Principles of Detergency and Their Application in Textile Processing[1]

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WITHIN recent years there has been an unusually increased interest in the study of surface activity, greatly stimulated by the advent of numerous successful synthetic surface active agents. From the practical standpoint surface activity includes such various effects as wetting, penetration, spreading, dispersing, suspending action, emulsification, and detergency. Of these numerous effects, which are seldom mutually exclusive or clearly distinguishable, detergency is doubtless the most complex.

In spite of the large amount of work which has been done in this field and the numerous detailed studies which have been reported, there have been relatively few attempts to analyze the detersive process explicitly and thoroughly from the physico-chemical point of view (1). It is the primary purpose of this paper to present such an analysis in outline form. A secondary purpose is to illustrate how this outline may be used as a guide to solving practical problems of detergency in the textile processing industry.

A typical detersive system consists of three essential elements:

1. A solid object to be cleaned, called the substrate.
2. "Soil" or "dirt," initially attached to the substrate, to be removed in the washing process.
3. A liquid "bath" which is applied to the soiled substrate.

Although many different types of substrates are of commercial and industrial importance this discussion will be limited to textile fabrics. Fabrics are among the most complicated substrates and offer all the problems and difficulties likely to be encountered in any detergency problem. The basic structural unit of a fabric, the fiber, is in many cases swellable, permeable, and relatively reactive. Furthermore, the geometrical configuration of the fiber surfaces in the fabric is such that the soil may be held mechanically as well as by physico-chemical forces.

A typical soil will consist of one or more solid or liquid phases, intimately mixed and closely attached to the substrate surfaces. The soil is considered to be substantially insoluble in water but may be amenable to partial solubilization in the bath if the latter contains a suitable surface active agent. The oil-lampblack artificial soil commonly used in detergency tests, which consists of one water-insoluble liquid phase and one water-insoluble, finely divided solid phase, is an excellent representative example for purposes of discussion. Gummy or plastic soil phases may be regarded as liquid if they are readily deformable by their own phase boundary forces under the conditions and within the time limits of the washing process. Otherwise they must be regarded as solid.

ALTHOUGH non-aqueous detersive systems are are not uncommon, only aqueous baths will be considered in this discussion. The bath is essentially a solution, and the solute may include several components. The principal solute component is the surface active agent, and its concentration in the bath is almost always higher than the critical concentration for micelle formation. In many practical baths two or more surface active solutes are present, advantage being taken of their synergistic effect. Additional solute components may include neutral or basic inorganic salts as well as colloidal additives such as carboxymethylcellulose, colloidal sodium silicates, etc. These products generally have no detersive action when used by themselves, but they serve to augment the action of the surface active agent. Although the mechanisms by which they increase the overall detersive efficiency may differ radically from one additive to another, all such additives are loosely grouped together under the name "builders."

The detersive process can be represented simply and clearly by the following equations, the first of which may be called the fundamental equation of detergency (2):

1. Soil-substrate complex + Bath $\rightleftarrows$ Soil + Substrate + Bath.
2. Soil + Bath $\rightleftarrows$ Soil-bath complex.
3. Substrate + Bath $\rightleftarrows$ Substrate-bath complex.

In considering the first equation, it is noted first of all that the reaction is reversible and can actually approach or reach an equilibrium. It is well known that a clean piece of fabric can be soiled by treating it with a reasonably concentrated suspension of soil in a detergent bath. This effect is usually spoken of as soil redeposition and is of great importance in practical washing operations (3). Of the two opposed reactions, cleaning and redeposition, each has its characteristic rate, and the ratio of the two rates will determine the extent to which cleaning takes place (4). The course of the overall reversible reaction is conditioned to a great extent by the two side reactions represented by equations 2 and 3. If the soil is effectively segregated by the bath components and forms some sort of stable complex with them, Reaction No. 1 will proceed toward the right and effective cleaning will result. This almost always happens to a greater or lesser extent in practical systems. If the substrate reacts with, adsorbs, or otherwise removes any of the effective bath components, it is obvious that the course of the reaction will be changed.

