# A Kinetic Study of Fabric Detergency[1]

**HANS SCHOTT**, Temple University School of Pharmacy, Philadelphia, Pennsylvania 19140


## ABSTRACT

The kinetics of soil removal were investigated under domestic laundry conditions by incorporating small swatches of four artificially soiled test fabrics into a standard load of clean cotton goods. This prevented soil redeposition from affecting the soil removal rate. Two runs were analyzed, one with an anionic and the other with a nonionic detergent. Assessment of the amount of soil remaining on the fabric was made by reflectivity measurements interpreted according to the Kubelka-Munk equation. First-order kinetics were found to prevail for periods ranging from the first 6 min of the wash cycle to the entire 20 min, depending upon test fabric and detergent. For these lengths of time, the rate of soil removal was directly proportional to the amount of soil remaining on the fabric. The 8 first-order rate constants had rather similar values, varying at most by a factor of 2.3. The average value, 0.109 $min^{-1}$, corresponds to a 6.4-min wash period for removing one-half of the soil and to a 21-min period for removing 90% of the soil from the soiled fabric. The magnitude of the response of the four artificially soiled test fabrics to the two detergents is compared and discussed in terms of the soiling materials. The nonionic detergent was more effective in cleaning a fabric soiled mainly with kaolin and wool fat, while the anionic detergent was more effective with a fabric containing large amounts of liquid oily soil plus carbon black and oleophilic bentonite.


## INTRODUCTION

There is a paucity of information on the kinetics of fabric detergency, i.e. on the rates of soil removal and of soil deposition or redeposition (1,2). Few published data are applicable to the kinetics of soil removal under domestic laundry conditions.

The following are some of the most common shortcomings. Bench-scale equipment differs from domestic washing machines in the kind and level of agitation, in the length of the wash cycle, and in the bath-to-cloth ratio. Extrapolating kinetic data obtained with the former to the latter is risky. The use of heavily soiled test fabrics promotes the buildup of soil in the bath. As soil redeposition (reverse process) becomes increasingly more important compared to soil removal (forward process), an apparent reduction in the soil removal rate is observed. An equilibrium between the two processes may be reached eventually.

The purpose of the present experiments was to study the kinetics of soil removal under actual domestic laundry conditions, using test fabrics because of their uniformity, while minimizing soil redeposition.

[1]Presented at the 169th National Meeting, American Chemical Society, Philadelphia, Pa., April 7-11, 1975.

## EXPERIMENTAL PROCEDURES

### Materials

The characteristics of the four artificially soiled cotton test fabrics employed are listed in Table I. Three of these fabrics are commercially available. Except for the Waeschereiforschung Krefeld (WFK) fabric, the test fabrics were soiled equally on both sides, i.e. both sides gave identical reflectance readings.

Two commercial detergents were employed at the recommended use levels. The actives were an alkylarylsulfonate and a nonionic polyoxyethylated surfactant for the detergent designated as anionic and as nonionic, respectively. Both were built with tripolyphosphate. Hot tap water was hardened to 180 ppm.

### Procedures

Swatches of the four test fabrics measuring ca. 9 x 10.5 cm were attached to 11 pieces of circular clean cotton cloth of 25 cm diameter by sewing along one edge only. These assemblies were incorporated into a 6-lb load of clean cotton pieces. Washing was conducted in a Kenmore top loading washer set at "full" and at "hot water" (white cycle). An electric heating coil was wound around the tub of the washing machine and covered with a layer of fiber glass batting for insulation. This made it possible to maintain the temperature of the wash liquor nearly constant. For the nonionic detergent, the temperature was 59 C at the beginning and 57 C at the end of the wash cycle. For the anionic detergent, the temperature remained at 56 C throughout.

At appropriate intervals during the wash cycle, circular cotton pieces with the test fabric swatches sewn on were withdrawn from the wash load and rinsed. The swatches were removed from the circular fabric, dried, and their reflectance was read on both sides. This was compared with the reflectance of the identical individual swatches which had been measured on both sides before the wash.

