Recent Advances in Detergency Theory[1]

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ABSTRACT

Practical detersive systems are inherently complicated, involving multiphase multicomponent soils adherent to a substrate, immersed in a multicomponent bath. Detergency is therefore not a simple colloidal effect, but the result of a large number of colloidal effects occurring simultaneously, each at its characteristic rate. To consider such systems meaningfully they are first resolved into a series of simpler model systems, each of which can usually be arranged to consist of three homogenous phases. Cleaning is the net result of the transitions of these model systems between the agglomerated (adherent) and the dispersed (separated) states. These transitions can be described and predicted in terms of well established, generally accepted concepts of modern colloid science. The resolution of typical detersive systems into their simple constituent models and the mechanisms of soil separation in these models are illustrated and discussed.

INTRODUCTION

Detergency is rightfully regarded in the first instance as a practical art, the very important art of cleaning things by washing them. If we use this as a starting point it is impossible to derive directly any single unified theory of detergency. The practical detersive system, consisting of a soiled solid substrate in a liquid bath, is a complicated conglomerate of a great many simpler systems, in which several disparate phenomena may be occurring simultaneously. Once we identify and dissect out these simpler systems, they can usually be reduced to models that are amenable to theoretical treatment, and the phenomena that occur during their transformations can be described in well established terms. This approach, which we propose to use in the present discussion, is in itself a relatively recent development, and only within the past few years has it come to be explicitly recognized and used by most investigators in the field. The first step in our present discussion will therefore be to break down the typical practical washing system and procedure into its constituent model systems. Using this as a framework, we will find that we can identify the phenomena that occur as well recognized phenomena of colloid science. In most instances these phenomena have been studied as such, without any reference to detergency, but they can nevertheless be very profitably applied in understanding and explaining detergency. The relationships between the model and practical systems will be indicated wherever they are not obvious.

Aside from this analysis the discussion will attempt to point out areas where significant advances are currently taking place, as well as areas where critical knowledge is still lacking. Only those aspects of detergency that belong in the realm of colloid science will be considered, i.e., the discussion will be limited to the type of soil removal that is a physically reversible phase separation. Soil removal by chemical dissolution (enzyme action, for example) or by bleaching, or the apparent removal of soil by fluorescent whitening agents, will not be considered.

MODEL SYSTEMS

Reduced to its simplest terms, a detersive system consists of three phases. There is a solid substrate phase, an initially adherent soil phase which may be either liquid or solid, and a liquid bath phase. The liquid soils and the bath usually consist of more than one component. In the practical detersive systems of primary interest the bath is aqueous and it contains at least one dissolved component that contributes markedly to the soil-removing effect. Geometrically, the three-phase detersive system initially includes three different phase interfaces (soil-substrate, soil-bath and substrate-bath) and one three-phase boundary line along which soil substrate and bath meet. Across each of the phase interfaces there is an initial acting of a net force of attraction, i.e., an adhesive force. This is especially true of the soil-substrate interface, the interface of primary interest in detergency. The adhesive bond between these two phases must be overcome to achieve cleaning. Detergency is the separation or disjoining of soil from substrate under the influence of the bath; the soil-substrate interface being replaced by soil-bath and substrate-bath interfaces. Generally the presence of the bath merely weakens the soil-substrate adhesive bond so that it becomes more easily broken by mechanical forces. In some cases it weakens the bond so much that the soil and substrate separate spontaneously under the influence of thermal currents or Brownian motion alone.

The two basic model detersive systems may accordingly be referred to as the liquid soil system (also called the oily soil system, implying an aqueous bath) and the solid soil system. In both systems the substrate is considered to be a homogeneous solid phase of uniform surface characteristics, and the bath is a homogeneous liquid phase. All real detersive systems can in theory be reduced to linear combinations of the two model types. In this connection, however, the following points should be noted. First, if the surface of the substrate is physicochemically nonuniform, and the uniform domains are large compared with the areas of soil attachment, it is evident that more than one model system is involved. Alternatively, if the uniform domains are small compared with the areas of soil attachment, the whole system can be reasonably well represented by a single model, using averaged values for the substrate surface properties. Secondly, a solid soil system, in which the soil particle has the same chemical composition and physicochemical surface character as the substrate, can be regarded as a simple agglomerated hyophobic colloid and can be treated as such. This is a very important concept in practical detergency as well as in theory. Lastly, it is quite possible in theory and in practice to have a soil consisting of two immiscible oily phases attached to each other and attached to the substrate at the same time, both oily phases being immiscible with the aqueous bath, e.g., a hydrocarbon and a fluorocarbon oil. Such a system would perforce behave differently, and in a more complicated manner, than the simple liquid soil system described above; it will not be considered in the subsequent discussion.