The detergency reaction, equation No. 1, is influenced only by those factors which influence the course of any chemical or physico-chemical reaction, namely the reaction conditions and the nature of the reacting substances. In this case they can be listed as follows:

I. Nature of the substrate, including its chemical properties, physical properties, and geometrical configuration or shape.
II. Nature of the soil.
III. Composition of the bath, which determines both its bulk and surface properties.

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IV. The physical and mechanical conditions of washing, which include temperature, duration of treatment, and type and degree of mechanical agitation.

V. The relative quantities of substrate, soil, and bath present in the system.

These are the five directly observable and controllable factors or variables which affect the course of the detersive process (5). A clear distinction should be made between these variables and the numerous molecular mechanisms which contribute to the total detersive action. Adsorption of detergent molecules, ions, or micelles on the soil particles, for example, is frequently referred to as a factor affecting detergency. It is more precisely one of the mechanisms which may contribute to the net cleaning effect. Whether this particular mechanism is brought into play depends upon at least two of the five factors mentioned, namely the nature of the soil and the composition of the bath.

EACH of the five factors above is in itself a complex quantity which can be resolved for any particular system into numerous sub-variables. The fact that the nature of the substrate has an important bearing on detergency is generally recognized by textile technologists. The difference between wool and cotton with regard to ease of cleaning, for example, is well known. The magnitude of this differential susceptibility to cleaning among various fibers is illustrated in Table I. In these experiments the fabrics were soiled according to the procedure recommended by Crowe (6) for soiling wool fabric. The soil consists essentially of lampblack, mineral oil, and glyceride oil. It is applied from carbon tetrachloride. The swatches were passed through the soiling solution until they showed 25% ± 2% reflectance. Washings were carried out in a Launderometer (7) at 50°C. for 10 minutes. One 8" x 8" swatch, 200 ml. of wash liquor, and 14 one-quarter inch stainless steel balls were used in each pint jar. After the swatches were rinsed and dried, their reflectance was measured with a Hunter Universal Reflectometer. The per cent soil removal was calculated according to the formula:

TABLE I

Soil Removal vs. Fabrics

Fabric	% Soil Removal	
	AAS[1]	Soap[1]
Cotton	18.0	20.9
Wool	36.8	0
Viscose	14.5	19.7
Viscose U. F.	4.7	9.5
Acetate	42.0	31.0
Nylon Knit	41.0	45.3
Fiberglass	40.5	53.8
Silk 1[2]	60.8	79.4
Silk 2[3]	0	0

[1]AAS = A 90% active alkyl aromatic sulfonate. Both the soap and the AAS were used at 0.2% concentration in bath.
[2]Silk 1 = A lightweight dress fabric.
[3]Silk 2 = Military powder bag silk.

$$\text{Per cent soil removal} = \frac{\text{Rw} - \text{Rs}}{\text{Ro} - \text{Rs}} \times 100.$$

Where RW is the reflectance of the washed swatch, Rs is the reflectance of the soiled unwashed swatch, and Ro is the reflectance of the original unsoiled fabric.

The fact that the chemical composition of the fiber influences detergency is illustrated not only by the different fibers but most emphatically by the case of the two viscose rayon fabrics. The viscose U. F. fabric has been treated with a crush-resistant urea formaldehyde finish but otherwise is exactly the same as the viscose fabric. The effect of differences in geometric configuration or construction of the fabric is illustrated by the case of the two silk fabrics, both made from the same fiber. The tightly woven, heavy powder bag fabric is extremely resistant to washing whereas the loosely woven dress fabric is one of the easiest to clean. Silk is a highly swellable fiber, and when the soiled heavy fabric is immersed in the bath, the interstices between fibers and yarns are closed up rapidly. The swelling fibers and yarns mechanically trap the soil particles and effectively prevent their removal. In the loosely woven fabric the interstices remain sufficiently open so that the soil is still held primarily by physico-chemical forces, and the bath is able to exert its full cleaning effect.