Reflectance measurements were made with a Gardner automatic color-difference meter, model AC-3 (Gardner Laboratory, Bethesda, Md.) Each swatch (single thickness) was backed by the ceramic standard.

TABLE I

Description of Soiled Cotton Test Fabrics

| Designation | Supplier | Particulate soil | Oily soil | Chloroform extractables, % |
|---|---|---|---|---|
| UST | U.S. Testing Co. | Oildag colloidal carbon black | Mineral oil + cottonseed oil | 1.4 |
| FDS | Foster D. Snell, Inc. | Carbon black + Bentone 34 oleophilic bentonite | Coconut oil + coconut oil free fatty acids + mineral oil | 11.5 |
| WFK | Waeschereiforschung Krefeld | Kaolin + lampblack + black and yellow iron oxides[a] | Wool fat[a] | 3.5 |
| VCD | Lever Brothers Co. | Vacuum cleaner dust | Free fatty acids | 2.5 |

[a]See ref. 3.

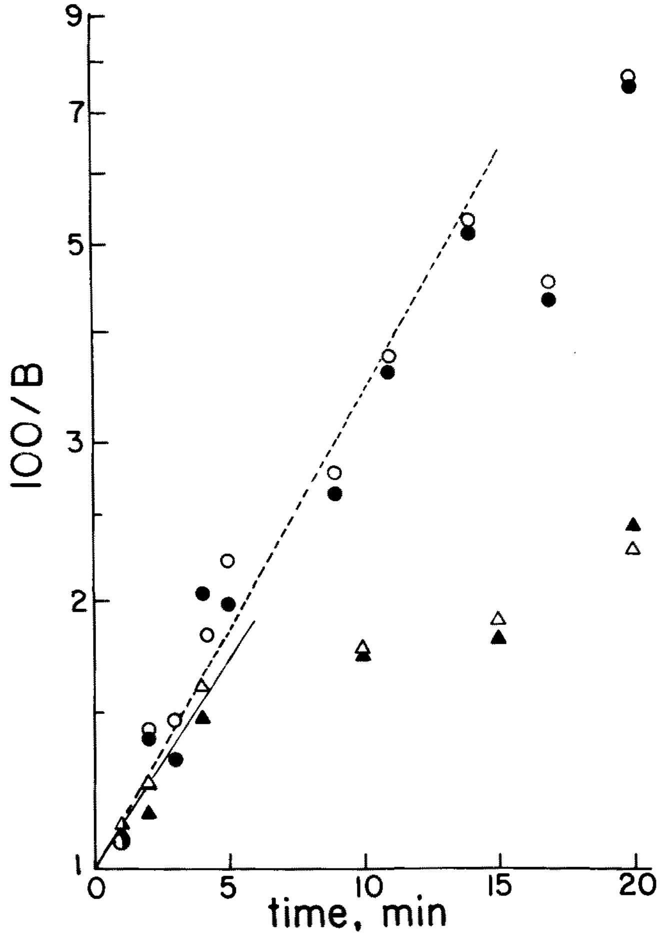


FIG. 1. Reciprocal of the fraction of soil remaining on Foster D. Snell (FDS) fabric (logarithmic scale) as a function of washing time. Circles = anionic detergent, triangles = nonionic detergent, open symbols = top of FDS test swatches, filled symbols = bottom, solid line = linear regression for nonionic detergent, and broken line = linear regression for anionic detergent.