SOIL REMOVAL IN LIQUID SOIL SYSTEMS

There are three basic mechanisms by which liquid soil may be removed in the model system: roll back, emulsification and solubilization. Although all three have been recognized for many years, recent investigations, both

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experimental and theoretical, have greatly augmented the knowledge of these mechanisms.

Roll Back

The basic theory of the roll back mechanism of liquid soil removal is old and well understood (1,2). As soon as the bath has displaced air from the soil substrate system, and the three-phase liquid-liquid-solid boundary line has become established, the system moves toward assuming the equilibrium contact angle. The value of this angle is governed by the Young's equation relationship among the three interfacial free energies. The higher the contact angle (measured in the soil phase) the easier it is for mechanical forces to separate soil-substrate, and a contact angle of 180 deg is tantamount to automatic complete separation.

It is evident that there are at least two broad avenues of inquiry into the roll back phenomenon. The first is physicochemical in nature. It concerns the final equilibrium states of the three interfaces, and the rates and routes through which these states are reached. The individual processes that are involved include mass transfer of compounds across all three interfaces to establish solubility and swelling equilibria, and adsorption at the interfaces. The rates at which these processes occur are possibly more important from the practical point of view than the final equilibrium state that is reached. This is because soil separation can occur as soon as the soil-substrate bond becomes weak enough, and this often happens well before equilibrium is reached.

The second type of action to be studied in connection with roll back is purely physical in nature, and involves both capillarity and hydrodynamics. Capillarity is broadly defined as the movement of a liquid along a solid surface under the influence of its own surface forces. This movement is easy to predict if the solid surface is smooth and planar, spherical or cylindrical. In a structure as geometrically complex as a textile fabric, however, it is almost impossible to predict precisely. A knowledge of this effect is nevertheless essential if the removal of oily soil from a fabric in a laundering bath is to be related to the basic roll back effect. Partial rather than complete separation of soil is the usual result of washing. This partial separation results from masses of oil being torn away by the mechanical action of the aqueous bath, a hydrodynamic effect that is not easily analyzed quantitatively, and is of great importance in the design of washing equipment.

Closely related to the roll back effect is the initial wetting action of the bath on the soiled substrate. This is essentially a displacement of air by the aqueous bath. Complete local wetting is essential before soil removal by any mechanism can occur, and the difficulty of achieving it is easily demonstrated by buoyancy measurements (3).

Emulsification

Theories of emulsification, as such, are outside the scope of this review. The role of emulsification in the removal of oily soil, however, has several interesting aspects. Consider an oily soil deposited in a relatively thin layer on a substrate, immersed in a bath which is capable of emulsifying the soil. Assume also that the degree of agitation in the bath is such that emulsion droplets of diameter d would be formed if the soil were present as a mass of oil unattached to the substrate. Then, as a first approximation, the bath will be able to remove soil from the substrate only until the soil layer reaches a thickness equal to d. Since d must always have a positive value it is evident that emulsification alone cannot remove soil completely. Conversely, consider a clean substrate immersed in an emulsion of oily soil and subjected to collisions with the moving oil droplets. If the contact angle at the oil-bath-substrate line is 180 deg (measured in the oil) the substrate will remain clean. If the contact angle is less than 180 deg, some oil will become attached and if the contact angle is zero the substrate will soon acquire a continuous layer of oil. The extent to which oily soil is removed or deposited in an emulsion system therefore depends to a great extent on the contact angle, i.e., on the roll back. This is especially true when the quantity of soil relative to substrate surface is small. With thick layers of soil the degree of removal depends on the same factors that influence emulsification in the absence of substrate, including degree of mechanical agitation.

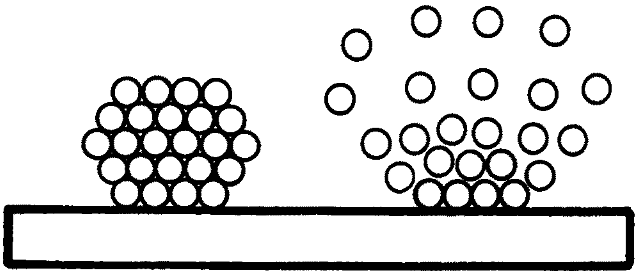

FIG. 1. Soil agglomerate. Particles adjacent to substrate remain adherent on dispersion.

