwashing formulations. Commercial alkaline silicates are characterized by the ratio of SiO_2 to Na_2O in the molecule. The silicates used in detergent formulations generally show a ratio >1, usually 2.0 to 2.4. The 1:1 compound, sodium metasilicate, is considered too corrosive to be widely used in consumer product formulations.

Zeolites. Certain zeolites have found application as builders in heavy-duty detergent formulations. The zeolite of choice is a so-called Type A zeolite, of empirical composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$ and particle size of the range of 10 μm. This builder functions by ion exchange in which sodium ions released from the zeolite crystal are replaced by calcium ions in hard water, thus lowering the free hardness in the wash. Its pore size accommodates calcium ions but is not sufficiently large for the highly hydrated magnesium ions. Zeolite A, therefore, is not an effective builder for magnesium hardness. Like sodium carbonate building, the ion exchange process is appreciably slower than soluble chelate formation by strong sequestrants like sodium tripolyphosphate. Type A zeolite is used principally to replace sodium tripolyphosphate in areas where phosphates are limited by law, ie, in the United States, Canada, and Western Europe. However, it is not practical as the sole builder in a nonphosphate detergent formulation (see also MOLECULAR SIEVES), since it does not contribute to alkalinity, soil suspension, or bind magnesium.

Clays. Clays (qv), such as kaolin, the montmorillonites, and bentonites, have been recommended and used from time to time as ingredients of washing compositions and other formulations containing surface-active agents. Under certain favorable conditions, particularly in soft water of low dissolved solids content, clay suspensions can have a marked detersive effect on ordinary soiled fabrics. Bentonite [1302-78-9] also acts as a suspending agent. In addition, sodium bentonite has some water softening effectiveness by virtue of its ability to sorb calcium ions. However, clays are considerably less effective than Type A zeolite in water softening.

In one U.S. laundry powder, a montmorillonite clay serves as the main softening component. It is combined with a waxlike cationic granule (4–7). Both are absorbed or filtered onto the cloth during the wash and spin rinse. The clay absorbs onto the fabric in thin sheetlike layers, providing a lubricating effect. The cationic particles melt in the heat of the automatic dryer providing an antistatic benefit and augmenting the softening benefit of the clay. A softening-in-the-wash effect is thus achieved with minimal interference with detergent performance.

Nitrilotriacetic Acid. The trisodium salt [5064-31-3] of nitrilotriacetic acid, $N(CH_2COOH)_3$, so-called NTA, is a powerful sequestrant builder, comparable to sodium tripolyphosphate. It is therefore noted here, even though it is an organic builder. NTA has been recommended and used as a phosphate replacement in areas where phosphate is banned. However, because of adverse laboratory reports of possible teratogenic effects, NTA has withdrawn in 1970 from consumer products at the suggestion of the U.S. Surgeon General. Because it is a smaller molecule than sodium tripolyphosphate, NTA is theoretically a more effective sequestrant on a weight basis. It is, however, less effective than sodium tripolyphosphate as a suspending agent and is not as easily processed in spray-dried laundry powders.

Alkalies. Caustic soda (sodium hydroxide) is used largely in mechanical bottle washing, glass washing, and metal cleaning. Sodium carbonate, either anhydrous (soda ash) or in hydrated form, has been used as builder or filler in soaps, surfactants, and with inorganic constituents in cleaners for hard surfaces and fabrics. It forms insoluble calcium carbonate with calcium ions in hard water but does not provide any suspending action. Sodium bicarbonate [144-55-8] $NaHCO_3$, sodium sesquicarbonate [6106-20-3] $NaHCO_3 \cdot Na_2CO_3$, and sodium borate [1330-43-4] $Na_2B_4O_7 \cdot 10H_2O$, borax [1303-96-4] are used in place of soda ash when a lower pH is desired. In cases where high solubility is required, the potassium analogues are used.

The alkalies do not sequester heavy-metal ions and have little soil-suspending effect. They are effective in maintaining a high pH and saponify the acidic constituents of soil and thus promote cleaning. In the cleaning of ceramics, glass, and metal surfaces, however, the alkalies act as primary detergents even in the absence of surfactants in these systems.

Neutral Soluble Salts. Sodium sulfate [7757-82-6] and, to a considerably lesser extent, sodium chloride [7647-14-5] are the principal neutral soluble salts used in laundering compositions. They are often considered to be fillers although they perform an important standardizing function enabling the formulator to manufacture powders of a desired, controlled density. Sodium sulfate, in addition, lowers the critical micelle concentration of organic surfactants and thus the concentration at which effective washing can be achieved.

In wool-scouring systems for textile processing that contain nonionic surfactants, sodium chloride acts as a true builder, ie, detergency promoter.

3.3. Organic Additives. Certain nonsurfactant organic additives improve cleaning performance and exhibit other desirable properties.

Such additives are usually present in low percentage and serve one or more of the following specific functions: reduced redeposition of soil from the detergentbath onto the substrate; increased whiteness or appearance of cleanliness; enhanced cleaning effect on specific types of solid and stains; promotion or inhibition of foaming power and stability; increased solubility or other modification of the physical form of the detergent composition; sequestering of heavy-metal ions, both in the concentrated detergent and in the diluted cleansing bath; reduced injurious effects the detergent may have on the substrate or the washing machine, such as tarnishing of silverware or etching of glassware, corrosion of metals, or irritation of skin in toilet and cosmetic applications.

Antiredeposition agents contribute to the appearance of washed fabrics. Sodium carboxymethylcellulose [9004-32-4], NaCMC is the most widely used, and on cotton fabrics, the most effective. With the advent of synthetic fabrics, other cellulose derivatives, eg, methylcellulose [9004-67-5], hydroxybutylcellulose, hydroxypropyl- and mixed methyl and hydroxybutycellulose ethers have been shown to be more effective than NaCMC (8) (see CELLULOSE ETHERS).

Fluorescent whitening agents (qv) were first disclosed in 1940 in combination with detergents (9). They absorb ultraviolet radiation and subsequently emit some of the radiation energy in the blue part of visible spectrum. As a result, they confer enhanced whiteness to the appearance of washed articles. Highly effective cotton-substantive fluorescent whitening agents were in widespread use at relatively high concentrations (ca 0.5%) in the 1950s and 1960s. For synthetic fabrics such as polyester, it has proved to be more effective to prebrighten the fabric by incorporating the fluorescent whitening agent in the spin-melt during manufacture rather than depend on adsorption from the detergent bath. As a result, the usage of fluorescent whitening agents in formulated laundry products has decreased in recent years.

Blueing agents, which are dyes, provide another approach to maintaining fabric whiteness by a mechanism in which a yellow cast of washed fabrics is covered by the blue dye. Since this approach reduces reflectance, it is less desirable than the use of fluorescent whitening agents that increase reflectance.

Proteolytic enzymes have been generally used in European detergent formulations. In the U.S., they were used in the late 1960s and early 1970s, but their use declined until they were present in only a few detergents. There has been a resurgence of their use in the last decade. Proteolytic enzymes in particular are widely used in premium products. They degrade proteinaceous stains and aid the cleaning performance of other formulation ingredients (10–12). Amylases and lipases have been used in a few U.S. detergents, the former to remove starches and the latter fatty esters and triglycerides. Cellulases have appeared in a few laundry detergents around the world. Since there are few, if any, cellulase-based soils present on home laundry, any laundering benefit from cellulase would be expected to come from action on cotton fabric. The nature and magnitude of such benefits is uncertain (see ENZYMES, INDUSTRIAL APPLICATIONS).

Bleaching agents (qv), such as sodium perborate trihydrate [28962-65-4], $NaBO_3 \cdot 3H_2O$, are commonly present in significant amounts in European laundry detergents. At high washing temperatures, sodium perborate effectively bleaches chemical stains such as wine, fruit juices, etc. As European wash temperatures have declined so has the efficacy of perborate alone. Bleach activators, primarily TAED (tetracetyl ethylenediamine) have been widely used in Europe to provide effective bleaching at these low temperatures. Because of the lower washing temperature in U.S. machines, sodium perborate is considerably less effective and its usage is restricted to some individual brands of laundry detergents (13,14). In the U.S., even TAED is ineffective due to still lower wash temperatures, shorter wash times, and lower product concentration. One U.S. detergent manufacturer has introduced detergents with the bleach activator sodium nonanoyloxybenzene sulfonate (15). This activator forms the surface active species pernonanoic acid that does provide a bleach benefit under U.S. conditions. In automatic-dishwashing formulations, bleaching agents are needed to remove food stains from dishware and break down proteinaceous soil. Chlorine is the most cost-effective agent available for this purpose and is present in all U.S. products as chlorinated isocyanurate (see CYANURIC AND BIOCYANURIC ACIDS).

Foam regulators such as amine oxides, alkanolamides, and betaines are present in products where high foam value is functionally or esthetically desirable, mainly hand-dishwashing liquids and shampoos. In automatic dishwashing products, on the other hand, copious foam volumes interfere with the efficiency of the mechanical rotors during operation. In this type of product, a foam depressant is often present.

Organic sequestering agents serve the same purpose as the sequestering phosphates, ie, to remove interfering metal ions from the detergent bath. They would appear to also provide some benefits through ionic strength and soil suspending effects. They are used where the less expensive phosphates are, for one reason or another, not applicable. Nitrilotriacetic acid, EDTA, and a variety of organic phosphonate structures are commonly used in a wide range of detergent compositions. With the elimination of phosphate, sodium citrate [68-04-2] and synthetic analogues such as sodium tartrate monosuccinate and sodium tartrate disuccinate (16) have found wide use, especially in heavy-duty liquids. They are used to some extent in detergent powders. In the latter case they can also be used to modify powder properties, as can sodium polyacrylates. Certain hard-surface cleaning products such as sanitizing cleaners for hospital use are examples of products generally containing small amounts of organic sequestrants.

4. Factors Influencing Detergency

Detergency is mainly affected by the concentration and structure of surfactant, hardness and builders present, and the nature of the soil and substrate. Other important factors include wash temperature; length of time of washing process; mechanical action; relative amounts of soil, substrate, and bath, generally expressed as the bath ratio, ie, the ratio of the bath weight to substrate weight; and rinse conditions.

4.1. Effect of Surfactant Concentration. A plot of soil removal versus surfactant concentration is generally sigmoid. It starts at the soil removal of water without surfactant, rises slowly, then more steeply until a plateau is reached when detergency is little affected by increase in surfactant concentration. This plateau can be correlated with the critical micelle concentration, CMC, of the surfactant, and is generally higher than the CMC. In general, detergency attains its maximum when the CMC of the surfactant is reached, taking into account surfactant adsorption on the soil and substrate. However, with certain surfactants, there is evidence that oily-soil detergency continues to increase above the CMC (17–20).

4.2. Surfactant Structure. The chemical structure of the surfactant is an important factor in detersive effectiveness. When relating detersive power to chemical constitution, within limited series certain regularities can be observed, but few if any general principles apply to the whole range of surfactants. Among the homologous fatty acid soaps and the straight-chain alkyl sulfates, optimum detergency under usual washing conditions occurs at a chain length of ca sixteen carbon atoms. Detergency among the ethoxylated nonionic surfactants varies in a regular manner with the length of the ethylene oxide chain as well as with the structure of the hydrophobic group. In general, optimum detergency occurs with 12–16 carbon atoms in the hydrophobe chain, and a hydrophile–lipophile balance, HLB, of about 12. For oily soil detergency by nonionics it is often found the optimum corresponds with the phase inversion temperature of the system under consideration (21).