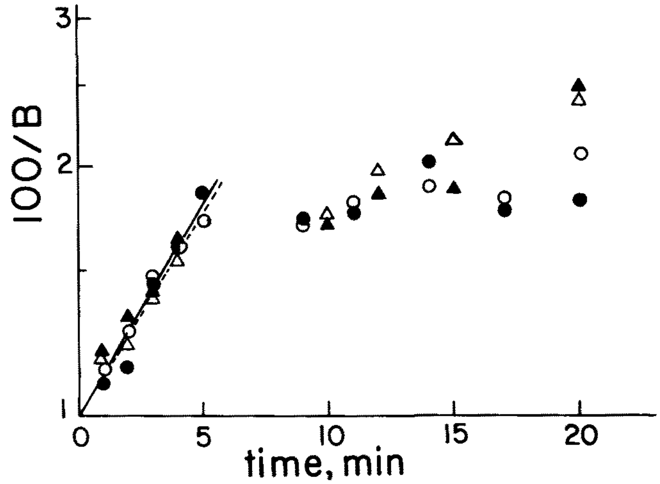


FIG. 2. Reciprocal of the fraction of soil remaining on U.S. Testing (UST) fabric (logarithmic scale) as a function of washing time. Circles = anionic detergent, triangles = nonionic detergent, open symbols = top of UST test swatches, filled symbols = bottom, solid line = linear regression for nonionic detergent, and broken line = linear regression for anionic detergent.

## TREATMENT OF DATA

The optical criterion of fabric whiteness was chosen, because it approximates consumer evaluation most closely and because the test fabrics were designed for optical evaluation. The measurements of reflectivity were interpreted by means of the uncorrected Kubelka-Munk equation, despite its limitations, in view of its convenience (2,4):

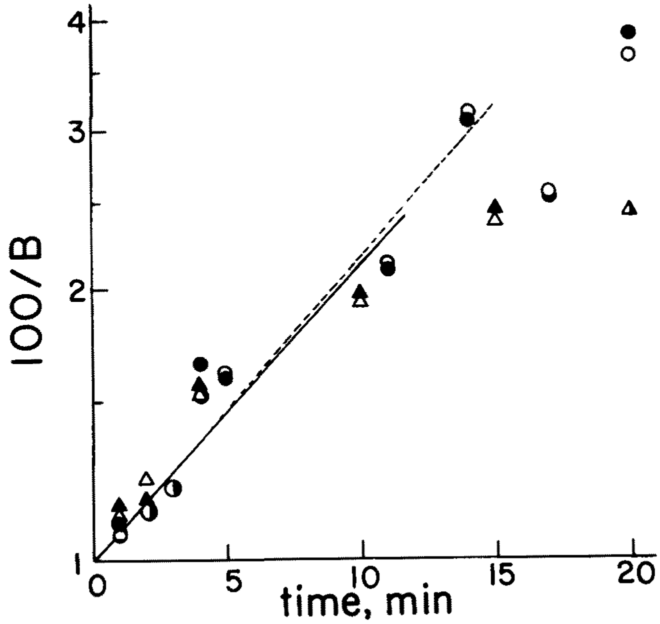


FIG. 3. Reciprocal of the fraction of soil remaining on vacuum cleaner dust (VCD) fabric (logarithmic scale) as a function of washing time. Circles = anionic detergent, triangles = nonionic detergent, open symbols = top of VCD test swatches, filled symbols = bottom, solid line = linear regression for nonionic detergent, and broken line = linear regression for anionic detergent.

$$(K/S) = (1-R)^2/2R, \tag{I}$$

where K is the light-absorption or reflectivity coefficient, S the light-scattering coefficient, and R the observed reflectance, all for monochromatic light. In the case of black or grey soil pigments on white fabrics, where the reflectance is the same at all wavelengths, R can be measured with white light. It is generally held that K increases proportionally with the amount of light-absorbing soil particles while S remains essentially constant, so that K/S is a linear function of the amount of dark particulate soil on the fabric (2,4).

The amount B of soil remaining on the fabric after a washing time t, expressed as a percentage of the amount of soil initially present, is then:

$$B = 100 \left[ \frac{(K/S)_L - (K/S)_O}{(K/S)_S - (K/S)_O} \right], \tag{II}$$

where the subscripts L, S, and O refer to laundered, soiled, and original unsoiled fabric swatches, respectively. Since $R_O$ is high compared to $R_S$ and $R_L$, $(K/S)_O$ is small compared to $(K/S)_S$ and $(K/S)_L$. Hence, the value of B is not much influenced by the value of $R_O$, which was known exactly for only two of the four test fabrics.