Solubilization

Solubilization of oily soils is a surfactant effect, and is probably the most important mechanism by which substrates are freed of small amounts of soil in practical detersive systems. As discussed above, roll back is seldom complete, especially when the surface is rough. Emulsification also has serious limitations as a practical soil-removing mechanism. Solubilization, in theory at least, can bring about essentially the same result as extraction with a true molecular solvent for the oil. The theory of solubilization, at both low and high concentrations of surfactant, has been worked out extensively in recent years and has been the subject of many excellent reviews and treatises (4). Closely linked to solubilization at high surfactant concentration is the formation of microemulsions (5), and the two mechanisms probably produce similar effects in soil removal.

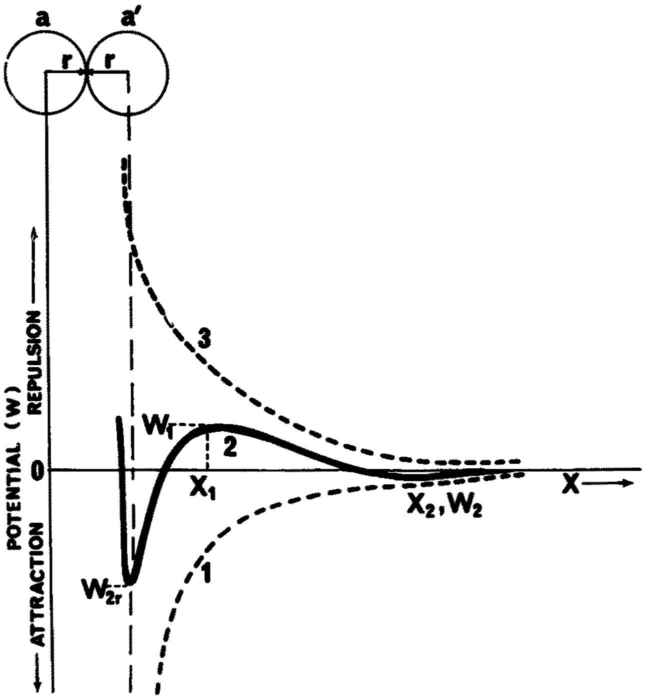

FIG. 2. Potential vs. distance between identical particles a and a'. Curve 2 is resultant of curves 1 (attraction) and 3 (repulsion). Barrier height maximum at W_1X_1. Secondary minimum at W_2X_2.

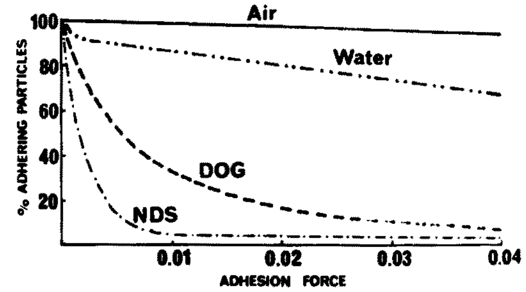

FIG. 3. Detachment of adherent particles in various media. DOG, ethoxylated dodecyl alcohol; NDS, sodium dodecyl sulfate (22).

Liquid Soil Removal in Practice

Since the test of a theoretical approach lies in the well-conceived and carefully-performed experiment, it is appropriate to mention at least briefly some of the more recent experimental work that relates liquid soil detergency as such to the model processes outlined above. The study of roll back is largely a matter of direct observation. Visual microscope methods have been refined, and the electron microscope and scanning electron microscope have been advantageously used in observing roll back on fiber surfaces. In instances where solubilization effects can be ruled out, roll back can also be studied by the buoyancy methods used in studying wetting. By far the most revealing method for studying liquid soil removal mechanisms has been radiotracers. Tagged oily soils were first used in the 1950s, and it was demonstrated that metal and glass surfaces cleaned to the stage where they were fully wetted by water still retained some oil (6). Later work on cellophane, nylon and polyester sheets and on fabrics has shown fractionation of mixed liquid soils, proving the solubilization mechanism, and has also added enormously to our knowledge of the specific cleaning effects of various baths and their individual components (7-10).

SOIL REMOVAL IN SOLID SOIL SYSTEMS

Solid soil detersive systems are, in practice, more complex than their liquid counterparts. Adherent to the substrate there may be a wide variety of solid species such as clays, silicas, metal oxides, lint, skin detritus, soot, etc. The individual particles vary widely in size and shape, so that they afford differing ratios of particle mass to true soil-substrate interfacial area (area of real contact) as well as of soil-bath area to soil-substrate area. Primary particles are often agglomerated into relatively large clumps with only a few particles holding the whole mass to the substrate as shown in Figure 1. It is evident that we could get much soil removal simply by dispersing such an agglomerate even if none of the adherent primary particles were removed from the substrate. It is quite a formidable research problem to define precisely most practical solid soil detersive systems, a problem which has been the subject of many technical publications (11,12).