Within a series with a fixed hydrophilic head group, detergency increases with increasing carbon chain length, reaches a maximum, and then decreases. This behavior frequently reflects a balance between increased surface activity of the monomer and decreased monomer concentration with increased surface activity. Similar effects are seen in surfactants in biological systems.

The numerous studies of the effect of surfactant structure in detergency include the classical paper on the series of sulfated secondary straight-chain alcohols (22) and various papers on detergent–builder combinations (23); nonionic–anionic mixtures (24,25); the polyethenoxy nonionic series (21,26,27); detergency of isomeric alkylbenzenesulfonates (28); practical home laundering (29); laundering and detergency effects in seawater (30); *o*- and *p*-alkylbenzene-sulfonates with straight and branched chains (31); and studies on alkylbenzene-sulfonates (32).

4.3. Water Hardness and Builders. The presence of heavy-metal ions, especially calcium and magnesium, has an effect on washing second only to that of the surfactant itself. Distilled water, used in a system where soil and substrate do not contain substantial calcium ions, is a surprisingly effective detergent, when the soils themselves contain fatty acids or sodium soaps. Detergency can be improved by the addition of surfactants in amounts smaller than might be expected. Conversely, the detergency of surfactants is generally decreased by the presence of hardness ions (Ca^{2+} and Mg^{2+}) and hard water alone is a poor soil remover. With traditional formulations containing anionic surfactants or soaps, cotton can be cleaned well by washing only if the calcium concentration is reduced to <0.01 mM. In current synthetic detergent compositions, builders sequester calcium and magnesium ions and thus reduce interaction with surfactants, soils, and fabrics as described above.

The sodium soaps of fatty acid form calcium soaps of such low solubility that they act as their own builders. Initial soap additions precipitate the calcium ion and the soap added thereafter functions in soft water. At high temperatures, the calcium soaps are relatively soluble compared to calcium tripolyphosphate. Thus sodium tripolyphosphate (STPP) can build (revert) soaps in a hot water wash. However, at low temperatures the relative affinity of STPP for calcium decreases so that STPP cannot build soaps in a cold water wash.

Calcium ion enters the system not only in the form of water hardness but also in the form of calcium salts contained in the soil. Other heavy-metal ions such as aluminum and ferric iron may also be present in the soil, and must be removed by an appropriate builder to achieve good soil removal. Effective builders for cotton washing are those for which the calcium dissociation constant, expressed as pK_{Ca}, or $-\log K_{Ca}$ is >4 and preferably >7 (33). Much of the work that led to elucidating the role of builders as calcium sequestering agents in detergency was done in connection with redeposition studies (34).

Legislatively mandated reductions in detergent phosphate concentrations have resulted in numerous attempts to compensate for the attendant cleaning losses. Problems caused by phosphate reduction can be ameliorated by changes in surfactant systems. Thus, calcium-sensitive surfactants such as linear alkylbenzenesulfonates (LAS) can be replaced by calcium insensitive ones such as alcohol ethoxylates (AE) or alcohol ether sulfates (AES). Proper blends greatly reduce surfactant sensitivity to calcium ions (35,36). Increasing the amount of surfactants partially compensates for phosphate reduction or elimination. Other calcium-lowering agents include NTA, citrate, zeolite, and carbonate. Citrate and NTA lower calcium levels in solution by sequestration, zeolite by ion exchange, and carbonate by ion pair formation and precipitation. To date, no entirely satisfactory single replacement for phosphate has been found. Indeed, some soil-cloth detergency data show that the 1978 nonphosphate products are less effective than the 1969 high-phosphate products (37). However, subsequent refinements in formulation technology have substantially improved nonphosphate product performance to equal that of their phosphate predecessors.

In the presynthetic surfactant era, soap was built (and still is) with alkaline salts such as soda ash, silicates, orthophosphates, and borates. These materials buffer the wash solution to a high pH and prevent soap protonation; thus the soap remains effective. Another type of builder is the neutral inorganic salt such as sodium chloride and sodium sulfate. These materials may improve detergency by increasing the ionic strength and altering the CMC of anionic surfactants.

4.4. Antiredeposition Agents. The redeposition effect is best illustrated by agitating a clean swatch of white cotton in a washing bath that has been used and is turbid with dispersed soil. Even though the bath may still be effective and capable of removing soil, the white swatch picks up some soil from the bath and darkens. Any agent that minimizes this redeposition improves net soil removal, and decreases the soil accumulation through several laundering cycles. Redeposition is in many ways the inverse of soil removal and is influenced by the same factors. Thus, calcium ion promotes redeposition in much the same way that it inhibits soil removal. Surfactants themselves are effective antiredeposition agents. Builders reduce redeposition independently of their ability to sequester hardness ions.

Sodium carboxymethylcellulose, NaCMC, greatly reduces redeposition in cotton-washing systems based on synthetic surfactants. It is effective at remarkably low concentrations of ca 1% of the standard washing compositions used at ca 0.1 to 0.2% in the bath. Thus, ca 0.001–0.002%, or 10–20 ppm NaCMC is sufficient to significantly inhibit redeposition.

A very large number of hydrophilic polymers have been tested with regard to their power of inhibiting redeposition, and it is remarkable how few materials can match NaCMC. Some proteins, polyvinylpyrrolidinones, and vinyl alcohol polymers with rather specific molecular weight ranges are in the same class as NaCMC. Certain starch derivatives, cellulose sulfates, and cellulose ethers are also effective. Currently, both NaCMC and cellulose ethers are used in home laundry products specifically to control redeposition. The cellulose ethers are used to control oily soil redeposition upon synthetic fibers, especially polyester. Using tracer methods, it was proved that NaCMC is adsorbed on the soil particles and also, under normal laundering conditions, on cotton fiber (38,39). Adsorption on cotton appears to be more important in preventing soil redeposition. This absorption occurs to a significant extent only in the presence of metallic cations that are furnished as sodium ions from STPP and the filler salts present in the detergent. In the absence of cations, except for the Na^+ present in the NaCMC itself, the adsorption is so slight as to be almost undetectable, and the antiredeposition effect is correspondingly lowered.

4.5. Liquid Soil. Liquid soils are frequently removed from fibers by a roll-up mechanism (40). In a study of wool grease removed from single fibers, it was found that the grease layer, originally continuous, rolled up in relatively large globules that detached themselves from the fiber. The detergent alters the contact angle at the fiber–grease–water interface. In pure water, the contact angle is $<90^\circ$, measured through the oil. Addition of detergent increases the angle to ca 180°. The receding contact angle, ie, that measured as the oil rolls up, is more important in detergency than is the advancing contact angle. Detergency mechanisms are similar on wool, viscose rayon, and cuprammonium rayon (41). The soil removal depends primarily on the nature of the oil. Those containing free fatty acids are removed more rapidly, followed by neutral glycerides and less polar mineral oils. Similarly, polar oils are more easily removed from wool than nonpolar oils (42). This difference correlates well with differences in contact angle.

Liquid soil can be removed by direct emulsification and solubilization as well as by roll-up. Oils that are more readily emulsified or solubilized are removed more rapidly and more completely.

4.6. Solid Soil Type and Size. Different solid soils differ greatly in ease of removal and redeposition behavior. These differences can be traced to particle size and soil–substrate bonding. The effect of particle size variation on detergency has been studied with soil removal and redeposition techniques.

In an early systematic investigation of this relationship, a series of carbon black samples was applied to chopped cotton fibers from an aqueous suspension with vigorous agitation (43). The degree of soiling was estimated by filtering the fibers with suction to form a mat, drying, and measuring the reflectance of the mat. The degree of soiling was found to be directly related to the particle size of the carbon black. As shown in Figure 1, when the primary particles of the carbon black are <50 nm, the soil deposition is severe, whereas at particle sizes >50 nm, the soil deposition is much lighter and relatively independent of particle size. Electron microscope studies of the cotton fiber show that 50 nm is about the upper limit of the crevice width on the surface of cotton fibers. Furthermore, the soil deposition by this procedure using fine-particle carbon blacks is practically irremovable, and the fibers are to all intents and purposes dyed a very fast gray. On this basis and on the basis of other supporting evidence, it was concluded that soiling in this system takes place by microocclusion, ie, that the particles of soil are so small that they can be trapped mechanically by

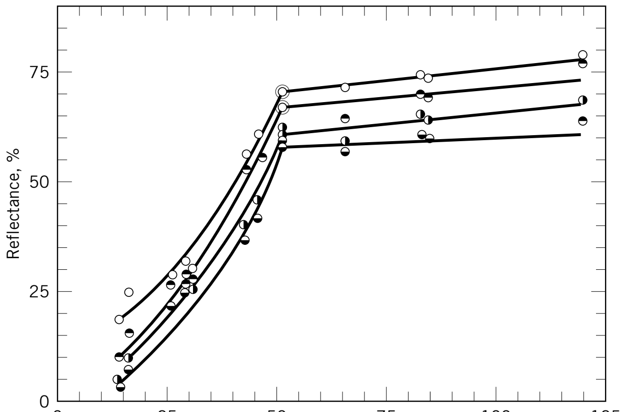

Fig. 1. Effect of primary particle size in a 1% carbon black dispersion on rate of change in reflectance. ○ = 5 min; ◓ = 20 min; ◑ = 180 min; ◒ = 360 min.

the irregularities of the fiber surface, even though these irregularities are scarcely larger than the dimension of a polymeric molecule. This theory accounts well for the observed facts, but the facts could also be accounted for by simply assuming that van der Waals forces control the attachment of the carbon particles to the fiber. Since these forces operate at the surface of the particle, there should be a critical particle size below which the surface forces become more important than the inertial and gravitational forces that are proportional to mass. Electron micrographs of soiled cotton show adherent soil particles in size ranges up to 0.5–2.0 μm clinging to apparently smooth surfaces (44–46). These and other supporting detergency data indicate that mechanical binding is not the basic mechanism of solid soil binding, even though the binding varies greatly with particle size.

As might be expected, large differences in the removability of solid particulate soil are due to differences in the chemical nature of the particle surface. Thus, iron oxides, lampblacks, and clays, all of the same particle size, differ greatly in their redeposition behavior and the manner in which they are removed.

4.7. Fabrics and Fibrous Substrates. Certain fibers are easier to wash than others. The hardness of the fiber surface, which varies not only with the basic fiber but also with the surface finish, affects both soilability and soil removal. Generally, soft finishes pick up and retain soil more readily than hard finishes, since soft surfaces permit greater soil–surface contact. The hydrophobicity of the fiber surface also influences soilability and soil removal, and the more hydrophobic fibers show greater soil retention especially for hydrophobic soils such as oils. These effects are explained by the high-energy interface existing between hydrophobic fibers and water (47). Many soil components lower the interfacial energy and therefore locate at the fiber–water interface.

Soils can also penetrate into the fiber. The interior of the cotton (qv) fiber, the lumen, is relatively hollow, and soils may collect there. Polyester fibers are solid, but if polyester is washed above its glass-transition temperature T_g it becomes relatively fluid (see FIBERS, POLYESTER). In this case, oils on the fiber surface can mix with the polyester itself. When soils penetrate into the fiber, they are nearly impossible to remove.

