

WETTING AND DETERGENCY

Erik Kissa

Jackson Laboratory, Chemicals and Pigments Department, E. I. du Pont de Nemours & Co., Wilmington, Delaware 19898, U.S.A.

Abstract - Wettability in real systems is difficult to define in quantitative terms. The usefulness of the contact angle is limited when measuring the wettability of nonideal surfaces. Immersion and sorption methods can provide more useful information on the wettability and the rate of wetting of fibers and fabrics.

Wetting of fibers and soil is essential for soil removal, but detergency is a complex process with many variables and the relationship between wetting and detergency is not simple. Liquid (oily) soils and particulate soils have different detergency mechanisms. Oily soil detergency depends on the wetting rate of the substrate and sorption of water in the fibers and fiber coatings. The main mechanism of oily soil removal involves diffusion of water to the soil-fiber interface and rolling up of soil. Other mechanisms are less important. Kinetic studies of oily soil removal reveal (a) an induction period during which water diffuses into the soiled substrate, (b) separation of soil from the hydrated soil-fiber interface, and (c) a final period of nearly insignificant soil removal. Detergency of particulate soil is not dominated by the wettability of fibers, but depends mainly on the location of the soil particle and its adhesion to the fiber surface. The strength of the adhesive bond depends on the attractive forces and the contact area between soil and fiber. The adhesion and retention of particulate soil depends on soiling conditions and increases with the force of the impact of the soil particle contacting the fiber surface.

INTRODUCTION

Detergency is the removal of an unwanted liquid or solid substance from a solid surface brought into contact with a liquid. Undoubtedly, wetting of the surfaces to be separated is an important part of the detergency process. However, the relationship between wetting and detergency is not simple in quantitative terms. Several mechanisms are operable in soil removal and many variables affect detergency, such as the nature and the location of soil, the nature of the substrate, the composition and concentration of the detergent, agitation during washing, etc.

The soil on textiles can be soluble or insoluble in water. The dissolution and extraction of water soluble soils is straightforward. The insoluble soils can be liquids (oily soils), solid particulates, or mixtures of liquid and solid soils. The kinetics and mechanisms of the removal of insoluble soils are complex and present an interesting challenge to the surface chemist.

MECHANISMS AND KINETICS OF OILY SOIL REMOVAL

The detergency of oily soil involves several mechanisms: rolling up of soil, penetration of soil, solubilization and emulsification. The roll-up mechanism (Fig. 1), first postulated by Adam (1), is the most important. The apparent



Fig. 1 Roll-up mechanism of oily soil removal.

contact angle of the oil on fibers changes from 0° to 90° and 180° , and the oil rolls up when the resultant force f of interfacial tensions is positive (2, 3)

$$f = \gamma_{FO} - \gamma_{FW} + \gamma_{OW} \cos \theta, \quad (1)$$

where γ_{FO} denotes the interfacial tension between fiber and soil, γ_{FW} the interfacial tension between fiber and water, γ_{OW} the interfacial tension between oil and water and θ is the contact angle of oil on fiber.

Since $\cos \theta$ can assume positive as well as negative values, the resultant is positive when

$$\gamma_{FO} - \gamma_{FW} > \gamma_{OW} \quad (2)$$

If the resultant f becomes zero before the contact angle θ has increased to 180° , the roll-up of oil stops and an external force has to be applied to complete the removal of soil.

This means that the conditions for oily soil removal are favorable when the interfacial tension between fiber and water γ_{FW} is small, the oil-fiber interfacial tension γ_{FO} is large, and the interfacial tension between oil and the wash liquor γ_{OW} is small. In other words, the fiber surface should be oleophobic and hydrophilic. However, a positive resultant of interfacial tensions is not a sufficient condition for the soil to separate. The rate of roll-up of oil depends on the viscosity of the oily soil. If the viscosity is too high to be overcome by the interfacial forces, an external force is needed to dislodge the soil.

Detergent micelles can solubilize oil on fibers as recently demonstrated by Carroll (4). However, water can, without a detergent, remove oil from hydrophilic fibers. Hence, solubilization is not the main mechanism of oily soil detergency.

Penetration and emulsification of oily soil by the detergent (5) can aid, but can also retard oily soil removal. One of the toughest oily soils to remove is used motor oil which is therefore frequently used in detergency studies. In an attempt to replace it with a model soil of a defined composition, we investigated the detergency of used motor oil and found its viscosity in aqueous detergent solution to be the cause of the refractory behavior. The viscosity of used motor oil does not differ much from that of "Nujol" oil, a hydrocarbon model soil that is relatively easy to wash from fibers (Fig. 2). Yet their behavior is quite different in an aqueous detergent. Unlike "Nujol" or unused

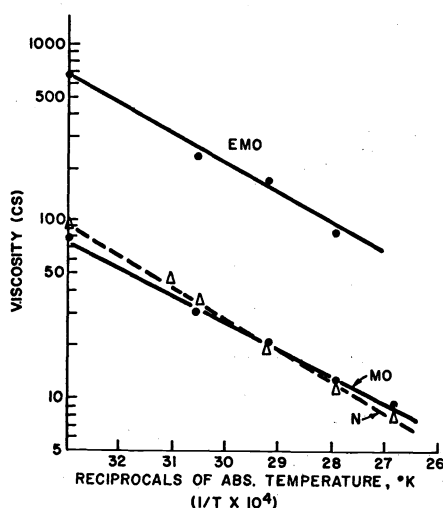


Fig. 2 Viscosity of oily soils used in detergency studies as a function of temperature: EMO - aqueous emulsion of used motor oil, MO - used motor oil, N - "Nujol" oil.

motor oil, used motor oil forms a viscous emulsion with water or an aqueous detergent solution. The temperature dependence of the viscosity of the emulsion formed correlates with the temperature dependence of the used motor oil retention (6).