There are two model systems for solid soil. The first consists of the liquid bath and a smooth substrate with adhering soil particles which are all of the same size, shape, chemical composition and surface properties; these chemical composition and surface properties differ from those of the substrate. The second model is simply an agglomerate of similar particles in the liquid bath, i.e., the classical lyophobic colloidal system, which has been the subject of much successful theorizing. Such a system exists in either the agglomerated (flocculated) or the disjoined (deflocculated) state, depending on the balance between the repulsion and attraction forces the particles exert on each other. The magnitude of these forces depends on the distance between the particles, as shown in the familiar potential energy vs. distance diagram (Fig. 2).

The attractive forces are generally of the van der Waals type and do not depend very greatly on the surrounding medium. The repulsive forces do depend greatly on the medium. The type of repulsive force that has been studied most thoroughly is due to the electrical double layer that surrounds any particle bearing an excess charge in an ionized medium. The basic quantitative theory of this type of system was worked out in the 1940's by Derjagin and Landau (13) in Russia and Verwey and Overbeck (14) in Holland. These investigators derived values for the repulsive forces in terms of the surface charge and the ionic content of the medium. The theory is still the subject of much refinement and embellishment. One very important advance has been the adaptation of this theory to systems in which the particles are of different species, i.e., to systems like the first model described above (15). Another significant advance has been the demonstration that in many actual solid soil detersive systems the double layer mechanism is indeed operative and may even be controlling. The observed effects of surface potential and ionic content of the bath (particularly polyvalent cations) match those predicted by the theory.

Systems of the above type have been referred to as "electrocratic". In addition to the electrocratic or coulombic mechanism of interparticle repulsion, another type of interparticle repulsion is often operative, especially in baths that contain surfactant above the critical micelle concentration level. This has been referred to as the "steric" mechanism, and it acts coincidently with but independently of the coulombic (16). Qualitatively the amphipathic surfactant molecule adsorbs onto the particles in oriented fashion, with the hydrophilic end or "head" in the solution. These heads are water soluble, i.e., strongly hydrated. Like any other soluble molecule or molecular grouping they repel each other enough in the aqueous medium to remain in the liquid state. If the density of these oriented surfactant molecules in the adsorbed layer on the particle surface is sufficiently high, and the particle itself is sufficiently small, i.e., has a high surface-to-mass ratio, the particle becomes lyophilic; the originally lyophobic suspension now behaves like a lyophilic colloid. Phenomenologically, this is often called the "protective colloid" effect. Few attempts have been made to work out quantitatively the magnitude of the inter-particle repulsion potentials associated with this effect. There is little doubt, however, that in practical detersive systems it frequently overshadows the coulombic effect, especially if relatively high concentrations of nonionic surfactants are present. The same effect can and does occur with adsorbable lyophilic polymers. Since the quantitative theory of protective colloid action for a homogeneous dispersion has not been worked out, it goes without saying that knowledge of the model solid soil system which is heterogeneous is even more empirical. It is possibly the greatest and most important gap in detergency theory today.

REDEPOSITION

Redeposition can occur in the liquid model system whenever the contact angle of a removed oil mass (whether or not it is emulsified) is less than 180 deg. If the liquid soil consists of only one component, and the system has been agitated sufficiently to have come to equilibrium, the quantity of soil on the "redeposition swatch" will in theory be equal to that on the "soiled swatch."

Redeposition in a solid soil model system is a more complicated phenomenon. If the soil is originally present as agglomerates, a consideration of Figure 1 shows that deflocculated particles can redeposit readily if the state of the system is such that the particles originally attached to the substrate remain attached. Redeposition can occur in nonideal systems if the originally agglomerated soil is heterodisperse. When it becomes deflocculated the finer particles may be redeposited while the coarser ones remain detached. In practical mixed soil systems, redeposition of solid particles can occur if they become deoiled in the bath after having been detached in a sheath of oil. Recent studies of redeposition have shown that primary deposition (clean fabric immersed in a bath-soil suspension) follows quite a different course from redeposition (clean fabric immersed in a bath) (17). Bath ingredients that inhibit primary deposition may be quite ineffective against redeposition. In theory at least, this can be due to the kinetics of the interactions; at the present writing, however, the actual causes have not yet been demonstrated.