4.8. Temperature and Mechanical Action. Absorption of external thermal or mechanical energy by a detersive system influences the rate and extent of soil removal. Raising the temperature generally increases the cleaning rate and, therefore, the amount of soil removed during any fixed-time laundering cycle. The effect is only strong at two critical temperatures; one is the temperature where the fatty soil in the system liquefies. As temperature increases through this region, the detergency increases markedly. Typical curves of detergency versus temperature are shown in Figure 2 (48). The second critical temperature is the boiling point. Boiling greatly increases detergency because of the localized mechanical action of steam bubbles forming, expanding, and breaking away at the solid– liquid interfaces. However, in the United States, boiling effects are never encountered in home washing machines. U.S. laundry wash temperatures have declined to an average wash temperature of about 35°C, and the average hot water wash temp is only 54°C. From 1970 to 1988 hot water wash declined from 48 to 20% of washes (49). Temperature effects are

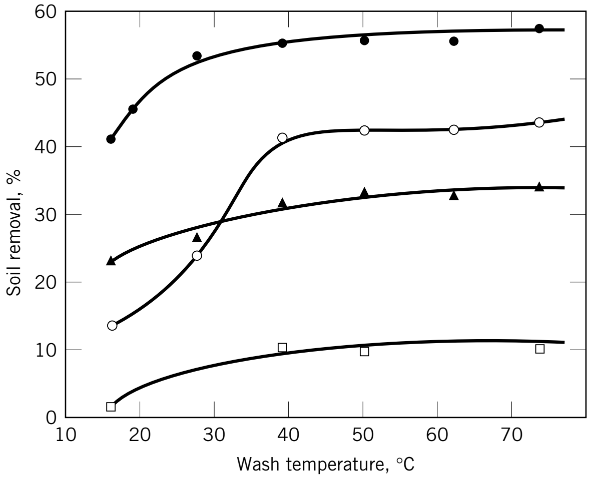

Fig. 2. Effect of wash temperature on removal of ● sebum, ○ lanolin, and ▲ lard from cotton (0.25% built detergent) (48). □, Represents sebum removal with no detergent.

also important with certain detergent additives. Thus the efficacy of certain bleaches and enzymes is markedly reduced at the low wash temperatures now popular. These effects emphasize the problems inherent in the current trend to lower wash temperatures.

As with the case of energy input, detergency generally reaches a plateau after a certain wash time as would be expected from a kinetic analysis. In a practical system, each of its numerous components has a different rate constant, hence its rate behavior generally does not exhibit any simple pattern. Many attempts have been made to fit soil removal (50) rates in practical systems to the usual rate equations of physical chemistry. The rate of soil removal in the Launder-Ometer could be reasonably well described by the equation of a first-order chemical reaction, ie, the rate was proportional to the amount of removable soil remaining on the fabric (51,52). In a study of soil removal rates from artificially soiled fabrics in the Terg-O-Tometer, the percent soil removal increased linearly with the log of cumulative wash time.

In detailed studies with a number of different artificial test cloths, first-order kinetics were obtained for soil removal during the first 6–20 min of the cycle (53).

In the washing of fabrics, machine and timing must be carefully adjusted. Too large an energy input for too long a time can injure fabric severely, and eventually tear it to shreds. The same effect is quite possible with purely mechanical agitation.

4.9. Foam. The relationship of foaming power to detergency has always been of interest, and foaming power has become associated in many consumers' minds with high detersive power (see also FOAMS). However, foam has no direct relationship to detergency in ordinary fabric-washing systems, and does not improve cleaning in a laundry or home-washing machine. Indeed, excessive foam can inhibit agitation and reduce cleaning. Additionally, excess foam levels may concentrate certain surface active cleaning agents in the foam, reducing their contact with the fabrics to be cleaned. In systems of low bath ratio, on the other hand, foam may play an important role. The individual foam laminae tend to imbibe and segregate particles of both liquid and solid soil that have been removed from the substrate. This prevents redeposition and enables the soil to be easily removed by scraping off or rinsing away the soil-laden foam. This effect is very important in the on-location shampooing of rugs, and to a certain extent in the shampooing of human hair. An excellent series of photomicrographs show the imbibition of liquid-soil droplets by foam films during the washing of oiled glass plates (54). The soil tends to be carried by capillary convention to the low-pressure region in plateau borders where three individual laminae join to form the edge of a foam cell.

5. Mechanisms

Even the simplest detersive system is surprisingly complex and heterogeneous. It can nevertheless be conceptually resolved into simpler systems that are amenable to theoretical treatment and understanding. These simpler systems are represented by models for substrate-solid soil and substrate-liquid soil. In practice, many soil systems include soli–liquid mixtures. However, removal of these systems can generally be analyzed in terms of the two simpler model systems. Although these two systems differ markedly in behavior and structure, and require separate treatment, there are certain overriding principles that apply to both.

The first principle is that soil systems can be regarded and treated as classical systems of colloid and surface chemistry. A cotton fiber bearing attached small particles of clay or carbon soil, immersed in an aqueous medium, is fully analogous to the sulfur sols or gold sols of classical colloid chemistry (see COLLOIDS). Although the fiber is not of colloidal dimensions, the area over which any individual soil particle contacts the fiber is of colloidal dimensions. Furthermore, the ratio of the soil particle's area to the area of contact, and the ratio of the soil particle's mass to the area of contact put this system in the colloidal range. These ratios are the same as the ratios prevailing when one sulfur sol particle makes contact with another. In addition, in the substrate-soil system two different types of surfaces are interacting, whereas in the classical sol systems the particles are all of the same chemical nature and the interacting surfaces are therefore similar. The problem of mixed sols has, however, been explored in classical colloid chemistry to at least a limited extent, and it is fully analogous to the problem of the model soil-detersive system. A fiber or steel plate covered with oil and immersed in an aqueous solution is a good representative of the liquid-liquid-solid system of classical surface chemistry. The well-established concepts of interaction at the liquid–liquid interface and at the three-phase boundary line are fully applicable.

A second principle applying to these model systems is derived from their colloidal nature. With the usual thermodynamic parameters fixed, the systems come to a steady state in which they are either agglomerated or dispersed. No dynamic equilibrium exists between dispersed and agglomerated states. In the solid-soil systems, the particles (provided they are monodisperse, ie, all of the same size and shape) either adhere to the substrate or separate from it. In the liquid-soil systems, the soil assumes a definite contact angle with the substrate, which may be anywhere from 0° (complete coverage of the substrate) to 180° (complete detachment). The governing thermodynamic parameters include pressure, temperature, concentration of dissolved components, and electrical conditions. This concept is at variance with the idea of a dynamic detergency equilibrium which was advanced as a working hypothesis by many of the early investigators. It is however, much more in keeping with the established concepts of colloid chemistry. In the classical theory of lyophobic colloids, no consideration is given to a dynamic equilibrium existing between the peptized state and the agglomerated state. This all-or-nothing behavior has been studied experimentally in model detersive systems by observing, with the help of microscopic techniques, the behavior of single textile fibers in aqueous carbon black suspensions containing dissolved soap (55). In the absence of soap, the carbon particles deposit on the fiber. When sufficient soap is added, the carbon particles do not deposit on the fiber but remain in suspension. The quantity of soap necessary to maintain the carbon in suspension is proportional to the amount of carbon present in the system. There is a sharp demarcation between the state in which the carbon is suspended and the state in which the carbon is attached to the fiber.

In applying this concept, the factor of particle size must be continuously borne in mind. A heterodisperse system can reach a steady state wherein the smaller particles are agglomerated and the larger particles are dispersed, giving the apparent effect of an equilibrium. In ideal monodisperse systems under steady conditions, however, no such effects are noted.

Purely mechanical disturbances (which are not usually considered thermodynamic variables) may influence the state of aggregation of a colloidal system; for example, floc size in carbon and iron oxide suspensions varies with the degree of agitation being imposed on the system (56). When the agitation is stopped, the flocs revert to their steady-state size. To have any effect, the shear field must be quite high and the particles relatively large. With particles $< 0.5\ \mu\text{m}$, thermal agitation becomes more important than even vigorous mechanical agitation in determining the state of aggregation.

A final consideration in resolving practical detersive systems into their simpler components relates to soil removal versus redeposition. Superficially, it would appear that the redeposition phenomenon contradicts the all-or-nothing concept that the system must exist in either the agglomerated or the dispersed state. Keeping in mind both the composite nature and the kinetics of a practical system, it is readily shown that no such contradiction exists. The soil particle that redeposits is in a different state from what it was during its initial removal from the substrate. It may have changed its state by becoming detached from adherent oil or from a cluster of similar solid particles. During the time interval between detachment and redeposition, it may have altered its surface character by adsorption or desorption. In this time interval, the state of the substrate surface may also have changed by adsorption or desorption, or by the loss or gain of an oily layer. Additionally, there are probably varying substrate types present in the wash, with varying affinities for the soils present. For example, oily soil could be detached from a cotton fiber, but then deposit on a polyester fiber for which it would have a greater affinity. Thus, the initial group of agglomerated systems, which composes the soil–substrate–bath complex before soil removal, is quite different from the agglomerated system composed of substrate and redeposited soil.

5.1. Solid-Soil Detergency.

Adsorption. Many studies have been made of the adsorption of soaps and synthetic surfactants on fibers in an attempt to relate detergency behavior to adsorption effects. Relatively fewer studies have been made of the adsorption of surfactants by soils (57). Plots of the adsorption of sodium soaps by a series of carbon blacks and charcoals show that the fatty acid and the alkali are adsorbed independently, within limits, although the presence of excess alkali reduces the sorption of total fatty acids (58). No straightforward relationship was noted between detergency and adsorption.

In a study of the adsorption of soap and several synthetic surfactants on a variety of textile fibers, it was found that cotton and nylon adsorbed less surfactant than wool under comparable conditions (59). Among the various surfactants, the cationic types were adsorbed to the greatest extent, whereas nonionic types were adsorbed least. The adsorption of nonionic surfactants decreased with increasing length of the polyoxyethylene chain. When soaps were adsorbed, the fatty acid and the alkali behaved more or less independently just as they did when adsorbed on carbon. The adsorption of sodium oleate by cotton has been shown independently to result in the deposition of acid soap (a composition intermediate between the free fatty acid and the sodium salt), if no heavy-metal ions are present in the system (60). In hard water, the adsorbate has large proportions of lime soap.

The adsorption behavior of commercial alkylbenzenesulfonates and several other anionic detergents on cotton, wool, and some of the synthetic fibers has been carefully plotted (61). The equilibrium adsorption isotherms, with a few exceptions, do not show any startling abnormalities. A number of other studies have attempted to correlate adsorption with detergency (62–64). In general, no significant correlations were found for a number of possible reasons. On porous fibers such as cotton, adsorption may occur on fiber areas that are not beneficial to detergency. The presence of soils on the fiber surface may significantly alter the adsorption behavior. The presence of trace amounts of surface-active agents in the soils themselves could modify adsorption of the active detergent component. For instance, soap present in natural soils could significantly change nonionic adsorption behavior. Finally, and perhaps most importantly, equilibrium adsorption measurements may not realistically reflect adsorption taking place in a 10 min wash cycle.

Adsorption of bath components is a necessary and possibly the most important and fundamental detergency effect. Adsorption (qv) is the mechanism whereby the interfacial free energy values between the bath and the solid components (solid soil and substrate) of the system are lowered, thereby increasing the tendency of the bath to separate the solid components from one another. Furthermore, the solid components acquire electrical charges that tend to keep them separated, or acquire a layer of strongly solvated radicals that have the same effect. If it were possible to follow the adsorption effects in a detersive system, in all their complex ramifications and interactions, the molecular picture of soil removal would be greatly clarified.