Detergency of oily soil occurs in three stages (6, 7): (a) an induction period during which the detergent solution diffuses into the soiled fabric, (b) the time period for soil separation from the fabric, mostly by the roll-up mechanism, and (c) the final period, during which soil removal is negligible or very slow (Fig. 3). Detergency is a kinetic process. The cycle of a wash-

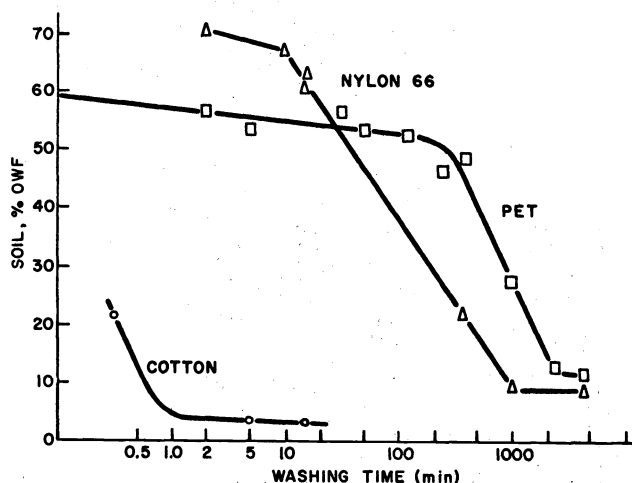


Fig. 3 Oily soil removal during washing with mild agitation (6). Used motor oil on nylon 66, polyethylene terephthalate (PET) and cotton poplin fabrics.

ing machine is of limited duration and soil not removed during the cycle is left on the fabric. The time needed to remove soil is also important when washing is done by hand. Residual soil is left on a fabric when either the induction period exceeds the wash cycle or the rate of soil removal is too slow (in the second period) or the soil is not completely removable under the conditions of washing (third period). The length of the induction period can vary from a few seconds to hours depending on the fabric and soil, and the agitation. The diffusion rate of water to the soil-fiber interface and oily soil removal can be enhanced by a hydrophilic coating on fibers which allows water to diffuse to the fiber surface under the soil (Fig. 4). The efficacy

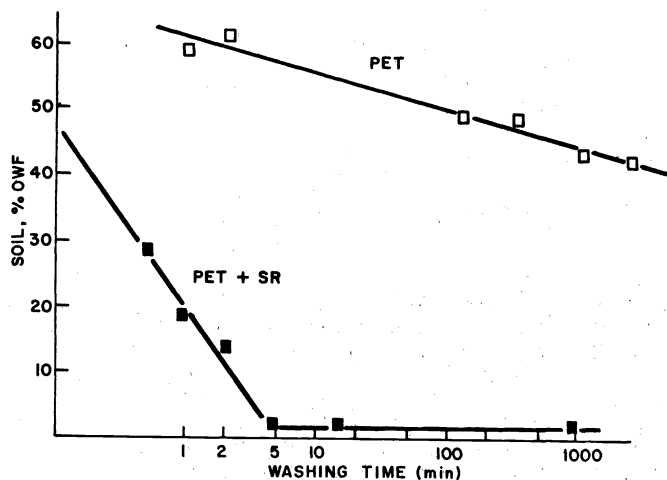


Fig. 4 Effect of hydrophilicity of the substrate on removal of oily soil ("Nujol") (6), PET - untreated polyethylene terephthalate fabric, PET + SR - polyethylene terephthalate fabric surface treated with a hydrophilic polymer.

of the detergency process does not depend only on wetting of fibers and soil, but depends also on the wetting rate, the detergent-soil interactions and the viscosity of the oily soil.

WETTING

Wetting is spontaneous when the sum of interfacial energies, E , decreases as the result of the solid-liquid contact

$$E = A_S \gamma_{SV} + A_L \gamma_{LV} + A_{SL} \gamma_{SL} = \Sigma A \gamma \quad (3)$$

where A denotes areas, γ surface tensions (surface energy per unit area) and the subscripts S , L and V designate solid, liquid and vapor, respectively.

Wetting can be defined as a displacement of a solid-gas interface by a solid-liquid interface.