The effect of variation in the soil is well known. It can be pointed out, for example, that a wool flannel soiled with lanolin and washed under the same conditions used to obtain the data in Table I would show 80% or better soil removal. A greige filament rayon fabric, partially desized, and scoured under these conditions, would come out practically clean. In this connection it should be emphasized that two phase soils may be removed differentially. If a mixed carbon-oil soil or graphite-oil is present on the fabric, it is quite possible to remove one phase and not the other. Usually it is the oil which is removed and the carbon which is left behind.

The third variable, bath composition, is so well recognized that no detailed consideration is considered necessary.

In considering the fourth variable, physical conditions of washing, the fact that temperature and duration of treatment will influence the soil removal is quite familiar to everyone who has had practical experience with cleaning. The importance of mechanical agitation, however, is sometimes underemphasized (8). The data in Table II illustrates how great an effect can be produced by apparently minor changes in the degree of agitation. These runs were made in the Launderometer instrument, varying the agitating elements, the swatch size, and the volume of the bath. The smaller swatch sizes and bath volumes allow for more vigorous agitation, and this effect alone can account for a 50% or greater increase in per cent soil removal. In these experiments Indian Head cotton fabric was used. The soiling operations

TABLE II

Agitation vs. Soil Removal

Agitating Elements	% Soil Removal[1]			
	Small		Large[2]	
	100[3]	200[3]	100[3]	200[3]
None	20.0	20.4	15.9	20.4
8⅝" Plastic Cubes	22.3	21.8	16.3	17.5
14¼" Steel Balls	28.5	23.9	18.3	20.6
6½" Glass Balls	33.9	27.4	19.5	18.4

[1]Indian Head cotton fabric, soiled with Crowe type soil. Launderometer washings 10 minutes at 70°C. Per cent soil removal estimated by ASTM method using reflectance photometer. 0.2% active alkyl aryl sulfonate used as bath.
[2]Large swatches 8" x 8". Small swatches 6½" x 3".
[3]Milliliters of wash liquor used in the standard pint jars.

and the reflectance measurements were carried out as described above for the experiments on soil removal vs. nature of the fabric substrate.

The fifth variable listed is of fundamental importance in this "detergency reaction" just as it is in a bona fide chemical reaction. A point of particular interest, which is applicable in a great many instances, concerns systems where the soil to substrate ratio is very low. In these cases it is often extremely difficult to remove the last traces of soil, particularly where the soil is a very finely divided solid such as carbon black (9). This effect may also be observed at times in the case of oily soils and has often been noted in the case of mineral oil on wool.

A detailed consideration of the physico-chemical mechanisms involved in the detergency reaction is beyond the scope of this discussion, but the more important effects which are known to play a part in the detersive process may be outlined as follows:

I. *Stability of the Soil Substrate Complex.*

The detersive process itself consists essentially in a disruption of the soil-substrate complex into its components by the action of the bath. In reacting with these soil and substrate components, the bath also effectively inhibits their reunion. At least three types of forces (which must be weakened or neutralized by the bath during the washing process) serve to hold together the soil-substrate complex. These are: a. Pure interfacial adhesional forces, i.e., Van der Waal's forces of intermolecular attraction. These are most important where the soil is liquid in nature. b. Coulombic or electrostatic forces. These are probably of major importance in the case of solid soils. c. Purely mechanical forces of juxtaposition and entanglement. These are a major factor in the case of coarse solid soils, where the fabric can often be cleaned by vigorous agitation in pure water.

II. *Modes of Interaction Among Bath, Substrate, and Soil.*

A. Wetting of substrate and soil by the bath. In the case of liquid soils this is tantamount to a preferential wetting of the substrate by the bath. It may also be regarded as causing an *increase* in the interfacial tension (or decrease in adhesion) between soil and substrate. The soil-substrate interface is replaced by soil-bath and substrate-bath interfaces of lower free energy content. Wetting is usually considered to be coincident with the adsorption of surface active ions or molecules.

