

TABLE II  
 Analysis of Soaps and Detergents

Sample	Type	% Cation					
		By flame spectrophotometry			By wet methods (1)		
		Sodium	Potassium	Magnesium	Sodium	Potassium	Magnesium
A	Spray-dried detergent	23.16	0	.....	23.76	0	.....
B	Light duty liquid detergent	2.10	9.82	.....	2.51	10.01	.....
C	Heavy duty liquid detergent	2.20	6.94	.....	2.31	7.06	.....
D	Bar Soap	5.89	2.11	.....	6.00	2.17	.....
E	Soap-synthetic bar	9.58	0.04	0.03	9.61	0.05	0.03

oxygen pressure with a hydrogen pressure of 1.75 psi, which is the pressure corresponding to maximum emission for magnesium, as a parameter. See Figure 3.

At an oxygen pressure of 10 psi slight variations in the pressure would not affect the luminosity. However, it was found that a calibration curve from 0 to 13 ppm magnesium could not be prepared when the oxygen pressure was 10 psi and hydrogen pressure was 1.75 psi. When the hydrogen pressure was changed to 2.5 psi the readings of the magnesium standard became continuous and a calibration curve could be drawn. If the hydrogen pressure drops from 2.50 psi to 2.45 psi, the transmission readings will increase 0.44 scale division, which amounts to about 0.1  $\mu$ g of magnesium.

*Examples of the Determination of Sodium, Potassium, and Magnesium in Soaps and Detergents.* To illustrate the usefulness of the method, five commercial products were analyzed for sodium, potassium, and magnesium. The types of samples analyzed and the results obtained are summarized in Table II. Excellent agreement between results obtained spectrophotometrically and by standard wet methods was obtained. The procedure followed was essentially the

same in each case, except that with liquid detergents the samples were dried at 110C prior to ashing. It was found that carbon was more readily burned off when using a platinum rather than porcelain dish. Also, the residue was more easily removed from the platinum than from porcelain or vitreosil dishes.

In conclusion, the determination of sodium, potassium, and magnesium in soap by means of flame spectrophotometry is useful because of the speed and accuracy of the method. Inherent difficulties, such as determining small quantities of magnesium in the presence of large amounts of sodium, were overcome by proper selection of wavelengths and instrumental conditions.

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## Kinetic Studies of Detergency. I. Analysis of Cleaning Curves

M. C. BOURNE<sup>1</sup> and W. G. JENNINGS, Department of Food Science and Technology, University of California, Davis, California

### Abstract

The kinetics of removal of thin films of pure radioactive tristearin from a stainless-steel surface by .03 M NaOH was studied in a circulation system. The data obtained are consistent with the presence of two species of tristearin, each species being removed simultaneously by a first-order process and behaving independently of the other. The principal evidence for the existence of the two species is the excellent agreement of the experimental data with the mathematical techniques of kinetics over a wide range of experimental conditions. Rate constants for the removal of each species and the relative proportions of the two species are given for different experimental conditions. It is shown that the difference between the two species must be based on some physical factor, and possible explanations are discussed. The presence of two species gives a satisfactory explanation for hitherto unexplained results of other workers.

### Introduction

DETERGENCY, A PRACTICAL EVERYDAY OPERATION, usually involves removal of a thin film from a surface by a liquid. Although standards of efficiency are

presently high, the literature shows that our understanding of detergent processes lags far behind practice. Most detergent research at the fundamental level has been concentrated on fibers and textiles, even though the cleaning of hard surfaces is conceivably more important as directly related to the wholesomeness of food.

In most detergency studies, the time factor is held constant while other variables are studied. In this investigation of the rate of soil removal, in contrast, the main variable under consideration was the time factor.

Rhodes and Brainard (31) pointed out the need for an index of detergent power that would be based on experimental data. They found that log-log plots of detergency vs. time were linear, and suggested that the slopes would be some index of detergent power. Bacon and Smith (4) stressed the importance of mechanical action in detergency and the effect of detergents in reducing the work requirement. They varied the force factor of their mechanical washing device 48-fold and found that their data fitted the equation

$$S = K (CFT)^n$$

where  $S$  = soil removed,  $C$  = detergent concentration,  $F$  = force,  $T$  = time,  $K$  and  $n$  are constants, and  $n$  is between 0 and 1.