Mass Transfer near the Substrate Surface. Mechanical action has a great effect on soil removal, probably by influencing mass transfer (qv), ie, the diffusion of soluble material away from the immersed fibers (65,66). Mechanical action tends to maintain a high concentration gradient near the fiber, and the resulting increased diffusion causes stronger diffusion currents to flow. These diffusion currents are presumably responsible for carrying away the soil particles that have already been detached or loosened from the fiber surface by physicochemical action. In a Terg-O-Tometer investigation of mass transfer, using only water soluble substances, the transfer coefficient was found to be directly proportional to agitator speed and stroke angle, inversely proportional to the water-holding capacity of the cloth load, and independent of bath volume (65,66). The soil removal behavior is very similar to the mass transfer behavior, supporting the idea that diffusion currents are an important operating factor in soil removal, even though they may play no part in breaking the primary soil–substrate bond. Considering the wide variety of soils and substrates encountered in washing, as well as the wide variation in particle size and fabric geometry, mass transfer effects could play a principal or minor role of the overall wash process, depending upon the specific system encountered.

Colloidal Stabilization. Surfactant adsorption reduces soil–substrate interactions and facilitates soil removal. For a better understanding of these interactions, a consideration of colloidal forces is required.

The model solid-soil detersive system is advantageously treated as a sol-agglomerate colloid system or, in more general terms, a lyophobic colloid. In the typical lyophobic colloid, consisting of a single disperse phase in an aqueous suspending medium, only one type of liquid-solid interface and one type of solid–solid interface is present. The simplest detersive system, however, has an added degree of complexity in the presence of two types of liquid–solid interface: soil–bath and substrate–bath. Also present are two effective types of solid–solid interface: soil–substrate and soil–soil. The soil–soil interface relates to flocculation or dispersion of soil particles remote from the substrate, and is not of primary concern in the present discussion. The soil–soil interface is, of course, important in practical detergency since soil aggregates can be regarded as large single particles.

There are two general theories of the stability of lyophobic colloids, or, more precisely, two general mechanisms controlling the dispersion and flocculation of these colloids. Both theories regard adsorption of dissolved species as a key process in stabilization. However, one theory is based on a consideration of ionic forces near the interface, whereas the other is based on steric forces. The two theories complement each other and are in no sense contradictory. In some systems, one mechanism may be predominant, and in others both mechanisms may operate simultaneously. The fundamental kinetic considerations common to both theories are based on Smoluchowski's classical theory of the coagulation of colloids.

As the particles in a colloidal dispersion diffuse, they collide with one another. In the simplest case, every collision between two particles results in the formation of one agglomerated particle,ie, there is no energy barrier to agglomeration. Applying Smoluchowski's theory to this system, the half-life, $t_{1/2}$, ie, the time for the number of particles to become halved, is expressed as follows, where η is the viscosity of the medium, k Boltzmann's constant; T temperature; and N_0 is the initial number of particles.

$$t_{1/2} = \frac{3\eta}{4kTN_0}$$

For dispersions at moderate concentrate, ca 10^9 particles per cm^3, $t_{1/2}$ has a value of the order of a few seconds. This expression assumes there is no barrier to collision and every collision is effective. For stable dispersions to exist, an energy barrier W is assumed that prevents collision. In this case, the expression for half-life becomes:

$$t_{1/2} = \frac{3\eta}{4kTN_0} \exp(2W/kT)$$

If W is 15–20 kT, the half-life is several days and the dispersion is reasonably stable. The problem of colloidal stability thus becomes a problem of the energy barrier, W, that lessens the unifying collisions.

Ionic Stabilization. The quantitative theory of colloid stability based on electrical barriers was developed independently in the USSR by Derjaguin and Landau (67) and by Verwey and Overbeek in Holland (68). It is generally referred to as DLVO theory. There are two opposing forces between particles: a force of attraction that is responsible for agglomeration when the particles approach close enough, and a force of repulsion that prevents close approach. The attractive forces are the London dispersion forces or van der Waals forces. These have the general form shown below, where r is the distance between particles and n is between 3 and 7, depending on the geometry of the interacting surfaces.

$$F = K/r^n$$

The repelling forces are caused by the electrical double layers that surround the particles in aqueous dispersions. The interaction of these two forces is conveniently shown in a plot of potential energy versus distance between particle centers, as in Figure 3. The ordinate in this plot can be either force or potential; for quantitative purposes, they are interconvertible through the definitive relationship that force is the negative gradient of potential. To separate two agglomerated particles ($r = 2a$), it is necessary to overcome the energy barrier $V + W$, to bring them to distance X_2 at which point repulsive forces predominate. Conversely, to cause agglomeration of two separated particles, it is necessary to overcome the barrier W at X_2.

According to DLVO theory, the shape of curve 2, which controls the shape of the effective curve 3, is determined by the thickness and charge density of the electrical double layer that surrounds each particle. These factors, in turn, are determined by the nature of the ionic species adsorbed at the interface, the degree of adsorption, and the ionic strength of the surrounding medium. The

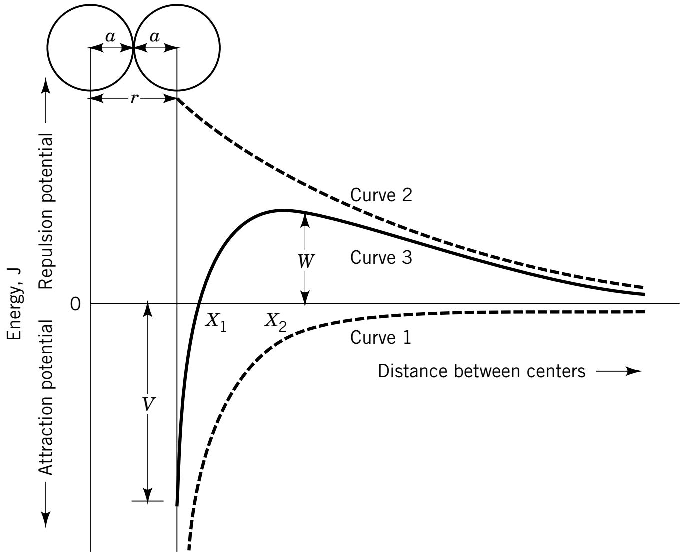

Fig. 3. Attraction–repulsion potentials as a function of distance between particle centers. Curve 1 represents the attractive potential caused by van der Waals forces, curve 2 is the repulsive potential caused by double-layer forces, and curve 3 is the resultant force experienced by the two particles.

quantitative aspects of the DLVO and the double-layer theory (ie, the structure, formation, and interactions of electrical double layers at phase interfaces) are beyond the scope of this article, and it is recommended that the reader consult the standard publications in this field. Qualitatively, high charge density increases the repulsion forces and thus shifts curve 3 upward, increasing the potential W and decreasing $|V|$. High ionic strength shrinks the double layer, lowering curve 3, lowering W, and tending to increase $|V|$.

Electrical potentials can, of course, be negative or positive. In most detersive systems, the charges acquired by both substrate and solid soil are negative. The adsorption of detergent anions increases the effective density of negative charge and tends to increase the double-layer-repulsion potentials. The counterions, in this case metallic cations, exert the controlling effect on the ionic strength factor, with increasing valence greatly magnifying the effect. Thus, calcium ions have a much greater effect than sodium ions in shrinking the double layer and promoting agglomeration. Aluminum ions have an even greater effect than calcium ions. This is in accord with the well-known Schulze–Hardy rule that was proposed as an empirical finding many years before this quantitative DLVO theory was developed.

The electrokinetic effect is one of the few experimental methods for estimating double-layer potentials. If two electrodes are placed in a colloidal suspension, and a voltage is impressed across them, the particles move toward the electrode of opposite charge. For nonconducting solid spherical particles, the equation controlling this motion is presented below, where u = velocity of particles; η = viscosity of medium; V = applied field, V/cm; R = factor for electrical relaxation; D = dielectric constant of medium; F = factor for size of spheres; and

ζ = zeta potential.

$$u = \frac{RFVD}{6\pi\eta}\zeta$$

This equation is a reasonable model of electrokinetic behavior, although for theoretical studies many possible corrections must be considered. Correction must always be made for electrokinetic effects at the wall of the cell, since this wall also carries a double layer. There are corrections for the motion of solvated ions through the medium, surface and bulk conductivity of the particles, nonspherical shape of the particles, etc. The parameter zeta, determined by measuring the particle velocity and substituting in the above equation, is a measure of the potential at the so-called surface of shear, ie, the surface dividing the moving particle and its adherent layer of solution from the stationary bulk of the solution. This surface of shear lies at an indeterminate distance from the true particle surface. Thus, the measured zeta potential can be related only semiquantitatively to the curves of Figure 3.

There have been many attempts to correlate detergency and deflocculation with measurements of zeta potential (69); such measurements have been made on both fibers and soil particles using various model detersive baths as the media. Aside from the expected result that high zeta potentials tend to correlate with deflocculation, few direct relationships of theoretical significance have become evident. In an extensive and productive study, it was pointed out that DLVO theory relates the height of the maximum in the potential curve (W in curve 3, Fig. 3) to the square of the zeta potential rather than to its first power (70). From the DLVO theory the surface potential ψ was calculated, which is necessary to give a barrier of height (in joules) $W = 15$ kT for soil particles of various size in electrolytes of various concentrations; ζ was measured experimentally. When the ratio ζ^2/ψ^2 was greater than unity, good stability was attained. In calculating soil–substrate interaction, good results were obtained using the ratio of $[(\zeta \text{ substrate})(\zeta \text{ soil})]/[\psi \text{ substrate})(\psi \text{ soil})]$. Application of DLVO theory to detergency has also been made very successfully when the shape factors and factors involving the structure of the double layer were taken into consideration (71).

The strong adverse influence of calcium ions on the stability of lyophobic suspensions is predicted by DLVO theory, and has been demonstrated with many types of simple soils. That calcium ions have an overwhelming effect on the redeposition of carbon soil onto cotton tends to support the idea that DLVO theory is a principal key in explaining detersive action. The redeposition of carbon onto cotton has been correlated quantitatively with the calcium ion content of the system, both in the presence and absence of surfactant (72). The adverse effect of calcium ions on wet soil removal in practical washing has also been well established (73). The effect of calcium in detergency cannot be explained solely, however, by its shrinking of the double layer. Calcium is very strongly adsorbed onto cotton through the carboxyl and hydroxyl groups present on the cellulose chains. This adsorption is so strong that cotton rinsed in even slightly hard water transfers a harmful amount of calcium to the next wash liquor. Calcium present in soil particles can act as a bonding agent at the soil–substrate interface, and inhibit soil removal by this secondary mechanism. In one of the most thorough studies of the above effects, it was also demonstrated that calcium promotes the deposition of oil onto cotton (74). The sorption of calcium during washing is complicated by its apparent ability to coadsorb with surfactants and complex phosphate builders, further obscuring the mechanism by which it exerts its adverse effect (75,76).

Despite its successes and its great usefulness as a guide, the limitations of the DLVO theory in explaining detergency are most evident when considering the nature of the soil−substrate bond. The DLVO theory in its simplest form postulates van der Waals' bonding as the primary agglomerating mechanism. Even revised theories of double layer interaction, that do not assign such an important role to van der Waals' forces, do not encompass agglomerating mechanisms such as polyvalent cation bridges and hydrogen bonding (77,78). There is ample evidence that these latter mechanisms prevail in some important detersive systems.