Wetting of a fibrous assembly, e.g. a fabric, involves the work of immersion, W_I , capillary sorption, W_P , adhesion, W_A , and the work of spreading, W_S ,

$$W_I = W_P = \gamma_{SV} - \gamma_{SL} \quad (4)$$

$$W_A = \gamma_{SV} - \gamma_{SL} + \gamma_{LV} \quad (5)$$

$$W_S = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \quad (6)$$

The work of immersion, W_I , appears in every one of the equations above. Unfortunately, neither solid-vapor interfacial free energy, γ_{SV} , or the solid-liquid interfacial free energy, γ_{SL} , can be directly measured. It is therefore more convenient to relate wettability to the balance of forces at the three-phase boundary. A drop of liquid resting on a solid surface forms a contact angle θ which is considered to be characteristic of the particular solid-liquid interaction (Fig. 5). The equilibrium contact angle θ has

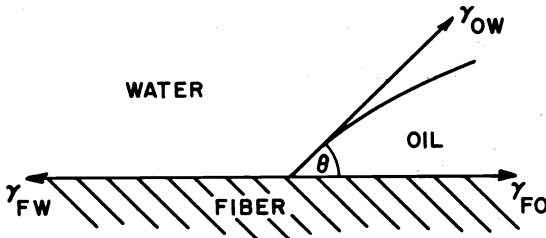


Fig. 5 Interfacial forces at the oil-water-fiber boundary.

served as a measure of wettability, but it has been sometimes overlooked that valid conclusions can be drawn only when equilibrium is assured. This has led to disputes and controversy in wetting studies.

Young (8) proposed the following equilibrium of forces at the three-phase boundary

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (7)$$

Combination of equations (5) and (7) yields the familiar Young-Dupré equation

$$W_A = \gamma_{LV} (1 + \cos \theta) \quad (8)$$

which appears to contain only measurable quantities. However, the equations (7) and (8) apply to three phases in equilibrium and are valid only in ideal systems characterized by smooth, impermeable and undeformable surfaces. In real systems the contact angle is not single valued but displays a different contact angle after it has advanced on a dry surface than after receding from a previously wet surface. The difference between the contact angles displayed by the advancing and the receding liquid has been attributed to sur-

face roughness (9), heterogeneity, adsorption of liquid on the solid, surface deformation, impurities, etc. (10). The systems subjected to detergency, such as fibers and fabrics, have surfaces with one or more of these nonideal characteristics. Although techniques have been developed for measuring contact angles on single fibers (11), the experimental difficulties in obtaining accurate contact angle data can be unsurmountable. Hence, alternate methods have been suggested for the determination of wettability (12). The measurement of contact angles on fabrics is even more difficult. Numerous wetting tests have been developed to side-step the contact angle determination. These tests have involved immersion or capillary sorption from a liquid reservoir of limited or unlimited volume.

WETTABILITY AND OILY SOIL DETERGENCY

Sorption from an unlimited reservoir

Sorption of a liquid from an unlimited reservoir has been the subject of numerous studies. Cameron and Bell, Lukas (13, 14) and Washburn (15) have shown that the distance l , covered in a time t by a liquid flowing under capillary pressure is given by

$$l = \left(\frac{r \gamma_{LV} t \cos \theta_A}{2 \eta} \right)^{0.5} \quad (9)$$

where γ_{LV} is the surface tension, and η the viscosity of the liquid, θ_A the advancing contact angle and r the effective capillary radius.

The fabric strip can be held in a vertical position or, to avoid complications by gravitational forces, in a horizontal position. Vaporization of the liquid from the wet fabric and absorption of vapor by the dry fabric can affect the diffusion rate of the liquid. The latter problem can be avoided by impregnating the fabric with a nonvolatile liquid and measuring its displacement by an immiscible liquid (7). The displacement of a nonvolatile hydrocarbon on a fabric by diffusion of either water or a detergent solution into the fabric simulates detergency of oily soil (Fig. 6). The rate at which

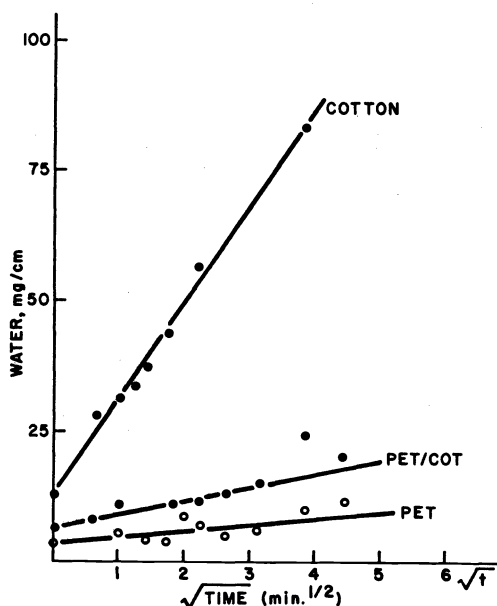


Fig. 6 Diffusion of water (mg H₂O per unit length of water/fabric contact boundary) into fabrics impregnated with "Nujol" oil (7): Cotton poplin, polyethylene terephthalate (PET) and a polyethylene terephthalate-cotton (65/35) blend (PET/COT).

oil is displaced increases with the initial water content (moisture regain) and consequently with the hydrophilicity of the fabric.

Total immersion

Some wetting tests, e.g., the Draves test (16), involve a total immersion of the yarn or fabric sample in a liquid. The floating sample is allowed to sink in the liquid and the sinking time serves as a measure of wettability. The sample, a yarn skein or a fabric disk, sinks when the liquid displaces most of the air or another liquid of lower density in the samples. Fowkes (17) has shown that the sinking time of a yarn bundle in surfactant solutions is a function of the advancing contact angle of the liquid on fibers.