<sup>1</sup> Present address: Dept. of Food Science and Technology, New York State Agricultural Experiment Station, Cornell University, Geneva, N.Y.

Pederson (28) studied the time factor in cleaning fabrics and found that his data fitted the equation

$$V = k_1 + k_2 \log t$$

where  $V$  = visual cleanness,  $t$  = time, and  $k_1$  and  $k_2$  are constants. Since, however, the relation between weight of soil and visual cleanness is not linear, Pederson's equation is of limited usefulness.

Vaughn et al. (37) found in multiple wash tests that the amount of soil removed per wash continually decreases with increasing number of washes. They concluded that "the rate of soil removal is a function of the removable soil content" and set up the equation

$$-d(c - s)/dt = f(c - s)$$

where  $s$  = amount of soil removed,  $c$  = removable soil content, and  $t$  = time. They integrated this equation to obtain:

$$s = c - (c/e^{Kt})$$

By trial and error they selected a value for  $K$  that made the function a linear plot. They showed that  $K$  has a physical significance as the "specific soil removal rate," that larger values of  $K$  indicate more rapid detergent action, and that  $K$  is independent of time and soil content, but would be expected to vary with detergent concentration, kind of detergent, temperature, type of soil, and degree of mechanical action. This work appears to be the first attempt to study the kinetics of detergency and reduce it to mathematical terms, but its accuracy suffers from the trial-and-error method of evaluating  $K$ .

Utermohlen and Wallace (34) rearranged the differential equation of Vaughn et al. and upon integration obtained:

$$\log(C - s) = -ft + R$$

where  $C$  = removable soil content,  $s$  = amount of soil removed,  $f$  = specific soil removal rate,  $t$  = time,  $R$  = constant.

By graphical methods they were able to obtain numerical values for  $f$  and  $R$ . Because a portion of the soil proved irremovable, they determined the relative amounts of "removable soil" and "irremovable soil," but apparently were not able to separate the two soils in their graphs and proceeded no further with their kinetic treatment of the data.

Patrick and Payne (27), studying the desorption of stearic acid from a metal surface by toluene, found that the desorption followed the classical decay equation

$$\phi = \phi E (1 - e^{-Kt})$$

where  $\phi$  = count/min in toluene,  $\phi E$  = equilibrium count/min,  $K$  = rate constant of desorption,  $t$  = time.

Jennings (16) showed that the removal of milk solids from stainless steel by NaOH solutions in a circulation system could be treated mathematically in the same way as the kinetics of a chemical reaction. His data showed, with a highly significant correlation, that the process is kinetically first-order in soil (milk solids) and first-order in detergent concentration (NaOH), and he used the equation:

$$-dS/dt = K(S)(OH^-)$$

where  $S$  = soil as per cent of original deposit,  $(OH^-)$  = hydroxide ion concentration,  $K$  = molar-velocity constant,  $t$  = time. Jennings showed that  $K$  has an Arrhenius temperature-dependence, and he pointed out that the determination of  $K$  values could be used to evaluate precisely the reaction of specific detergents

with specific soils, and compatibility and synergism with mixtures of detergents.

There are objections to Jennings' use of chemical kinetics for a physical process occurring in a two-phase system. Because the study reported here makes extensive use of the kinetic treatment developed by Jennings, it is proper to consider these objections at this time.

The first objection is to the use of chemical kinetics for a process that is not a chemical reaction. Here, the use of the word "chemical" is misleading. A first-order kinetic process is one in which the rate of change of a substance is proportional to the amount present of that substance. Although the mathematics and theory of kinetics have been developed by chemists, there are many processes that empirically follow first-order kinetics although not chemical in nature. Examples include: radioactive decay; the growth of populations when not restricted; the death of bacteria at lethal temperatures; the desorption of stearic acid from a metal surface (27); the diffusion of color, ascorbic acid, and total acid in frozen syrup-packed strawberries (8); the rate of uptake of a gas at a sparsely covered surface (20). It appears that first-order processes represent a widespread natural law. In this study the expression "first order" is used when the rate of change in the amount of tristearin is proportional to the amount of tristearin present. The word "chemical" is deliberately omitted because the processes involved are not true chemical reactions.