Steric Stabilization. Double-layer repulsion cannot satisfactorily explain stabilization of lyophobic suspensions by nonionic surfactants nor nonionic detergency in solutions of high salt content. Not only nonionic surfactants but even anionic ones can overcome the agglomerating effects of salt. To explain these phenomena, steric interaction between the surfactant molecules adsorbed at the solid−solution interface must be considered. The adsorbed molecules are oriented with the hydrocarbon tails adherent to the essentially hydrophobic solid surface and the water-soluble heads sticking into the solution. This adsorption and orientation is governed by the same factors governing micelle formation, ie, the amphipathic nature of the surfactant molecule and solution forces. The head groups at both nonionic and anionic surfactants are heavily hydrated. As a result the lyophilic particle is surrounded by an inner layer of hydrophobic surfactant tails and an outer layer of hydrated surfactant heads. In Figure 3, it can be seen that the attractive potential does not greatly increase until the particles are relatively close to each other.

The bulk of the hydrated head groups prevents the particles from approaching near enough to each other for the attractive forces to cause agglomeration. In the case of polyoxyethylene nonionic surfactants, the head group is quite large, extending for several nanometers into solution; the head group is associated with a large amount of water of hydration caused by ether−water interaction. The bulk of a hydrated anionic head group is not so great; however, the anionic surfactant retains some ionic stabilization even in salt solution. Agglomeration is achieved only if the particles overcome the energies involved in steric compression of the head groups and desolvation of the head groups. Conversely, if two particles, adherent over a small area of contact, are immersed in a surfactant solution, oriented adsorption on the noncontacting areas, followed by hydration, presumably breaks the adhesive bond and forces the particles apart. This picture would suggest some degree of correlation between the wetting power of a surfactant for a given material and its stabilizing power for sols of the same material. Such a correlation has indeed been found, using paraffin wax with both nonionic and anionic surfactants (79).

5.2. Oily-Soil Detergency. *Roll-up.* The principal means by which oily soil is removed is probably roll-up. The applicable theory is simply the theory of wetting. In briefest outline, a droplet of oily soil attached to the substrate forms at equilibrium a definite contact angle at the oil-solid-air boundary line.

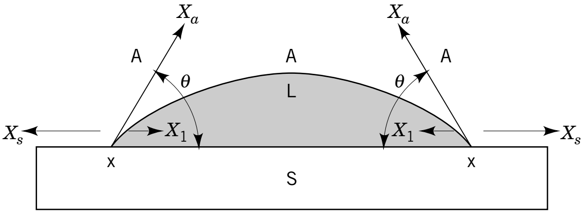

Fig. 4. Contact angle at the oil–solid–air boundary line in the roll-back process of oily solid detergency. X_s,X_1, and X_a are force vectors at the surface and tangential to the droplet.

This contact angle (Fig. 4) is the result of the interaction of interfacial forces in the three phase boundaries of the system. These interfacial forces, expressed in mN/m(= dyn/cm), or interfacial free energy values expressed in mJ/m^2 (erg/cm^{2}s) are conveniently designated γ_{LA}, γ_{SA}, and γ_{SL}; the subscripts relate to the liquid–air, solid–air, and solid–liquid interfaces, respectively. The equilibrium contact angle at the boundary line θ_{SLA} may be regarded as a thermodynamic quantity since it is functionally related to the free energy values through the Young-Dupre equation:

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA}\cos\,\theta_{SLA}$$

When the solid substrate is placed in the bath, the air is displaced by the bath, *B*, and the *SA* interface is replaced by an *SB* interface. Similarly, an *LB* interface replaces the *LA* interface. The equilibrium free energy values of these new interfaces are not established immediately but gradually through mass transfer (if there is any mutual solubility between *L* and *B*; it is assumed that *B* does not dissolve *S*) and through adsorption of dissolved components. When these processes have gone to completion the new relationship is

$$\gamma_{SB} = \gamma_{SL} + \gamma_{LB}\cos\,\theta_{SLB}$$

In general, γ_{SB} and γ_{LB} are lower than γ_{SA} and γ_{LA}. If *B* contains a surface-active agent, they tend to become exceptionally low and θ_{SLB} is therefore much greater than θ_{SLA}. Because θ_{SLB} is greater than 90°, even though less than 180°, hydraulic action is capable of removing the oil droplet from the soil and surface.

Rearrangement of the above equation gives

$$\cos\,\theta = \frac{\gamma_{SB} - \gamma_{SL}}{\gamma_{LB}}$$

For $\theta > 90°$, there must be $\cos\,\theta < 0$. Since the interfacial tension terms are themselves positive, for $\cos\,\theta < 0$, it follows that $\gamma_{SL} > \gamma_{SB}$. In other words, for effective roll-up, ie, $\theta > 90°$, the interfacial tension between the solid and bath must be less than that between the solid and liquid. As shown in Figure 5, the area of contact can be reduced to zero while maintaining the contact angle and its equilibrium value, and avoiding any necking down and division of the droplet. If

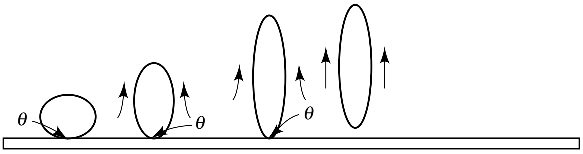

Fig. 5. With θ remaining constant at >90°, oil droplet can be removed completely by hydraulic currents (arrows).

θ_{SLB} is less than 90°, it is impossible to separate the oil completely from the surface by hydraulic action alone. As the droplet is withdrawn and the area of contact is reduced, a neck is formed directly above the contact region. If the contact angle is maintained at equilibrium, the drop must divide at this neck, leaving a small quantity of oil adherent to the substrate. This effect is shown in Figure 6.

The value of θ_{SLB} can be estimated on purely theoretical grounds from estimates of the adsorption of surfactant which, in turn, can be estimated from the Gibbs adsorption equation relating adsorption to surface-tension lowering.

Even when the equilibrium value of θ_{SLB} approaches 180°, it is quite difficult in practice to displace all the oil from the substrate by the bath for the following reasons: the contact angle of the oil, as it is rolling back, is a receding contact angle that is considerably smaller than the equilibrium angle. Any surface roughness further increases the hysteresis. Thus, an actual angle of 180° may not be achieved even though the theoretical equilibrium angle has this maximum value. Solid surfaces are notoriously inhomogeneous. Even a small surface area exhibits roughness or spots of high interfacial energy where the moving boundary tends to stick. The hydraulic currents then tear away the bulk of the droplet, leaving some oil at the rough or sticky spot.

In this model, the surface is oil-free under steady-state conditions only when θ_{SLB} is 180°. At any lower value, free-floating oil droplets redeposit and become attached to the substrate, and at equilibrium (on the all-or-nothing basis) all the oil is attached. When θ_{SLB} is high, however, even though it is not 180°, agitation keeps a large proportion of oil separated from the substrate and moving around in the bath. Thus, if the substrate is removed from the agitated bath and rinsed, it is freed of most of its soil burden.

This model for oily soil removal does not apply to systems where the oil soil becomes emulsified. Emulsified oil droplets are characterized by a surface layer that acts either as a physical barrier or as a potential energy barrier against coalescence, or against coming into intimate contact with the substrate. Such

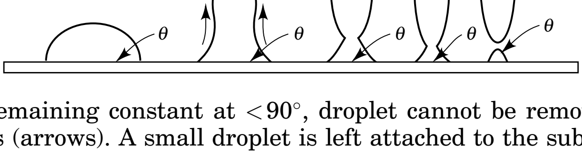

Fig. 6. With θ remaining constant at <90°, droplet cannot be removed completely by hydraulic currents (arrows). A small droplet is left attached to the substrate.

droplets must overcome this potential barrier to redeposit on the substrate, whereas the free-floating unemulsified oil droplets of the roll-up model redeposit on contact without surmounting any barrier, energetic or physical. The mathematical model for emulsification can be found in standard treatises on emulsification. It resembles the model for solid-soil dispersion outlined above, although there are many important differences of detail.

Solubilization. The role of micellar solubilization (as the term is used in the physical chemistry of surfactants) in oily-soil removal has been debated for many years. The amount of oily soil that could be present in a normal wash load could not all be removed and held in micellar solution by anionic surfactants. On the other hand, nonionic surfactants could do so, because of their greater solubilizing ability. High solubilizing power is definitely linked with good detergency (80). Thus, a very direct relationship between the solubilizing power of a surfactant for the test dyestuff Orange OT and its ability to remove polar solid from steel surfaces was established (81). In a practical detergency range lying between the surfactant concentration that gives 90% soil removal and a surfactant concentration twice that high, the relationship is expressed by the equation below, where D is the detergency value, S is the solubilization value, and K_1 and K_2 are constants:

$$D = K_1 S + K_2$$

Furthermore, in a series of polyoxyethylene nonylphenol nonionic surfactants, the value of K_1 varied linearly with the HLB number of the surfactant. The value of K_2 varied linearly with the log of the interfacial tension measured at the surfactant concentration that gives 90% soil removal. Carrying the correlations still further, it was found that from the detergency equation of a single surfactant with three different polar soils, K_1 was a function of the soil's dipole moment and K_2 a function of the soil's surface tension (81).

Detailed thermodynamic and mechanistic analyses of solubilization and related mechanisms are given in References 17 and (82–84). These works show that under proper circumstances, solubilization can make a significant contribution to oily-soil removal.

Phase Changes at the Soil–Bath Interface. Closely related to solubilization is a phenomenon that involves polar organic soils and surfactant solutions. If a complete phase diagram is plotted for a ternary system containing sodium dodecyl sulfate (or glycerol oleate), and water, several important and unusual features are noted. A large area represents a liquid phase consisting of a microemulsion, where the dispersed particles are so small that the system is isotropic, like the familiar soluble oils. Also, over another large area, a liquid crystalline phase is formed, containing all three components. This liquid crystalline phase flows like a liquid, at least in one direction. Flow perpendicular to the oriented planes is accomplished by folding the planes cylindrically, but the physical flow is still of the purely viscous type, with no yield point evident. These two phases, particularly the liquid–crystal phase, play an important part in detergency (85). Furthermore, liquid–crystal formation lowers interfacial tension (86). Although this phenomenon was demonstrated in tertiary oil recovery, the principles could also apply to oily-soil detergency.

When the polar organic component is a solid at ordinary temperatures, the addition of detergent and water markedly lowers the melting point; more specifically, as the temperature is raised, a point is reached where surfactant and water penetrate the solid. Thus, the ternary liquid–crystal phase might form spontaneously at room temperature by mixing the components, or, more precisely, an aqueous detergent solution can literally melt and liquefy a relatively large proportion of solid polar fatty matter (see LIQUID CRYSTALS). What actually happens when these two phases are placed together at a low temperature and slowly warmed is a slow interaction. At a definite critical temperature, however, penetration of the detergent solution into the polar material starts to take place rapidly and the mass soon becomes fluid (17). This interaction is especially favorable in the case of nonionic surfactants that are relatively soluble in polar organic compounds and are the active ingredients of choice when forming microemulsions. In addition, above certain temperatures they display multilayer adsorption isotherms (87–92).