If the washing process follows first-order kinetics, the rate of soil removal is directly proportional to the amount of soil present on the fabric:

$$-dB/dt = kB, \tag{III}$$

which on integration becomes

$$\log (100/B) = kt/2.303, \tag{IV}$$

where B is the amount (percentage) of soil still present after t min of washing, and k is the first-order rate constant expressed in reciprocal min. This equation is of the form:

$$y = bx, \tag{V}$$

where y, the dependent variable, is the logarithm of the quotient (amount of soil present initially/amount of soil remaining on the fabric after time t); x, the independent variable, is time. On the first-order plot according to equation IV, the slope b is k/2.303. The straight line must pass through the origin because when x = t = 0, B = 100, making y = log (100/B) = log 1 = 0.

Plots of log (100/B) vs t were linear for periods ranging from the first 6 min to the entire 20 min of the wash cycle (Fig. 1-4 and the sixth column of Table II). This indicates that the soil removal process followed first-order kinetics for a sizable portion of the wash cycle or for all of it.

The slope or regression coefficient b for the linear portion (and from it the rate constant k) was calculated by the method of least squares (5) according to:

$$b = \Sigma x_i y_i / \Sigma x_i^2, \qquad \text{(VI)}$$

where $\Sigma$ stands for summation and the subscript i refers to an individual point. The variance from regression was calculated by:

$$s_{y \cdot x}^2 = \Sigma (y_i - Y_i)^2 /(n-1), \qquad \text{(VII)}$$

where $Y_i$ is the value of y calculated by the least-squares equation (Equation IV or V), and n is the number of points of the linear portion of the plot besides the origin. The variance of the slope is:

$$s_b^2 = s_{y \cdot x}^2 / \left\{ \Sigma x_i^2 - (\Sigma x_i)^2/n \right\}. \qquad \text{(VIII)}$$

Since k = 2.303 b, the standard deviation of the rate constant is given by:

$$s_k = 2.303\, s_b. \qquad \text{(IX)}$$

The Student t tests for the comparison of slopes and of rate constants were carried out as described by Youden (5).

## RESULTS AND DISCUSSION

The pertinent data are summarized in Table II.

### Fabric Symmetry

The differences between the pairs of rate constants obtained from the top and the bottom side of each of the four test fabrics were not statistically significant. This applied even to the WFK fabric, where the $R_S$ values of one side were 5.2 reflectance units lower than those of the other side. In subsequent calculations, the data and the two rate constants obtained for the top and the bottom of a given test fabric with one detergent were combined.