The second objection to Jennings' use of kinetics is that his system is heterogeneous, involving reaction between a solid phase and a liquid phase. Nevertheless, the good fit of Jennings' data to first-order kinetics supports the use of his methods. Vaughn et al. (37), and Utermohlen and Wallace (34), found a first-order process in the detergent systems they studied, although they were hampered with difficulties as noted above. Matantsev (24) found the removal from stainless steel of scale films 4-5  $\mu$  thick by nitric acid to be kinetically first-order. This is an example of a true chemical reaction following first-order kinetics in a heterogeneous two-phase system.

## Experimental

### Test Apparatus

The cleaning system consists of an insulated stainless-steel tank containing 50 gal of .03  $M$  NaOH (A.R.) in distilled water. A centrifugal pump, operating completely flooded, draws this solution from the base of the tank and circulates it through the test section and back to the tank. The test section was a 24 in. length of glass pipe, 1.37 in. I.D., mounted vertically on the outlet side of the pump. Flow through the test section was regulated with a 1½ in. valve between the test section and the pump outlet. In operation, the NaOH solution interface moves across the soiled strips uniformly and reproducibly. A 1½ in. pipe is connected to the upper end of the test section and returns the solution beneath the liquid surface in the tank. A quick-action snap clamp is placed in the line just above the glass pipe to allow the pipe to be opened for insertion and removal of the test strips. Small bars, diametrically placed and welded just below and above the glass test section, serve as supports for the test strip. A quick-acting valve in the highest point of the pipe permits the test section to be drained quickly and with little or no turbulence. This minimizes any additional soaking of the test strip, and permits its recovery as it

existed at the end of the cleaning period. Temperatures were regulated to within  $\pm 0.2^\circ\text{C}$  by means of a coil of  $\frac{3}{4}$  in. copper tubing located in the bottom of the tank and connected to steam and water lines.

In operation, NaOH solution is pumped through the apparatus at the required flow rate and temperature, and test strip is preheated to this temperature in a hot-air oven. With the pump off, the test section is drained and opened. The preheated soiled stainless-steel test strip is quickly inserted, the test section is closed, and the solution is pumped past the test strip for the required time. With the pump off, the pipe is again quickly drained, the test strip removed and allowed to drain dry, and its activity counted. Tristearin removed from the thin soil film is carried to the solution tank, where it floats on the surface, eliminating the possibility of redeposition on the strip, or of an equilibrium between the removed and unremoved tristearin. As discussed below, the rate of hydrolysis of tristearin is very low under these conditions. If displaced tristearin had not been removed by skimming, and if the total quantity removed had hydrolyzed, the concentrations of sodium stearate and glycerol would have reached 7 and  $2.4 \times 10^{-5}$  M, respectively, in the most extreme case. Because the reservoir solution was changed frequently, it is doubtful that even these concentrations were ever achieved.

#### Test Strips

Stainless steel was selected as the hard surface because of its corrosion resistance, and because it is one of the hard surfaces most frequently cleaned in practice. Test strips of  $3.6 \times 32$  cm were cut from a single new sheet of type 302 annealed 22-gauge stainless steel with a 2B finish.

Two small holes were drilled in each end of each test strip, for fastening to the counting apparatus, and to accommodate removable guide pins that located the strip centrally in the test section during a run. At high rates of flow, a mild steel bar,  $\frac{1}{4} \times \frac{3}{4}$  in.  $\times$  ca. 30 in. was bolted to the back of the test strip to prevent twisting. These flow rates were corrected for the cross-sectional area of the bar. A rigorous procedure, based on that of Anderson et al. (2), was used to prepare test strips. Strips were first immersed in  $\text{CCl}_4$  at room temperature for 5–10 min to remove the residual tristearin from previous runs. This was followed by two 1 min immersions in hot, undiluted nonionic surfactant (Igepal CO-630; 100% active), interspersed and followed by thorough rinses with 95% ethanol. Strips were then twice vapor-washed by suspension in a 6-L Erlenmeyer flask containing ca. 200 cc of boiling  $\text{CCl}_4$ , immersed 1 min in 95–98°C 0.2% HCl, and washed with cold distilled water. They were then immersed 1 min in 95–98°C 0.5% NaOH, repeatedly rinsed with boiling distilled water, and allowed to drain dry. They were then immersed again in the vapor of boiling  $\text{CCl}_4$ , and the tristearin solution was immediately applied to the surface.