These phenomena are most rapid and easiest to observe in fairly concentrated aqueous detergent solutions, that is, minimally 2–5% detergent solutions. In a practical qualitative way, this is a familiar effect, and there are many examples of the extraordinary solvency and cleaning power of concentrated detergent solutions, for example, in the case of fabric pretreatment with neat heavy-duty liquid detergents. Penetration can also be demonstrated at low detergent concentrations. As observed microscopically, the penetration occurs in a characteristic manner with the formation of a sheathlike structure, termed myelin; they are filled with isotropic liquid but have a liquid crystalline birefringent skin.

In a detersive system containing a dilute surfactant solution and a substrate bearing a solid polar soil, the first effect is adsorption of surfactant at the soil–bath interface. This adsorption is equivalent to the formation of a thin layer of relatively concentrated surfactant solution at the interface, which is continuously renewable and can penetrate the soil phase. Osmotic flow of water and the extrusion of myelin forms follows the penetration, with ultimate formation of an equilibrium phase. This equilibrium phase may be microemulsion rather than liquid crystalline, but in any event it is fluid and flushable from the substrate surface. This phase change effect explains the detersive behavior of sucrose fatty esters in admixture with alkylarenesulfonates (93).

6. Measurement of Detergency

The measurement of detergency can be approached from two different points of view. The theoretical approach is concerned with the relative quantity of soil bound to the substrate before and after washing. In this case, measurement is a necessary analytical procedure in the study of the detergency mechanism. The second approach emphasizes the development of reproducible laboratory methods that predict the results of practical cleaning operations. In the development of new household-cleaning compositions, for example, the formulator must know whether his products outperform others under actual use conditions. Realism, or accuracy as it is usually termed, is a prime requisite of any detergency test. It means good correlation between laboratory evaluation and the results of field testing. The practical field evaluation is usually made on the basis of specifications, sometimes implied rather than explicitly expressed, that determine whether or not the cleaning results were satisfactory. In removing spinning lubricants from wool yarns, for example, the most satisfactory cleaning procedure is that which removes most soil from the substrate. In certain metal-cleaning operations, however, the satisfactory outcome is a piece of metal free of solid soil but carrying an even and easily perceivable layer of rust-preventive oil. In judging the cleanness of white fabrics, more interest is usually shown in fabric whiteness rather than in its actual soil content. Thus, most detergency evaluations in which white fabric is the substrate specify cleanness in terms of fabric whiteness or reflectance.

With these limitations in mind, the measurement of detergency in the laboratory requires the following components: A means for measuring or estimating the amount of soil on the substrate or the degree of cleanness both before and after washing; satisfactory substrates and soiling compositions; a means for applying soil to substrate in a realistic manner; and a realistic and reproducible cleaning device. These fundamental requirements apply regardless of the particular type of substrate that is being cleaned. More attention in this area has been centered on textile fabrics than on other substrates, but the various substrates and even human skin can be considered from the same point of view.

6.1. Fabric Detergency. *Laundering.* Reflectance is the most commonly used measurement for the whiteness of fabrics, although the transmittance of light by fabric specimens can also be used. The most commonly used instrument for reflectance measurement is the Gardner colorimeter, although the Zeiss Elrepho is also used. For general detergency, the grayness of the fabric is measured. Color effects can also be measured, and fabric yellowing is especially important. It is masked by fluorescent whitening agents (FWA). Special filters are available to eliminate this effect, and whitening caused by soil removal can be distinguished from that of FWA deposition.

As would be expected, no single artificial soil or combination of artificial soils can adequately model natural soils in the household laundry. Natural soils vary widely within a single household, between households, and between regions. In addition, natural soiling includes effects of aging and repetitive soiling that are difficult to simulate artificially. Consequently, there is no single set of test conditions that can consistently rate a group of detergents in a completely realistic manner. Limited correlations are usually obtained by suitably adjusting both the laboratory procedure and the practical full-scale procedure.

These problems can be dealt with by using artificial test cloths impregnated with various approximations of natural soils such as vacuum cleaner dust, dirt from air conditioner filters, clays, carbon black, fatty acids, dirty motor oil, and artificial sebum, either alone or in combination (37,94–98). The soils are applied by spraying, immersion, or padding. If the soils are carefully applied, reproducible results can be obtained. Soil test cloths can be of great help in detergency studies, when used with an understanding of their limitations.

The device most widely used for laboratory fabric detergency measurements is the Terg-O-Tometer (U.S. Testing Co.), a miniature agitator washer. Just as it is difficult to model natural soils, it is difficult to model a full-scale washing machine. The Terg-O-Tometer consists of four or six small agitator washers in

2-L beakers. Water and detergent are placed into the beakers, and the temperature controlled by a water bath. Standard-soil cloths are added and washed for 5–15 min. The speed as well as the angle of oscillation of the agitators is adjustable. The soil cloths are then rinsed, usually in the Terg-O-Tometer, dried, and the reflectances read. The performance of various detergent mixtures can be compared on the basis of the final reflectance R_f of the washed soil cloths. However, it is generally more useful to express the cleaning as percentage detergency, $\%D$ where R_i is the initial reflectance (before the wash) of the soil cloths and R_o the reflectance of the unsoiled fabric used to prepare the soil cloths, as shown in the equation below.

$$\%D = \frac{R_f - R_i}{R_o - R_i} \times 100$$

Redeposition of soil can be estimated simultaneously with net soil removal (detergency) by including a white swatch with the soiled swatches. It also can be estimated separately by adding a measured amount of soil to a fresh wash bath, then treating the white swatch in this standard-soil bath. The former method is, superficially at least, more realistic. The latter method, however, is frequently of greater value in development work because both the quantity and composition of the soil are known and can be controlled.

Grayness of a fabric swatch is not directly proportional to its content of black pigment (or artificial soil). A basic formula relating reflectance to the pigment content or concentration can be applied to the evaluation of detergency test swatches (51,99–101). In simple form, an adaptation of the Kubelka-Munk equation, it states that the quantity $(1 - R)^2/2R$ (where R is the fraction of light reflected from the sample) is a linear function of the soil content of the sample.

In some cases, it may be impossible, or undesirable, to measure the amount of soil by reflectance. Soil can also be determined by extraction and weighing the cloths, or weighing the washed cloths.

A number of excellent studies have used a variety of radiolabeled soils to investigate the removal of small amounts of colorless soils such as oils (102–104). By proper use of different radiolabels (such as ^{3}H and ^{14}C), the preferential removal of various components in a soil mixture can be followed. In these cases in particular, detergency can also be calculated from measurements of the amount of radioactivity that is removed from the fabric and is found in the wash liquor.

The above tests all measure the ability of a washing system to remove soil from a fabric in a single wash. However, the detergent or washing machine is often judged by the way the linen appears after several soil-wash cycles. After a series of soilings and washings, the linen acquires an off-white gray or yellowish shade caused by soil accumulation and chemical changes in the soil. Although soil accumulation tests are more tedious than soil removal tests, they give the most realistic results. A laboratory-scale soil accumulation test using vacuum cleaner dirt and small swatches of fabric has been described (105).

Textile Mill Operations. Detergency is important in textile finishing because small quantities of foreign matter on the goods can interfere seriously with dyeing and other finishing treatments. Furthermore, the goods are expected to be uniformly and thoroughly clean when sold. Many detergency tests in this area are of the semipractical type, ie, test swatches are analyzed for soil content. This analysis generally consists of gravimetric determination of the soil content either directly from the fabric weight, or by extraction (see TEXTILES).

6.2. Hard Surface Detergency. Despite the variety of hard-surface objects that are purposefully cleaned at regular intervals, detergency has been studied quantitatively in relatively few cases only. The small-scale user normally judges washing results as satisfactory or unsatisfactory. If satisfactory results are obtained with the amount of detergent and the degree of mechanical action employed, the user is not interested in minor qualitative differences. In those areas where specifications are important and where differences among detergents or mechanical washing equipment are readily perceivable, quantitative methods for measuring detergency have been developed.

In specific cases of metal cleaning where small amounts of residual soil must be detected and are difficult to measure by conventional means, radiotracer methods have been employed (106). Interest in these techniques has been stimulated by the development of methods for decontaminating hard surfaces subjected to atomic fallout (107).

Quantitative measurements have been obtained for ceramics and glass, metals, and organic surfaces such as painted and plastic tile.

Glassware and Dishwashing. Dishes are washed either by hand or in an automatic dishwashing machine. Hand-dishwashing detergents are generally high foaming compositions containing organic surfactants as the main ingredient. The consumer judges efficiency not only by the cleanness of plates but also by foam persisting throughout the operation. Evaluation of hand-dishwashing products by manufacturers simulates this procedure. The number of plates that can be washed clean, judged visually without or with a color or fluorescence indicator, and the number of plates necessary to kill the foam in the dishpan is taken as the measure of detersive efficiency (108,109).

More objective laboratory methods employ a mechanical device such as a Terg-O-Tometer (110). Food soils are applied to microscope slides or glass tape rather than to actual plates. The soils are tagged with fluorescent materials or with dark pigment to facilitate measurement of residual soil. Reflectance or transmittance may also be read directly (111).

The foam stability of hand-dishwashing compositions can also be measured more directly and more quantitatively using mechanical means to whip up a foam and adding increments of food soil to a predetermined no-foam end point (112).

The detergents in automatic-dishwashing compositions are largely inorganic, but evaluation of residual soil is essentially the same as in hand-dishwashing tests. Low foam avoids inhibition of the free movement of the rotor. Clarity of glassware is a particularly prized performance feature of home dishwashers and special photometric methods have been reported for measuring freedom from water spots or filming (haze) (113). More frequently, however, the presence of spots and filming is assessed visually in a box in which light is beamed at the interior of inverted glasses in an otherwise black environment.

In restaurant operations, sterilization of dishes is an additional requirement (see STERILIZATION TECHNIQUES). Sterilization is determined by the usual swabbing and culturing methods or by employing bacteria tagged with radioactive phosphorus and counting residual radioactivity on the washed dishes (108).

Metal Cleaning. The purpose of cleaning steel is to remove dirt and leave the article in a state where it can be delivered for use without further finishing (see METAL SURFACE TREATMENTS). The surface must therefore be covered with a tenacious corrosion-resistant coating as it emerges from the cleaning bath. Many emulsion cleaners remove lubricants and other unwanted dirt while depositing an anticorrosive coating on the metal. The primary test for efficacy in this situation is a corrosive test of the cleaned article.

A more thorough cleaning prepares the surface for further finishing, eg, electroplating or painting, or application of an oxide finish. The basic objective in this case is to ensure maximum adhesion of the finish by freeing the surface of all foreign matter (114). Frequently, the cleaning compositions are straight organic solvents, hydrocarbons or chlorinated hydrocarbons, but in many cases aqueous detergent solutions are used. Regardless of the composition of the cleaning product, detergency test methods involve soiled test specimen, a standard method or device for performing the cleaning operation, and a quantitative method for estimating the extent of soil removal. The test specimens are mostly metal panels, or coupons, 10–300 cm^2 in area. They are carefully cleaned, usually by abrasive action, and then soiled. Soils may vary widely but often are based on lubricating oil or asphalt. A dark pigment or fluorescent marker is added if the cleaning result is to be evaluated visually or by photometry. A radioactive tracer, compatible or identical with the soil, may also be added for assessment of residual soil. The cleaning device is often a miniature version of large-scale cleaning equipment that provides soaking of the test article and agitation by hydraulic action or boiling.