An apparatus for measuring the sinking time of a fabric disk is shown in Fig. 7. The fabric disk is lowered carefully onto the liquid with a minimal

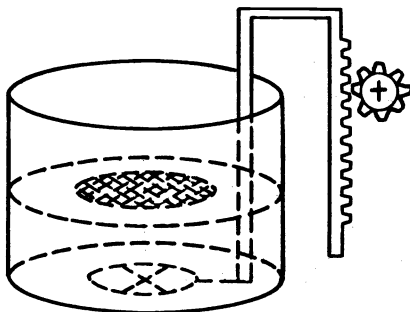


Fig. 7. Apparatus for measuring sinking time.

disturbance of the surface. Care is taken to avoid leaving air pockets between the fabric and the liquid. The fabric is more flexible and conforms more readily to the surface of the liquid when impregnated with an immiscible liquid of lower density than the liquid used as the sinking medium.

The sinking time of a fabric disk in a liquid depends on the geometry of the fabric and the fibers. The sinking time is therefore not directly related to the wettability of fiber surfaces. Relative wettability values can be obtained by measuring the sinking times in two or more different liquids, e.g., in a hydrocarbon and in water, or better in an aqueous detergent solution (7). A very useful hydrophilicity/oleophobicity index is the ratio of the sinking times of a fabric disk in a hydrocarbon and in an aqueous detergent. We have used a mixture of "Nujol" oil and hexadecane (1:1) and a 1.0-g/L solution of the AATCC standard detergent 124 as the two liquids for the determination of the hydrophilicity/oleophilicity index.

TABLE 1. Detergency of oily soil and wettability of substrate.

Property measured	Untreated polyethylene terephthalate fabric	Polyethylene terephthalate fabric treated with nonylphenol-15 ethylene oxide adduct (18)
Sinking time (sec) at 25°C:		
In hexadecane-"Nujol" (1:1)	13.5	17.9
In aqueous detergent (a)	20.4	8.5
In aqueous detergent (a) after impregnating the fabric with hexadecane	6600	252
Hydrophilicity-oleophilicity index	0.60	2.1
Retention (%) of "Nujol" oil (Test method ref. 22)	48	14

(a) 1.5 g/L AATCC standard detergent 124 in water

Table 1 shows the hydrophilicity/oleophilicity index and the oily soil retention of a polyethylene terephthalate fabric before and after a hydrophilic surface treatment. The fabric was made hydrophilic by bonding a polyoxyethylene derivative, $C_9H_{19} \cdot C_6H_4(OC_2H_4)_{15}OH$ to the fiber surface softened by heat (18). The hydrophilic surface treatment increased the rate of water sorption, decreased the rate of soil sorption, and consequently increased the hydrophilicity/oleophilicity index. The time of displacing hexadecane/"Nujol" oil by the detergent solution was greatly reduced by the hydrophilic treatment. The displacement of oil simulates detergency without an external force and represents a spontaneous release of soil.

Sorption of a drop

The sorption of a drop can indicate the wettability of a fabric either by the time of its sorption by the fabric or by the area of the wet spot formed by the liquid spreading within the fabric. The wettability of a fabric can also be estimated by a method using a series of liquids having different surface tensions. A measured drop of each liquid is placed on the fabric and the surface tensions of liquids noted which sink or do not sink into the fabric. This technique is used in oil repellency tests. The AATCC oil repellency test (19) uses eight hydrocarbons (n-alkanes) numbered in the decreasing order of their surface tensions. The repellency rating is indicated by the number of the liquid having the lowest surface tension of the liquids which do not wet the fabric in 30 sec.

The kinetics of sorption of a limited amount of liquid, such as a drop are more complicated than those of sorption of liquid from an unlimited reservoir. Gillespie (20) studied spreading of nonvolatile liquids in paper and developed the equation

$$R^2 [R^4 - R_0^4] = Bv^2 \gamma / \eta t \quad (10)$$

where

$$B = \frac{27 b q_s \cos \theta_A}{8\pi^2 h^2 c^3} \quad (11)$$

R denotes the radius of the stain, R_0 is the radius of the stain at time zero, v is the volume of the liquid, γ the surface tension, η the viscosity of the liquid, t is spreading time, b is a constant descriptive of the substrate, q_s the permeability of the substrate, θ_A the advancing contact angle, h the thickness of the substrate and c the saturation concentration of the liquid in the substrate.

The exact measurement of the radius R is difficult when the liquid spreads rapidly or when the substrate is not isotropic. We developed therefore a photographic technique for an instantaneous measurement of the spot area (21).

Equation 10 can be written in the form

$$A (A^2 - A_0^2) = \frac{K_s \gamma v^2 t}{\eta} \quad (12)$$

where A is the area covered by the spreading liquid, A_0 the area at time 0, and the capillary sorption coefficient K_s given by

$$K_s = \frac{27\pi b q_s \cos \theta}{8h^2 c^3} \quad (13)$$

We have found that the equation holds for capillary sorption of liquids contained within a fabric, but the use of the equation is complicated by the intrinsic area, A_0 , covered by the drop at time zero. The intrinsic area A_0 depends on the viscosity, surface tension and volume of the drop and other variables. The area A_0 can be neglected if the exponents of the equation are adjusted to fit the data (21).

If A_0 in equation (12) is neglected, the area covered by the spreading liquid is given by

$$A \approx K (\gamma/\eta)^{0.33} v^{0.67} t^{0.33} \quad (14)$$

Equation (14) may be written in the general form

$$A = K (\gamma/\eta)^u v^m t^n, \quad (15)$$

where u , m and n are constants, and K is a coefficient.