B. Adsorption of inorganic ions, or other ions of high specific charge, on soil and/or substrate. These can modify the electrostatic attractive forces between soil and substrate (even without being truly adsorbed). They are also effective in suspending the removed soil and preventing its redeposition.

C. Adsorption of colloidal particles on soil and/or substrate. These colloidal particles may be micelles of the surface active agent or may come from colloidal additives in the bath. They are considered effective in deflocculating the soil and preventing its re-agglomeration.

D. Solubilization of the soil in the bath.

Soil segregation (and the prevention of redeposition) can be accomplished by any or all of the four mechanisms above since these result in emulsification of liquid soils, suspension of solid soils, and a lowered attraction of both liquid and solid soil particles for the fiber.

It should be noted that this lowered attraction between soil and fiber is sometimes a much more important consideration than soil suspension in the bath. It is often the case that a bath with very little soil suspending power will show excellent detergency. The dirt, after having been removed, may again contact the fabric but will not adhere to it. Suspended soil, however, is much more easily rinsed than flocculated but non-adherent soil. This is because suspended soil cannot be held so easily by purely mechanical means.

It is unusually difficult to tell which mechanisms are operating and which are playing the predominant roles in any given detersive system. Except in very special cases detergent effects cannot be predicted, even qualitatively, from measurements of surface or interfacial tension on the bath, nor from any other physical measurements on the bath alone. It is theoretically possible that detergency could be predicted accurately if sufficient data on interfacial energies, electrokinetic effects, and adsorption effects were available for the various soil-substrate-bath combinations. At present, however, detergent effects are predicted entirely on an empirical basis by extrapolating and interpolating from the mass of available data.

The foregoing considerations, although seemingly general in nature, can be surprisingly helpful in solving the practical scouring and cleaning problems of textile processing.

TYPICAL detersive operations in the textile industry include: 1. Raw wool scouring. 2. Woolen yarn scouring. 3. Woolen and worsted piece goods scouring. 4. Scouring or boil-off of viscose rayon and acetate rayon piece goods, or greige goods made from other synthetic fibers. 5. Degumming of silk. 6. Kier boiling or open boiling of cotton. 7. The soaping-off or scouring of fast-color prints and dyeings on cellulosic fabrics. 8. The scouring of crease-resistant or other specially finished goods. The objective, as in any other industrial operation, is to obtain satisfactory results (or the highest percentage of satisfactory batches) at minimum costs for installation, labor, overhead, and chemicals used. Scouring processes of this type can be considered as follows, in light of the five major variables affecting detergency:

I. The nature of the substrate is usually fixed and cannot practically be changed. It is important to keep in mind, however, that scouring compositions and scouring conditions which work well on one fiber may be useless on another. A scouring formula which has worked well for acetate rayon, for example, should not be expected to work well on viscose rayon. Even when working with the same fibers, a permanent type finish may profoundly alter the scourability of a substrate, as has been pointed out in the case of urea-formaldehyde finished rayon. Differences in construction may also necessitate changes in the scouring procedure in order to obtain optimum results. Conversely, a particular detergent bath or a scouring procedure which fails to produce good results on one type of fabric should not be condemned. It may be excellent for another fabric.