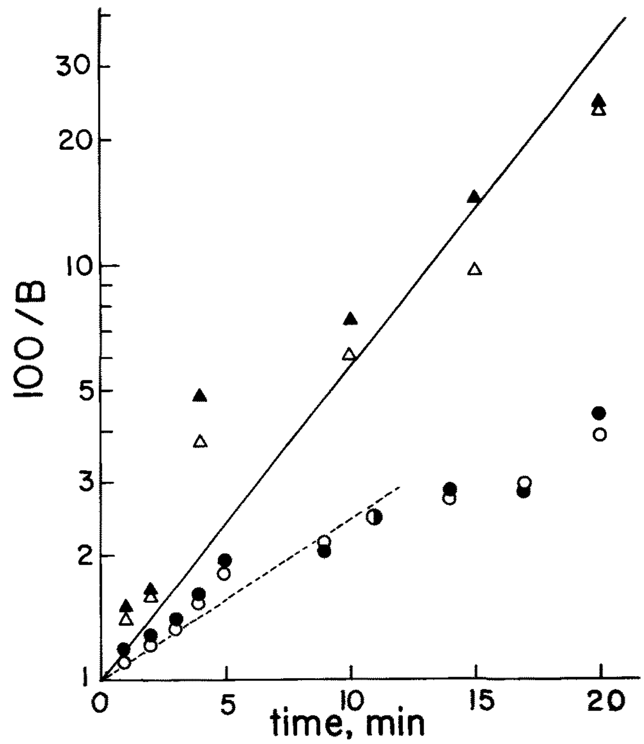


FIG. 4. Reciprocal of the fraction of soil remaining on Waeschereiforschung Krefeld (WFK) fabric (logarithmic scale) as a function of washing time. Circles = anionic detergent, triangles = nonionic detergent, open symbols = top of WFK test swatches, filled symbols = bottom, solid line = linear regression for nonionic detergent, and broken line = linear regression for anionic detergent.

TABLE II

First-Order Rate Constants k and their Standard Deviations $s_k$ for Four Test Fabrics and Two Detergents

| Detergent[a] | Fabric[b] | Side[c] | k, | $s_k$ | Range of first order[d], | n[e] |
|---|---|---|---|---|---|---|
| | | | min$^{-1}$ | | min | |
| N | FDS | T | 0.118 | 0.003 | 6 | 3 |
| | | B | 0.095 | 0.016 | 6 | 3 |
| N | UST | T | 0.109 | 0.017 | 6 | 4 |
| | | B | 0.125 | 0.018 | 6 | 4 |
| N | VCD | T | 0.073 | 0.012 | 12 | 5 |
| | | B | 0.076 | 0.013 | 12 | 5 |
| N | WFK | T | 0.167 | 0.024 | 20 | 7 |
| | | B | 0.180 | 0.029 | 20 | 7 |
| A | FDS | T | 0.118 | 0.009 | 15 | 8 |
| | | B | 0.123 | 0.008 | 15 | 8 |
| A | UST | T | 0.114 | 0.009 | 6 | 5 |
| | | B | 0.115 | 0.017 | 6 | 5 |
| A | VCD | T | 0.078 | 0.008 | 15 | 7 |
| | | B | 0.077 | 0.007 | 15 | 7 |
| A | WFK | T | 0.090 | 0.010 | 12 | 7 |
| | | B | 0.090 | 0.013 | 12 | 7 |

[a]N = nonionic and A = anionic.

[b]FDS = Foster D. Snell, UST = U.S. Testing, VCD = vacuum cleaner dust, and WFK = Waeschereiforschung Krefeld.

[c]T = top and B = bottom.

[d]Range over which k was constant, i.e. over which the plot log (100/B) vs time was linear.

[e]Number of measurements in the linar or first-order range, in additon to log (100/B) = 0, time t = 0.

TABLE III

Reflectance Readings of Test Fabrics during Wash Cycle

| Fabric[a] | Detergent[b] | Reflectance readings | | | |
| --- | --- | --- | --- | --- | --- |
| | | $R_S$ | $R_{L,10}$[c] | $R_{L,20}$[d] | $R_{L,20}-R_S$ |
| FDS | N | 16.3 | 23.8 | 28.8 | 12.5 |
| | A | 16.4 | 32.9[e] | 47.5 | 31.1 |
| UST | N | 22.0 | 29.5 | 34.9 | 12.9 |
| | A | 21.7 | 29.0[e] | 32.4 | 10.7 |
| VCD | N | 43.4 | 54.3 | 57.8 | 14.4 |
| | A | 43.0 | 53.1[e] | 62.6 | 19.6 |
| WFK | N,T[f] | 48.3 | 71.8 | 81.1 | 32.8 |
| | N,B[f] | 43.0 | 70.7 | 79.7 | 36.7 |
| | A,T | 47.8 | 59.0[e] | 67.3 | 19.5 |
| | A,B | 42.6 | 55.0[e] | 64.7 | 22.1 |

[a]FDS = Foster D. Snell, UST = U.S. Testing, VCD = vacuum cleaner dust, and WFK = Waeschereiforschung Krefeld.

[b]N = nonionic and A = anionic.