In accord with equations (14) and (15), a plot of the area covered by a spreading liquid against time is linear on logarithmic scales (Fig. 8). The

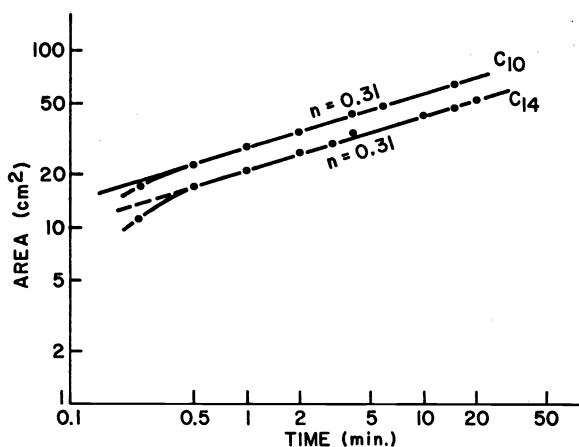


Fig. 8. Spreading of n-alkanes (drop size 0.10 mL) in 65/35 polyethylene terephthalate-cotton blend fabric: C₁₀ - n-decane, C₁₄ - n-tetradecane.

value of the slope, about 0.3, is reasonably close to the value 0.33 expected from the Gillespie equation with the exception of the first sorption phase, during which a part of the drop rests on the fabric surface and exerts a hydrostatic pressure on the spreading liquid. When the spreading time and the drop volume are kept constant and the same liquid is used for testing the effect of surface treatments on the wettability of a fabric, then the areas covered by the liquid are proportional to the coefficient K , which is a function of $\cos \theta$ and indicates wettability. It has to be assumed, of course, that the surface treatments do not change the geometry of the fabric.

The application of this sorption method to detergency related wetting problems is shown below with two examples. The first example shows the oil repellency of a polyester-cotton fabric treated with eight different fluoropolymers and the resistance to the spreading of oily soil in the fabric (Fig. 9). The oil repellency test is a contact angle phenomenon since the liquid does not flow into a repellent fabric. However, repellency, which is a condition of nonwettability, can be measured also under dynamic conditions by measuring the area covered by a liquid having a sufficiently low surface tension to be sorbed and spread within the fabric. The correlation of the areas covered by n-heptane with oil repellency ratings obtained by the static method (Fig. 9) is quite reasonable when considering the limited precision of the repellency test.

The second example shows a relationship between oily soil detergency and the wettability of a polyester fabric by water (Fig. 10). The polyester fabric was made hydrophilic by a heat treatment with ethoxylated alkanols having HLB values from 4.9 to 16.9 (18). The wettability of these fabrics was determined by measuring the area covered by a 0.10-mL drop of water in 120 sec. The effect of the hydrophilic surface treatment on detergency was determined with "Nujol" oil by two methods described in our previous publications. One method uses suction to apply oily soil to two disks cut from the fabric; the disks are washed in jars with mild agitation (6). The other method applies a 0.10-mL drop of oil to each of two 10 x 10-cm fabric samples. The oil is allowed to wick for 16 hours before the fabrics are washed in a wash machine (22). Both methods show that the wettability of the fabrics by water

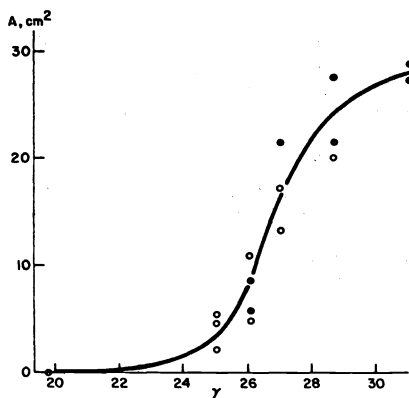


Fig. 9. Spreading of oily soil as a function of oil repellency of a fabric: Area covered by 0.10 mL n-heptane spreading for 180 sec in a 65/35 polyethylene terephthalate-cotton blend fabric versus lowest surface tension (γ) of a series of n-alkanes not wetting the fabric in 30 sec.
 ○ - fabric not washed after repellent treatment
 ● - fabric washed and dried after repellent treatment

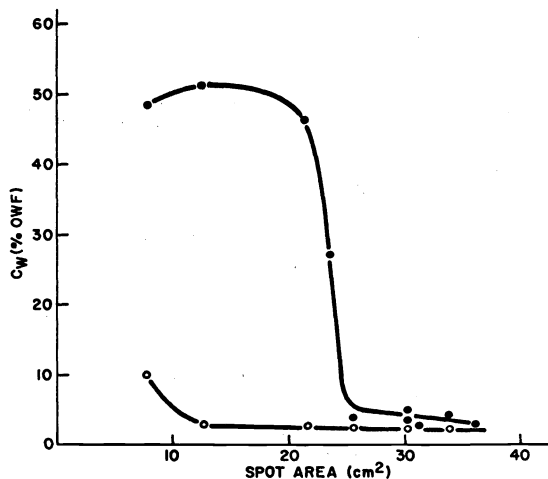


Fig. 10. The removal of "Nujol" oil vs. the area covered by 0.10 mL of water in 60 sec on polyethylene terephthalate fabric made hydrophilic by a heat treatment (18) with ethoxylated alkanols:
 ● - "Nujol" oil applied by suction, soiled fabrics washed in jars with mild agitation (6)
 ○ - 0.10 mL "Nujol" oil allowed to wick into fabric, solid fabrics washed in a wash machine (22)

increases the detergency of oily soil (Fig. 10). However, the effect of a hydrophilic surface treatment is more dramatic when the amount of soil on the fabric is large and agitation during washing is mild. Vigorous agitation can compensate for insufficient wettability and help to remove soil not released spontaneously. The example illustrates that the relationship between wetting and detergency is complicated by other factors, in this case the input of mechanical work into the detergency process.