When a quantitative estimate of residual soil is not called for and the suitability of a metal surface for further finishing needs to be assessed, the water-break test is used. The term water-break refers to the behavior of a water film on a smooth greasy surface. When the film becomes sufficiently thin by drainage, it suddenly breaks into islands or droplets between which the surface appears dry. On the other hand, when a film drains from a clean water-wettable, non-greasy surface, it becomes progressively thinner and finally disappears by evaporation without ever breaking into droplets. Such a surface is said to be free from water-break.

In a similar procedure, the atomizer test, which depends on the behavior of an advancing rather than a receding contact angle, a fine mist of water is applied to the metal surface and the spreading of water is observed. On a clean surface, water spreads to a uniform film. With oleic acid as the test soil, the atomizer test can detect the presence of 10^{-5} mg of soil per cm^2, less than a monomolecular layer (115). For steel that is to be electroplated, the copper dip test is often employed. Steel is dipped into a cupric salt solution and the evenness of the resulting metallic copper deposit is noted.

Correlation of all aspects of the test method with the practical system of interest is always important. The test used for dairy cleaning is an excellent example (116). Milk is used to tag the soil with radioactive ^{45}Ca by an exchange with radioactive $CaCl_2$. This treatment is applied to stainless steel planchets by suspending the planchets in milk under actual pasteurizing conditions.

Organic Surfaces. Tests for detergency on organic surfaces such as painted walls and plastic tile generally include a rubbing or sponging step corresponding to the manner in which such surfaces are cleaned in practice. The method adopted by the Chemical Specialties Manufacturers' Association includes scrubbing a painted glass surface soiled with a marking pencil in a Gardner Straight Line Washability Machine and assessing detersive efficacy, visually on a seven point scale (117). In a similar method, a preconditioned linoleum tile is coated with an oily pigment soil and scrubbed in a Gardner machine; the detersive efficacy is measured by reflectance change (118).

7. Detergent Manufacture

7.1. Liquid Products. The manufacture of liquid detergent products is generally a straightforward process requiring batch equipment with provisions for metered addition of individual ingredients, agitation, and if needed, heating and cooling. Capital cost can vary depending on the degree of automation.

7.2. Spray-Dried Products. The manufacture of powdered product is more complicated. High-pressure spray-drying of an aqueous slurry has replaced the earlier process in which a solidified cake of the product had to be broken up mechanically. Spray-drying equipment requires a relatively high capital outlay. The resulting product, however, is characterized by several desirable features: a high concentration of surfactant can be accommodated in the finished product; the product consists of hollow beads that dissolve readily in the washing solution; powders are considerably less dusty than those produced by the earlier process; powders generally do not lump and most compositions can be packaged in cartons without special liners; and bulk densities are obtainable within the general range of 0.25–0.65 g/L.

The first stage in preparing spray-dried products involves producing a slurry of liquid and solid ingredients. Two processes are available, a batch process or a continuous process. The batch process involves preparing a slurry in a crutcher, which is a mixing vessel with heavy-duty agitation and provision for heating. Solid and liquid components are combined to form a homogeneous slurry. It is normal with a batch process that two crutchers are employed; while one crutcher batch is discharged to the spray-drying tower, another batch is prepared in the second crutcher. The automated batch process is preferred when there are reaction, hydration and crystallization processes involved.

The continuous process can offer shorter residence times and requires a high degree of automation (119). In addition, continuous slurry preparation can permit high solids concentrations and hence reduce the evaporative load in the spray-drying tower. The resulting energy savings can be significant in large installations.

Acids such as fatty acids and alkylbenzenesulfonic acids are neutralized with NaOH during slurry preparation to form soap and sodium alkylbenzenesulfonate, respectively.

After preparation, the slurry is transported to an aging vessel. During residence time of 20–30 min, the neutralization process, hydration of sodium tripolyphosphate and structural changes in the slurry are completed to provide a homogeneous composition. By means of a high pressure pump, the slurry is conveyed to the spray-drying tower under a pressure of ca 10 MPa (100 atm). A representative spray drying tower layout is shown in Figure 7.

The slurry, at 80–100°C, is forced through nozzles of 2.5–3.5 mm dia arranged on a nozzle ring. In the tower, the slurry encounters hot air that has entered the tower at 250–350°C. Air flow is normally countercurrent. Air circulation is provided by two blowers. A third blower provides suction that carries fines into the collecting cyclones. From there the fines may be reintroduced into the upper part of the tower where they are contacted by wet slurry descending in the tower. Alternatively, the fines may be added to subsequent crutcher batches. Upon exit, the powder is conditioned during passage via a belt conveyer and an airlift to the packaging machinery.

The capacity of spray-drying towers is influenced by the formulation of the powder being produced. For large spray-drying towers, throughputs of up to 30 tons per hour can be expected.

Because of stringent air pollution rules the exit gases are wet-scrubbed in brine since high NaCl concentrations reduce foam formation. NaOH scrubs out SO_2 from sulfur-containing fuel. The scrubbing solution, saturated with detergent fines, is recycled to the water tank for slurry preparation. As shown in Figure 7, the tower is also provided with a cleaning ring that is moved along the tower walls.

Although spray-drying accommodates relatively high content of surfactants, certain types, such as the alkanolamides and some nonionic surfactants are best added to the product after spray-drying. Post addition not only protects the surfactant from the heat of the tower but also prevents the formation of aerosols in the exit gas. Aerosols are more difficult to trap in the scrubbing system than solid fines. They are formed by unsulfonated matter from the manufacture of LAS and nonionic surfactants with short ethylene oxide chains (120).

7.3. Dry-Blended Product. In addition to lower capital outlay, dry-blending requires considerably less processing energy. Final product density, which is usually near unity, depends on the density of the starting materials and the nature of equipment used to blend these materials. Modern mixing and blending equipment, if properly controlled, can give product density and particle sizes comparable to spray-dried products.

7.4. Agglomerated Products. The process of agglomeration is intermediate between spray-drying and dry-blending. Process water concentrations are between 35 to 40% in a crutcher slurry and essentially zero in dry blending. In agglomeration, a liquid is sprayed onto a continuously agitated powder. Equipment designs include stationary mixers, rotating mixers with spray nozzles, and rotating blenders with a liquid dispersion bar, either twin shell or continuous zigzag (121). Automatic dishwashing detergents are mostly manufactured by agglomeration (122). Liquid components of the formulation, for example silicate, detergent actives, and water, can be used as the agglomerating liquid. Other examples of agglomeration processes include the hydration of sodium tripolyphosphate, coloring (speckling) of detergent powders, and the agglomeration of spray tower fines.

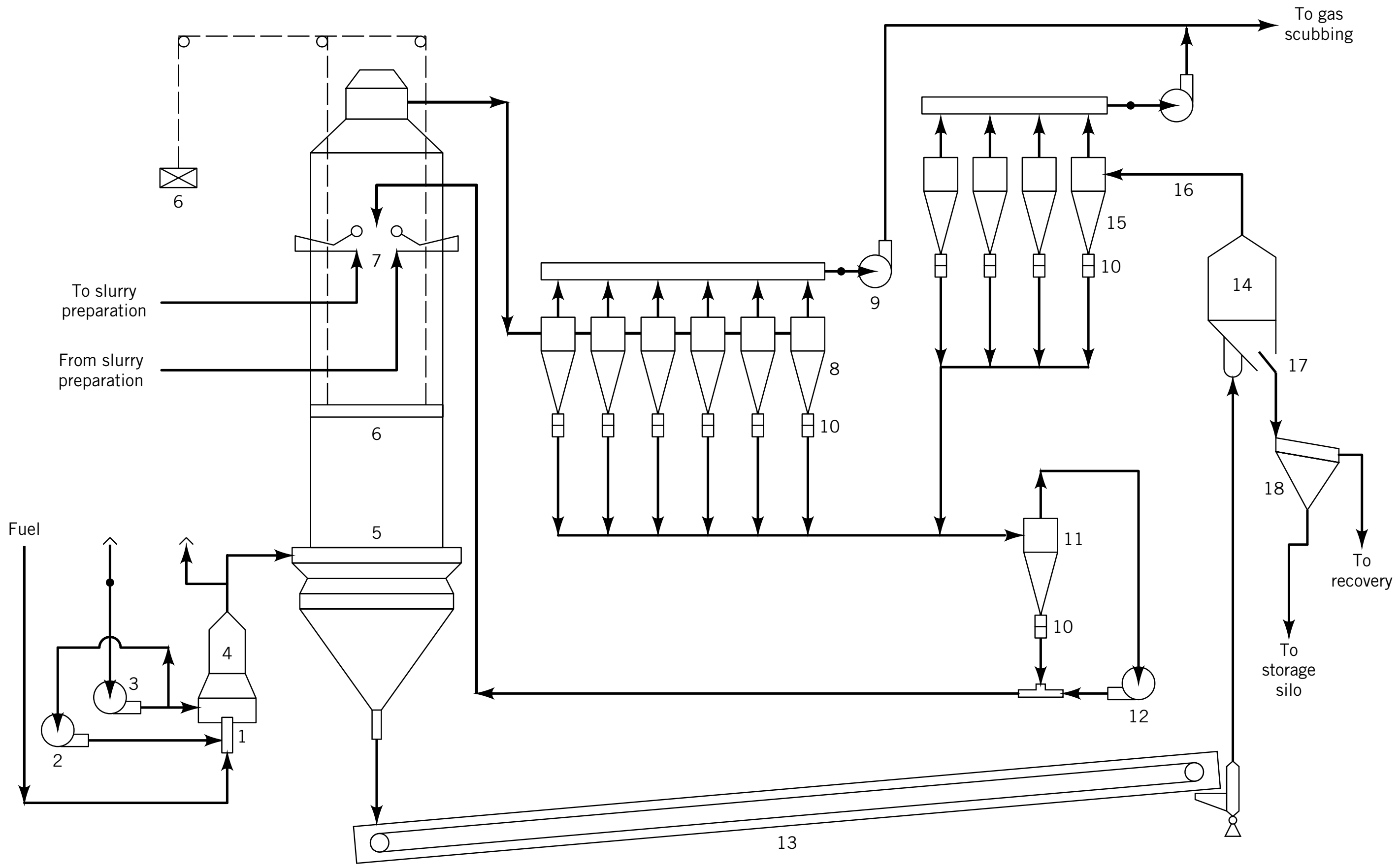

Fig. 7. Plant for spray-drying of detergents and soaps. 1, Burner; 2, air combustion; 3, cold air fan; 4, hot air generator; 5, spray-drying tower; 6, cleaning ring; 7, nozzles circuit; 8, tower suction cyclones group; 9, tower suction fan; 10, double-flap dischargers; 11, recovery powder cyclone; 12, recovery powder fan; 13, belt conveyor; 14, air lift; 15, air lift suction cyclones; 16, air lift suction fan; 17, double-flip dischargers; 18, vibrating sieve.

8. Analytical Methods

The literature on analytical methods is voluminous and not easily summarized (123–130). Often the greatest expertise in the analysis of complex detergent mixtures resides with in-house personnel in individual companies who may regard their methods as proprietary information.

An unknown commercial detergent may contain some combination of anionic, nonionic, cationic, and possibly amphoteric surfactants, inorganic builders and fillers as well as some minor additives. In general, the analytical scheme includes separation of nonsurfactant and inorganic components from the total mixture, classification of the surfactants, separation of individual surfactants, and quantitative determination (131).

9. Health and Safety Factors

As a class, surfactants and detergent products are among the most widely used chemical compositions. Almost everyone is exposed to these products on a daily basis in situations that range from ingestion of food-grade emulsifiers to intimate contact of skin and eyes with personal-care and laundry products. Safety is therefore a matter of great importance (132,133). Ranges of surfactant LD_{50} values are shown in Table 2.