KINETICS OF DETERGENCY

After air has been displaced by the bath from the soil substrate complex it takes a finite time (sometimes a long time) for separation of soil from substrate to occur. During this time the interfacial free energy levels are being lowered to the critical values necessary for separation. This lowering is due to adsorption of bath constituents at the interfaces or to the bulk equilibration of the bath with soil and substrate, or both. Adsorption occurs only if it results in lowered interfacial free energy, and therefore the degree of adsorption should be at least an indirect index of detersive potential. Many studies have been made of the adsorption of typical bath ingredients (surfactants, builders, antiredeposition agents, etc.) on various substrates, especially the common textile fiber substrates. Similar studies have been made on typical model solid soils such as carbon black, silica and clay. Very little data is available, however, on the rates of adsorption in these systems. Such data would appear more pertinent to detergency than the simple equilibrium values.

Another relatively unexplored aspect of detergency kinetics is the rate of solubilization of liquid soils by surfactant-containing baths. This is probably diffusion controlled, but the quantitative data needed for a useful theoretical treatment are lacking.

The rate at which roll back occurs in even quasi-practical detersive systems has received little attention despite its obvious importance. There has, however, been considerable recent work on rates of spreading and on dynamic contact angles in analogous systems (18), which define the parameters of the roll back process and open the door to more direct detergency studies.

DYNAMICS AND MECHANICS OF DETERGENCY

Aside from the physicochemical dynamics of interfacial free energy changes, thermal energy effects and the effects of pure mechanical energy play an important role in detergency. Relatively little work has been done on thermal effects in model systems, although temperature is well known to be of great importance in practical detergency and much empirical data on the effects of temperature is available. Temperature affects viscosity, which in turn influences the rate of roll abck and emulsification. Temperature also affects rates of sorption and the final sorption equilibria. Finally, it affects Brownian motion, which is probably a major mechanism of solid soil removal. Qualitatively it is usually not difficult to predict the effect of temperature changes on a detersive system. The theoretical basis for predicting these effects quantitatively remains to be developed.

Since it has always been known that elbow grease gets the washing done, there have been many efforts to relate mechanical energy input to soil removal in practical systems (19). The more recent studies have largely been made in the laboratories of washing machine manufacturers, and the results have generally been in the form of empirical engineering equations (20). Various methods of applying mechanical energy, such as sonics and ultrasonics, also come into this general area of investigation. From the theoretical point of view, it is of the greatest interest to measure the effect of various baths on the force (or energy) necessary to remove a solid soil particle from the substrate. Considerable success has recently been achieved in this difficult experimental task using well chosen model systems. Two different methods of applying the dislodging force have been used: the centrifugal method and tangential hydraulic current method, of which the centrifugal method is the more direct and easier to calculate. In this method the model substrate forms the outer surface of the rotor of a high speed centrifuge. The soil particles, monodisperse and homogeneous, are attached to it and the assembly is immersed in the experimental bath. On rotating, the bath moves along with the rotor so that the only dislodging force is radial. The centrifuge is spun until a critical speed is reached at which most of the particles are removed, thus affording a direct measure of the force required to dislodge (21). For a given substrate soil system this force is found to vary greatly with the composition of the bath liquid, as shown in Figure 3 (22).

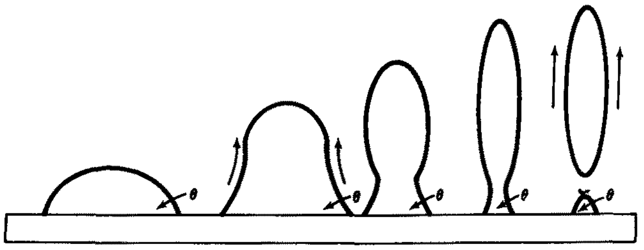

FIG. 4. Incomplete detachment of oily soil droplet by hydraulic currents. Contact angle remains constant.

The mechanical forces and energies required to remove liquid soil in roll back are more difficult to measure and to predict, even in the ideal model system where the geometry of the substrate surface is tractable. Unless the contact angle comes to 180 deg the soil can be removed only by a yielding and breaking of the bath-soil interface, as shown in Figure 4. To calculate the necessary forces is a complicated problem in hydrodynamics. With substrates of complex geometry, such as textile fabrics, the calculation becomes extremely difficult. The starting point is the equilibrium configuration of the liquid-liquid interface in the presence of the substrate surface. This in itself is difficult to predict, although some theoretical and experimental progress in this area has been made in recent years (23,24).

In conclusion, this necessarily cursory review has attempted to highlight, first of all, the rewarding results of taking a practical detersive system and resolving it into its simple model component systems before attempting to theorize about it; secondly, the fact that these simple models are generally amenable to treatment in terms of established theories of modern colloid science; thirdly, some of the actual advances that have been made in understanding the mechanisms of detergency; and, lastly, the large gaps that remain to be filled in before the behavior of practical detersive systems can be quantitatively interpreted and predicted.

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