The discussion assumed so far that the fibers were impermeable to the liquid placed onto the fabric. When the liquid can diffuse into the fibers or into a surface coating on the fibers, the kinetics of sorption and spreading are much more complicated. Diffusion of the liquid into the fibers accelerates the sorption of the drop by the fabric. However, the spreading rate of the

liquid within the fabric is reduced, because absorption in fibers reduces the volume of liquid available for spreading in the capillary spaces, causes swelling of the fibers and decreases the spaces between the fibers. The effect of sorption inside the fibers on capillary sorption is shown with a drop of water on cotton poplin fabric (Fig. 11). The water drop sinks rapidly

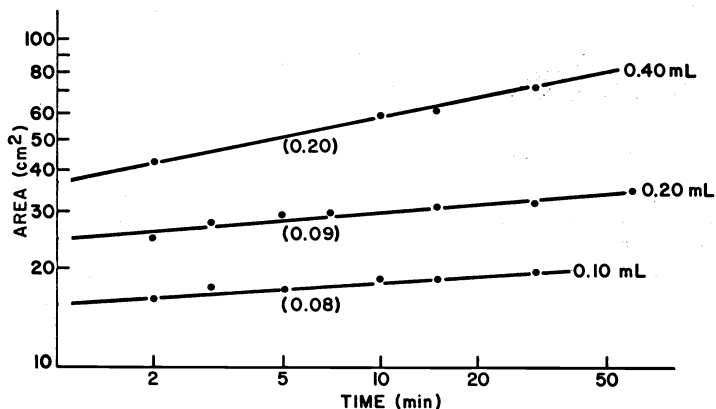


Fig. 11. Spreading of water in cotton poplin fabric. Drop volume 0.10, 0.20 or 0.40 mL.

into the fabric, but once water is within the fabric, spreading is relatively slow. The exponent n in equation 15, indicated by the slope of the curves in Fig. 11, is small until the drop volume is increased. When the liquid is absorbed by the fibers, the rate at which the liquid spreads within the fabric is no longer a valid indication of its wettability. Hence, both the absorption of a liquid in the fibers and the capillary sorption in spaces between the fibers have to be known to characterize the wetting properties of a fabric. The relationship between wettability and oily soil detergency is not always simple, because the transport of the wash liquor to the fiber surface covered with soil can occur via three different routes (Fig. 12): (A) along the fiber surface, (B) through a permeable fiber coating, and (C) through the fibers. Although the wettability of the fibers by water is the most impor-

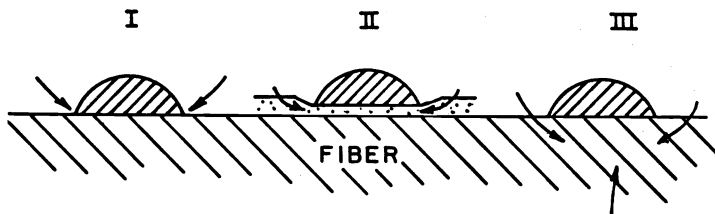


Fig. 12. Diffusion routes to the soil-fiber interface.

tant factor in determining detergency of oily soil in an aqueous bath, other factors, such as the viscosity of the soil, the detergent, wash temperature, agitation, etc., can affect the rate of soil removal and hide the correlation with wettability.

Particulate soil

The removal of a soil particle (3) involves penetration of the detergent solution (wash liquor) into the soil-fiber interface, wetting of the separated surfaces and the transport of the particle to a distance exceeding range of the attractive forces between the surfaces separated (Fig. 13). The spreading pressure of the adsorbed detergent is usually not sufficient to overcome the adhesional forces and a mechanical force has to be applied to dislodge the particle from the fiber surface. Hence, the detergency of particulate soil is not dominated by the wettability of the fiber surface. Other factors, are more important, such as the location of the soil and the adhesion of soil particles to the fiber surface. The adhesion of a soil particle de-

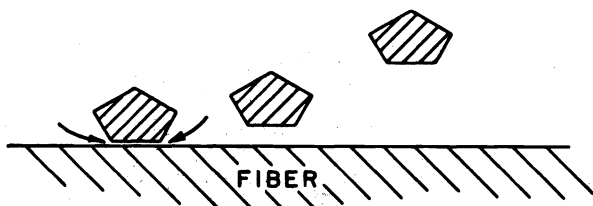


Fig. 13. Mechanism of particulate soil removal.

depends on the adhesive, mainly dispersion forces, and the contact area between the particle and the fiber. Deformation resulting in plastic flow of the soil particle or the fiber surface increases the contact area and the adhesion (Fig. 14). Since the deformation depends on the impacting force of the parti-

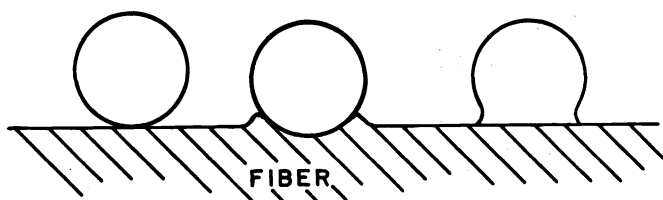


Fig. 14. Plastic flow on impact of a soil particle.

cle, the adhesion of the particle, as well as its location in the fabric, depends on the soiling conditions.