Under conditions of normal use, detergent products are not hazardous to users. Nonetheless, surfactants possess some toxicity, and they are mild irritants. Particularly under conditions of misuse, such as accidental ingestion or spillage, they can produce irritation and discomfort in the form of nausea and vomiting, as well as irritation to skin and eyes. The long-term effects, however, are minimal (134).

In the last two decades (1980s and 1990s), governmental concern with the safety of chemicals has led to a number of legislative acts that regulate the manufacture and sale of chemicals including detergents. Even before this, the Food and Drug Act was passed in 1938. Food-grade emulsifiers fall under its provisions, as well as products containing antimicrobial agents such as deodorant soap bars.

Like other chemicals, new substances introduced into detergent products are regulated by the TSCA of 1977. Since its purpose is to prevent chemicals with long-term deleterious effects from entering the marketplace, the emphasis in testing is on long-term effects such as carcinogenicity, mutagenicity, and teratogenicity.

Table 2. **Rat Oral LD_{50} Values of Surfactant**[a]

Type of compounds	Oral LD_{50}, mg/kg
alkylbenzenesulfonates	700–2,480
alcohol ethoxylates	1,600 to greater than 25,000
sulfated alcohol ethoxylates	7,000 to greater than 50,000
alcohol suflates	5,000–15,000

[a] Ref. 132.

Table 3. **Detergent Animal Acute Oral LD_{50} Versus Probable Lethal Dose for a Human Adult**[a]

Animal acute oral LD_{50}, g/kg	Toxicity rating	Probable lethal oral dose for 70 kg person, g[b,c]
<0.005	6 super toxic	taste, <0.35
0.005–0.050	5 extremely toxic	0.35–4.9
0.05–0.50	4 very toxic	4.9–28.3
0.5–5.0	3 moderately toxic	28.3–453
5.0–15.0	2 slightly toxic	453–1000
>15	1 practically nontoxic	>1000

[a] Ref. 135.

[b] 0.35 g = 7 drops; 4.9 g = 1 tsp; 28.3 g = 1 oz.

[c] To convert g to lb, multiply by 0.0022. 1 lb is approximately 1 pt.

The manufacture of surfactants and of detergent products is regulated by OSHA. Dust concentration in detergent plants as well as factory noise levels are the primary areas of relevance, since the individual components in these products are essentially nonhazardous. Of more immediate concern to the detergent industry is the Federal Hazardous Substances Act (FHSA) of 1960 and the Consumer Products Safety Act (CPSA) of 1972. The FHSA defines specific labeling requirements, such as “Danger” for extremely flammable, corrosive, or highly toxic substances, and “Warning” or “Caution” for less hazardous materials.

To assess the degree of hazard, animal acute oral toxicity data are generally relied upon even though such data have limitations in their applicability for predicting possible human effects in the case of a specific exposure. Ranges of detergent LD_{50} values ratings are given in Table 3.

The range of values for several representative categories of detergent products is given in Table 4.

Table 4. **Acute Oral LD_{50} Ranges for Detergent Product**[a]

Detergent type	Albino rat, oral LD_{50}, g/kg
heavy-duty, laundry	
granular	2–7
liquid	2–9
hand-dishwashing, liquid	5–20
automatic dishwashing	2–7
floor and wall cleaner	
crystalline	4–6
liquid	8– >16
rug cleaner	7–9
laundry presoak with enzyme, granular	3–11
fabric softener	>10
toilet bar, soap, or synthetic base	7–20
shampoo	
plain	>10
medicated	3–10

[a] Ref. 136.

Because of emesis, it is unlikely that appreciable quantities of most common soaps and detergents could be ingested accidentally.

Methods of testing for eye and skin irritation potential have been reviewed (137). The official FHSA procedure for evaluating ocular irritation potential of detergent products is a modified Draize rabbit eye test (138). Some controversy surrounds this method at present, and a search for a procedure less injurious to test animals is in progress. In general, the order of irritation is cationic > anionic > nonionic (139).

Skin irritation potential is assessed by patch tests. More serious than simple irritation is the potential of a product to cause sensitization, ie, to cause a subject to become allergic to even very small amounts of the product.

Several test methods have been devised for sensitization. In the Magnussen-Kligman procedure, guinea pigs are injected just below the skin with a slightly irritating dose of the test substance with and without an antigen. After some days, a patch test is taken on the injection site to stimulate the skin to react. After several weeks, another patch test is taken, this time on an untreated site. A positive reaction is an indication of the sensitizing potential of the test substance (140).

Photosensitization, the potential of a product to cause sensitization in the presence of sunlight, is similarly evaluated by taking a patch test on guinea pigs before and after exposure to uv radiation (141).

Controversy over test methodology, and concern with the welfare of test animals, has been highly publicized in the last decade, and various states have proposed legislation to ban animal tests. Significant effort has been devoted to developing nonanimal alternative tests and predictive methods. Progress has been made, but no entirely satisfactory substitute has been found to date (142).

10. Environmental Considerations

The introduction of surfactant products into the environment, after use by consumers or as part of waste disposed during manufacture, is regulated by the Clean Water Act, the Clean Air Act, and the Resource Conservation and Recovery Act. In this respect, surfactants are subject to the same regulations as chemicals in general. There are, however, two areas of specific relevance to surfactants and detergent products, ie, biodegradability and eutrophication.

As early as 1947, incidents of foam blankets on bodies of water were reported. This was at a time when detergents containing synthetic surfactants were in the process of displacing soap as the principal heavy-duty laundry product. It was suspected that they were the cause of foam formation since they were less readily degraded by the microorganisms present in water. In contrast to soap with a straight-chain hydrophobe, alkylbenzenesulfonate, ABS, the predominant surfactant at the time, contained a highly branched hydrophobe, eg, a propylene tetramer alkyl group. The U.S. surfactant industry, represented by The Soap and Detergent Association (SDA), took the lead in the investigation of the problem, sponsoring a large number of field studies in the development of test methods and analytical procedures for measuring the presence of surfactants in the environment. For anionic surfactants like ABS, the Methylene Blue

Active Substance (MBAS) test, which depends on the formation of a chloroform-soluble complex of the anionic surfactant with cationic methylene blue, provides the first indication of the extent to which a surfactant has been degraded (143). Nonionic surfactants are assayed by complex formation with cobalt thiocyanate (144).

Among the methods for simulating the fate of the surfactant in the environment, the river die-away test (145) and the shake-flask method (146) have proved acceptable for fast screening and routine use. The semicontinuous activated sludge (SCAS) method is more time-consuming, but is more accurate and reproducible (147). Determination of biological oxygen demand (BOD) also provides useful data on biodegradation (148).

The extensive investigations led to the conclusion that a branched hydrophobe impedes the rate and extent of degradation of surfactants by microorganisms. The most immediately apparent remedy, therefore, was to replace the propylene tetramer in ABS with a straight hydrocarbon chain giving straight-chain alkylbenzenesulfonate, so-called linear alkanesulfonate (LAS). At the same time, commercialization of the Ziegler process for the oligomerization of ethylene provided another route to straight-chain hydrophobes that could easily be converted to detergent alcohols and straight-chain nonionic surfactants. By 1965, the U.S. detergent industry had completed a voluntary switch from hard to soft surfactants at a cost that has been estimated at ca $\$150 \times 10^6$. In addition to ABS, other surfactants based on propylene oligomers, such as alkylphenol derivatives, have largely disappeared from U.S. consumer laundry products.

Even though the biodegradability problem has been solved for all practical purposes, the subject continues to receive considerable attention. The biodegradation of LAS has been studied intensively, and several mechanistic pathways have been identified such as β- and φ-oxidation as well as reductive and oxidative desulfonation (149). Investigation of the biodegradation of LAS, alcohol ethoxylates, and alkylphenol ethoxylates in the laboratory and under sewage plant operating conditions showed that LAS and straight-chain alcohol ethoxylates and their sulfates degrade to CO_2 and H_2O (150,151).

10.1. Eutrophication.

This term, which denotes excessive nutrition or overfertilization, has been applied to the contribution excessive amounts of phosphorus may make to the growth of algae under certain conditions. Phosphorus in water supply originates from run-off of agricultural fertilizers, human excrement, and sodium tripolyphosphate present in detergent formulations. It has been estimated that 25–30% of the phosphorus in waste water comes from laundry detergents, and that detergents contribute about 3% of the phosphorus annually entering U.S. surface waters (152). Excessive algal growth in stagnant bodies of water contributes to oxygen depletion, which causes starvation of marine life and eventually leads to the death of lakes through silting. Phosphorus can be removed from the effluent of sewage treatment facilities by treatment with materials such as alum. Expansion of sewage treatment has been the method of choice in some areas of the world, notably Sweden, to assure acceptably low phosphorus content in environmental waters (153). In the United States, and later in Western Europe, detergent phosphates were singled out in the early 1960s as the cause of eutrophication, and their removal from consumer laundry formulations was proposed as a feasible approach to improvement of environmental water quality. Many states and a number of local jurisdictions have banned detergent products containing phosphate.

The efforts of the detergent industry toward solution of its part of the eutrophication problem are, at this point, less complete than its response to the biodegradability problem. Soda ash, Na_2CO_3, sodium silicate, and, to a lesser extent, sodium citrate formed the basis of the early formulations marketed in the areas where phosphates were banned. Technically, these substances are considerably less effective than sodium tripolyphosphate. As a precipitant builder, soda ash can lead to undesirable deposits of calcium carbonate on textiles and on washing machines.

At the same time, the industry embarked on an intensive search for phosphate substitutes. Of a very large number of experimental organic builders, a few substances reached commercialization or near-commercialization including trisodium nitrilotriaceate (NTA), trisodium carboxymethoxysuccinate (CMOS) (154) and trisodium carboxymethyltartronate (155). As discussed above, sodium citrate ether carboxylates have achieved widespread use as phosphate substitutes. Polymeric builders (polyelectrolytes) proved to be effective calcium sequestrants, but failed to satisfy the criterion of acceptable biodegradability. Interestingly, some monomeric polycarboxylates proved to be even more powerful calcium sequestrants than sodium tripolyphosphate but were not sufficiently biodegradable (156).

Trisodium nitrilotriaceate, a sequestrant of effectiveness comparable to sodium tripolyphosphate, reached commercialization in the late 1960s. However, because some laboratory findings suggested potential teratogenicity, it was withdrawn from the market in 1970 at the request of the U.S. Surgeon General. It has continued to be used in Canada and elsewhere. On the basis of many studies supporting the safety of NTA, the EPA dropped its opposition to NTA and this builder, in combination with type-A zeolite, briefly appeared in some nonphosphate consumer laundry products. However, continuing opposition to NTA on the state level resulted in its withdrawal from detergents and its reappearance seems unlikely at this time.

Laboratory assessment of the eutrophication potential of an experimental substance is less clear-cut than that of biodegradation. A frequently used method is the algal assay procedure in which a variety of algal cultures is grown in open shake flasks and the effect of test material on their growth is determined (152). In a second procedure, the MAAP test, one observes the behavior of a microcosm, consisting of bacteria, algae, zooplankton, sediment, and water taken from an oligotrophic lake. The diversity index, an indication of the number of algal species present, is a measure of the nutritive index of the system. A reduction in the diversity index is taken as an indication of the eutrophic potential of the test substance (158).

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