II. The detergent problems of the textile industry are considerably simplified by the fact that the nature of the soils is usually known quite accurately. This is in sharp contrast to many other industries where the soil is qualitatively and quantitatively unknown. At least two instances may be cited where it is common practice to change the composition of the soil purposely so as to simplify the subsequent cleaning process. Wool oils have always been specially designed with the scourability as well as the lubricating properties in mind. By applying modern knowledge of surface active agents and detergency to this field the so-called self-scouring wool oils have been developed. These substances wash off more readily and under much milder conditions than the older types. In the formulation of warp sizings for rayons and other yarns the question of future scourability is also taken into account. If a boil-off operation is not working satisfactorily, it may sometimes be corrected by either changing the sizing formula or modifying the desizing operation. Either of these changes is, in effect, a change in the nature of the soil. It is sometimes possible to change or modify the soil just before the soiled goods are washed or even during the washing process. The addition of solvents or softening oils to the goods or to the bath is an example of this type of operation. The solvent dissolves in the soil and becomes a part of the soil, making it softer, more fluid, and more easily removed.

III. Changes in the bath composition usually receive the most attention, and they are often overemphasized while the other four variables are being overlooked. In fact it is one sub-variable of bath composition, namely the surface active agent itself, which usually receives the most attention. There are many discussions as to the relative merits of soaps versus synthetics and various synthetics versus one another. These considerations are important, but it is also very important to regard the total bath, rather than any single ingredient of it, as the cleaning agent. The presence of builders, synergistic additives, inorganic salts, colloidal additives, acids, or bases may completely alter the effects obtained with pure solutions of the primary surface active agent. Working out an optimum bath composition is accordingly a long and laborious proposition. In recent years, however, the trend has been to work out different formulas to suit the various soil-substrate combinations and the various operating conditions encountered. Complete bath compositions rather than individual surface active agents or builders are rightfully receiving more attention from both the producer and user of detergents.

IV. The three major physical sub-variables, namely temperature, time, and mechanical agitation are sometimes fixed by the limitations of the fabric being handled or the design of the scouring equipment, but their variation within allowable limits can frequently increase the efficiency of scouring to a significant extent. The design of scouring equipment, for example, can sometimes be modified to afford more efficient agitation without endangering the fabric. Since time is an important economic factor, it is usually desirable to change other variables in the process (bath composition, for example) so as to decrease the time necessary for scouring. The same considerations hold true for variations in the temperature of operation.

V. Of the several points of practical interest in connection with the fifth variable (namely the relative quantities of substrate, bath, and soil present) two may be selected for purposes of illustration. In the first place the soil carrying capacity of different baths varies within wide limits and should always be checked before any bath composition is adopted. Some fresh baths will show remarkably high detergency but will lose their effectiveness rapidly when they become even slightly fouled. Other baths will retain a reasonable degree of scouring power even after they have become thick with suspended dirt. This soil-carrying capacity is of greatest importance in continuous or semi-continuous operations, such as raw wool scouring.

ANOTHER place where the relative quantities of detergent and soiled goods are important is in calculating the make-up of the bath. It is quite common operation in wet textile processing to calculate the weight of chemicals used as a percentage on the weight of goods processed. This is necessary for cost accounting purposes, and in some processes, such as dyeing, it is satisfactory for actual operations. In scouring, however, the concentration of the bath (i.e. the weight of detergent per unit weight of liquor) is usually a much more important single factor than percentage of detergent relative to the weight of goods. By way of illustration it may be considered that a 0.2% unbuilt soap solution is a poor wool washing bath but 0.3% soap makes an effective bath. With the latter bath, at a 10 to 1 bath ratio, good scouring will be obtained and the total soap consumption on the weight of the goods will be 3%. Using the 0.2% bath the bath ratio can be increased to 100 to 1, or 20% soap on the weight of the goods, and still the scouring will be inadequate. It is important therefore to make sure that the bath is sufficiently concentrated to be effective and subsequently to economize, if necessary, by shortening the bath ratio.

The physico-chemical mechanisms of detergency are a primary concern of the research scientist but are only of indirect interest to the practical textile processor. It is important, however, that the processor realize the large number and complexity of the effects involved. Such realization prevents undue importance being attached to any single basic measurement such as a surface tension concentration curve or a spreading coefficient. It also serves to focus attention on the five primary variables which are directly observable and controllable and which form a more reasonable guide to solving detergency problems at the practical level.

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