The effect of pressure on adhesion of soil is shown with ferric oxide on polyester and cotton fabrics (Fig. 15). Two fabric squares with iron oxide evenly

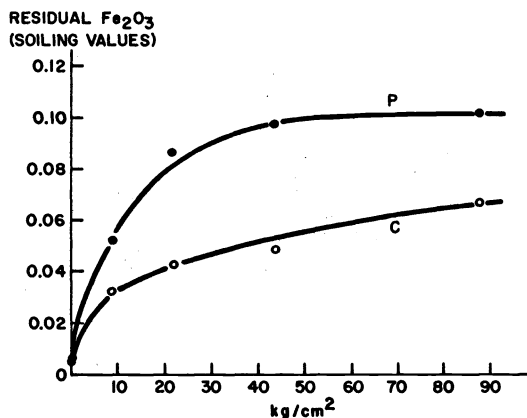


Fig. 15. Effect of pressure applied to ferric oxide on polyethylene terephthalate (P) or cotton poplin (C) fabrics on the amount of ferric oxide retained by the fabric after washing (one 15-min. wash cycle).

spread between them were covered with polished steel plates and placed under a hydraulic press. The amount of ferric oxide adhering to the fabrics after washing increased with increasing pressure.

To study quantitatively the effect of soiling conditions on detergency of particulate soil, we developed a technique for uniform soil application under precisely controlled conditions (23). We employed for this purpose the Accelerator, an instrument designed for abrasion testing of fabrics, after removing

its abrasive collar. A motor driven impeller rotates the soil and the fabric samples in a closed chamber. The mechanical work and the degree of soiling can be continuously varied by varying the rotational speed, the soiling time and the amount of soil (24).

The soiling conditions affect both the amount of soil adhering to fibers before washing, c_s , and the residual soil on the washed fabric, c_w (25). Within the range of our experimental conditions the amount of soil left on a fabric after laundering c_w is given by

$$c_w = K_w s^{0.5} t_s^{0.5} u \quad (16)$$

where s denotes the amount of soil rotated with the fabric (expressed as % of the weight of the fabric), t_s time (min.), u the rotational speed (rpm), and K_w a coefficient.

Soil retention, defined as c_w/c_s , increases with the number of rotations performed. However, rotation at higher speed increases the soil retention more than an equal number of rotations performed at a slower speed (Fig. 16). In-

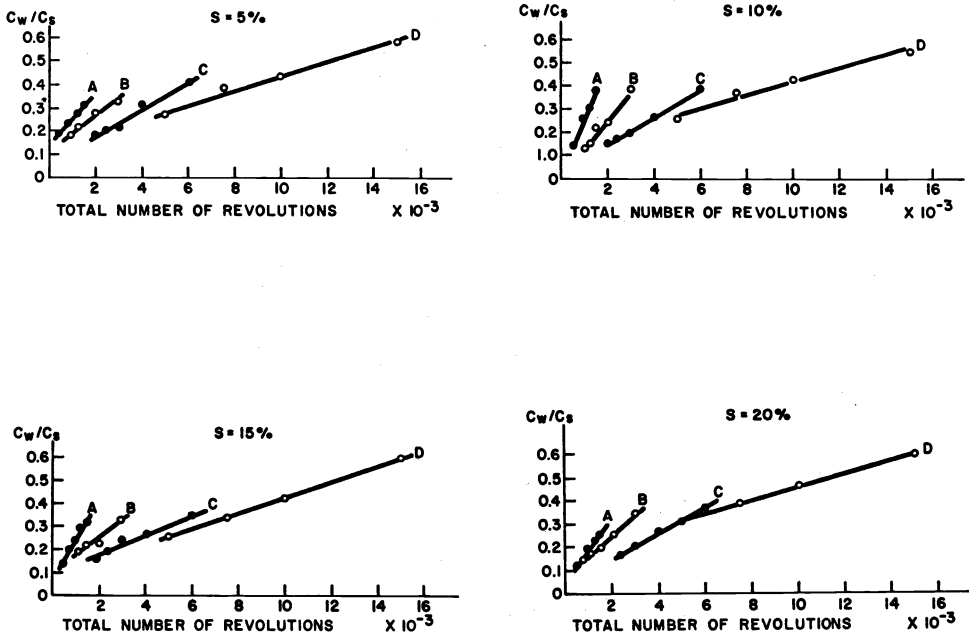


Fig. 16. The effect of mechanical work performed during soiling on the retention after one wash cycle (c_w/c_s) of ferric oxide on cotton poplin fabric: Soiling times: A - 30 sec, B - 60 sec, C - 120 sec, D - 300 sec. The data points in each group are in the order of rotational velocities increasing from 1000 to 3000 rpm.

creasing the rotational speed increases the kinetic energy of the impacting particle, and because of increased flexing of the fabric, transports the particles deeper into the fabric. Since soil retention depends on soiling conditions, two fabrics with the same soil content may not wash equally clean. The soiling conditions are therefore important variables in detergency studies, but it is only recently that quantitatively controlled methods of soil application have been developed.