[c]Reflectance after 10 min laundering.

[d]Reflectance after 20 min laundering.

[e]Interpolated,

[f]T = top and B = bottom.

### Rate Constants

Despite the considerable differences among the four test fabrics and between the two detergents, the eight mean first-order rate constants were relatively similar. The highest k value was a mere 2.3 times larger than the lowest.

The overall average value of k is 0.1091 $min^{-1}$. This corresponds to a 6.36-min wash period to remove one-half of the soil from the soiled fabric, and to a 21-min wash period to remove 90% of the soil.

### Effect of Nature of Detergent upon k

Only the WFK fabric, among the four test fabrics, could discriminate between the nonionic and the anionic detergent according to the kinetic criterion. The rate constant of the nonionic detergent on the WFK fabric was 1.93 times greater than that of the anionic detergent. The differences between the rate constants obtained with the two detergents on each of the other three test fabrics were small and not statistically significant.

### Effect of Nature of Test Fabric upon k

The order of effectiveness of the anionic detergent in cleansing the four test fabrics according to the four k values was FDS $\cong$ UST > WFK > VCD. For the nonionic detergent, the k values were ranked in the order WFK $\geqslant$ UST $\cong$ FDS > VCD. Rate constants obtained with the fabrics to the left of the > signs are significantly greater than those to the right. The rate constant to the left of the $\geqslant$ sign is greater than those to the right, but the difference is not statistically significant at the 5% probability level. Thus, the rate constant obtained with the nonionic detergent for the WFK fabric was larger than those for the UST and FDS fabrics, but the two differences carry no statistical significance. However, the three rate constants obtained with the nonionic detergent for the WFK, UST, and FDS fabrics were significantly greater than that for the VCD fabric.

### Comparison of Test Fabrics

The data of Table III were assembled because comparative studies of artificially soiled test fabrics are rare. The greatest increase in reflectance, both after 10 and 20 min laundering, was achieved by the nonionic detergent on the WFK fabric, followed by the anionic detergent on the FDS fabric and on the WFK fabric. The UST fabric showed the smallest increases in reflectance.

The WFK and the FDS fabrics responded quite differently to the anionic and to the nonionic detergent. The nonionic detergent cleansed the WFK fabric more extensively than did the anionic detergent, paralleling the greater k value observed with the former. On the other hand, the anionic detergent cleansed the FDS fabric more extensively than did the nonionic detergent after both 10 and 20 min laundering. This is not reflected by the two first-order rate constants for the FDS fabric. While the anionic detergent had a slightly higher k value (for the initial 15 min) than the nonionic detergent (for the initial 6 min) on the FDS fabric, the difference between these two k values is without statistical significance due to the scatter of points about the straight lines.

The WFK fabric contained over 1% of a mixture of particulate soil which consisted of 86% kaolin, 8% carbon black, and 6% iron oxides (3). Nonionic actives are known to be much more effective than anionic actives in removing particulate soil, especially clays, from cotton (6,7). The FDS fabric, on the other hand, was soiled largely with oily soil. Its particulate soil (25% carbon black, 10% oleophilic bentonite) is oleophilic and, therefore, cannot adhere well to the hydrophilic cellulose substrate. Moreover, the particles are embedded in the more abundant oily soil. The anionic active is probably a better wetting and emulsifying agent than the nonionic active, removing the oily soil more extensively and, with it, the embedded particulate soil. Alternatively, the builders may have helped the anionic active to remove the oily, plus particulate oleophilic, soil more extensively than the nonionic active, i.e. they had a greater synergistic effect upon the oily and oleophilic soils with the anionic than with the nonionic active.

ACKNOWLEDGMENTS

Experimental data on which this study is based were obtained in the Detergency Evaluation Section, The Lever Brothers Company Research Center, Edgewater, N.J. W.E. Gaffney supervised the laundry runs and optical measurements, and The Lever Brothers Company granted permission to use the data.

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[Received November 27, 1974]