Naturally occurring soils are usually mixtures of particulate soil and fatty or oily soil. The adhesion of such soils depends on wetting of the fibers by the fatty soil component. The detergency of such mixed soils depends on the removal of the fabric by the aqueous detergent and the hydrophilicity of the fiber surface.

Redeposition of soil

Some of the soil dislodged during washing is redeposited onto fibers. Although soil removal is opposed by soil deposition, soil removal is not truly reversible and an equilibrium is not attained during washing (26). Soil redeposition is, like soil removal, strongly influenced, but not dominated, by wetting of the fibers and soil. The redeposition of oily soil is mainly governed by preferential wetting of the fibers by water and the soil. The redeposition of solid soil depends, in addition of the wettabilities of the surfaces involved, also by the hardness of the soil particle and the fiber surface immersed in water. Ionic interactions can also influence soil redeposition. These factors can overshadow the wettability of the fibers by water.

CONCLUSIONS

Research on detergency has left a gap between fundamental theories of surface phenomena and the understanding of the practical detergency process. The advanced knowledge of wetting, contact angles, surface energies, electrokinetic potentials, etc., has provided insight into the detergency mechanisms. However, the progress made in surface chemistry has not eliminated the need for empirical testing of detergents with naturally soiled fabrics and visual estimation of residual soil on fibers (27, 28). Research on wetting has centered around the contact angle on plane surfaces, while wetting of textile fabrics involves curved surfaces which the liquid may deform or permeate. More can be learned about the relationship between wettability and detergency in the real world by measuring the displacement of one liquid by another, and by studying the kinetics of wetting and sorption in textile fabrics.

Detergency is a complex process with many variables. In order to elucidate detergency mechanisms and isolate the effect of each variable, the detergency process can be divided into elementary processes studied individually. The techniques we have developed for reproducible, uniform and realistic soil application (23, 24, 29) have made it possible to study quantitatively the effect of soiling conditions on detergency (25). These techniques will help to define model soils (30) which can represent most types of soils encountered in the detergency process. Systematic investigation of the elements of detergency using modern analytical techniques will further strengthen the link between basic surface chemistry and practical detergency.

Acknowledgment - The author thanks Drs. M. W. Duch, C. J. Hensler and T. A. Liss for reading the manuscript and their helpful comments.

REFERENCES

1. N. J. Adam, *J. Soc. Dyers Colourists* 53, 121 (1937).
2. W. Kling, *Kolloidz.* 115, 37 (1949).
3. H. Lange, "Physical Chemistry of Cleansing Action", in "Solvent Properties of Surfactant Solutions", p. 117, K. Shinoda, ed., New York, Dekker (1967).
4. B. J. Carroll, *J. Coll. Interf. Sci.* 79, 126 (1981).
5. A.S.C. Lawrence in "Surface Activity and Detergency", K. Durham, ed., Macmillan, New York, 1958, p. 158.
6. E. Kissa, *Textile Res. J.* 41, 760 (1971).
7. E. Kissa, *Textile Res. J.* 45, 736 (1975).
8. T. Young, *Phil. Trans. Roy. Soc. (London)*, 95, 255 (1858).
9. R. E. Johnson and R. H. Dettre, *Advan. Chem. Ser.* 43, 112 (1964); R. H. Dettre and R. E. Johnson, *ibid.* 43, 136 (1964).
10. R. J. Good, in *Surface and Colloid Science*, 11, 1 (1979).
11. A. W. Neumann and R. J. Good, in *Surface and Colloid Science*, 11, 31 (1979).
12. B. Miller, "The Wetting of Fibers", in "Surface Characteristics of Fibers and Textiles", M. J. Schick, ed., New York, Dekker (1977), p. 417.
13. F. K. Cameron and J. M. Bell, *J. Phys. Chem.* 10, 658 (1906).
14. R. Lukas, *Kolloidz.* 23, 15 (1918).
15. E. W. Washburn, *Phys. Rev.*, 2nd Series 27, 273 (1921).
16. C. Z. Draves and R. G. Clarkson, *Amer. Dyest. Rep.* 20, 201 (1931).

17. F. M. Fowkes, *J. Phys. Chem.* 57, 98 (1953).
18. E. Kissa and R. Dettre, *Textile Res. J.* 45, 773 (1975).
19. AATCC Test Method 118-1978, *AATCC Technical Manual* 55, 242 (1979).
20. T. J. Gillespie, *J. Colloid Sci.* 14, 1123 (1959).
21. E. Kissa, *J. Colloid Interf. Sci.*, accepted for publication.
22. E. Kissa, *Textile Chem. Col.* 3, (10) 224 (1971).
23. E. Kissa, *Textile Res. J.* 41, 621 (1971).
24. E. Kissa, *Textile Res. J.* 43, 86 (1973).
25. E. Kissa, *Textile Res. J.* 49, 384 (1979).
26. T. H. Grindstaff, H. T. Patterson and H. R. Billica, *Text. Res. J.* 40, 35 (1970).
27. A. L. de Jong, *J. Am. Oil Chem. Soc.* 55, 163 (1978).
28. H. Krüssmann, *J. Am. Oil Chem. Soc.* 55, 165 (1978).
29. A. M. Dave and E. Kissa, *Textile Res. J.*, accepted for publication.
30. E. Kissa, *Textile Chem. Col.* 5, 251 (1973).