The effectiveness of the method of cleaning is shown by following the decrease in radioactivity of a strip soiled with radioactive tristearin:

Treatment	Subsequent counts (10 min)
freshly soiled strip	100,000 (ca.)
immersion in $\text{CCl}_4$ (5 min)	3,348
immersion in surfactant ( $2 \times 1$ min)	967
immersion in $\text{CCl}_4$ vapor ( $2 \times$ )	893
immersion in HCl (1 min)	730
immersion in NaOH (1 min)	296
immersion in $\text{CCl}_4$ vapor	311

The residual activity (ca. 30 count/min), being less than the statistical counting error, was ignored. It probably represents a small amount of tristearin either adsorbed on very strongly attractive sites, or mechanically held within the structure of the metal surface.

#### Soil Films

Pure tristearin (Eastman Organic Chemicals) was selected as a model soil because it is a stable saturated fat and its chemical and physical properties are well-known. Ten per cent of  $\text{C}^{14}$ -labelled tristearin (Tracerlab, Inc. 1.37 mc/mM) was added as a tracer. A total of 1 ml of  $\text{CCl}_4$ , containing 5 mg tristearin was applied uniformly to the central 27 cm of a test strip in five applications of 0.2 ml each (representing 25–30 molecular thicknesses). The solution was stroked over the surface from a 0.2-ml pipet, and the strip was allowed to dry between each application. After soiling, the strips were baked for 10 min at  $125^\circ\text{C}$  in a hot-air oven to melt the tristearin. The strips were removed and, while still hot, a piece of polyethylene film, wrapped around a short length of rubber tubing, was wiped across the surface to help ensure an even film. All cleaning treatments on the strips were completed within 24 hr of soiling to avoid the aging effect reported in an earlier work (5).

Preliminary experiments in which the loss of radioactivity was measured at zero flow rate for many hours at several temperatures showed that hydrolysis of the tristearin by the NaOH proceeded extremely slowly, compared with the physical removal of tristearin as complete tristearin molecules, and that it could be safely ignored for the purpose of these determinations. (See discussion of purity of tristearin below.) Lachampt et al. (19) studied the saponification of emulsified triglycerides and found that fine emulsions required some minutes to be saponified in 35% NaOH at  $70^\circ\text{C}$ . In this study .03 M (0.12%) NaOH was used.

#### Determination of Radioactivities

The strip was bolted, face up, to a brass plate  $45 \times 5.2$  cm. The brass plate was placed in the top slot of a tracerlab SCIOA sample holder and tube mount. A thin-window G.M. tube ( $1.4 \text{ mg/cm}^2$ ) was placed in the tube mount. A small synchronous electric motor, mounted on the side of the sample holder and fitted with two small gears, was used to drive the brass plate forward by engaging the two track gears, which were soldered to the underside of the brass plate. In this way, the 27 cm of soiled test strip was scanned by the G.M. tube, with constant geometry, over a 10-min period. The counts were recorded on a Tracerlab 1000 Scaler. The 10-min counts, corrected for coincidence and background, were taken to be a measure of the quantity of tristearin on a strip at a given time. The level of activity was adjusted to give a 10-min count of ca. 100,000 with an initial soil load of 5 mg tristearin. Replicate counting of freshly soiled and cleaned strips indicated this technique was a highly reliable method of measurement.

#### Results and Discussion

A typical cleaning curve is shown in Figure 1, where log tristearin (measured as counts per 10 min) is plotted against the number of 10 sec washing treatments. If the removal of the tristearin followed first-order kinetics, this semi-logarithmic plot should be linear from zero washes. Instead, it is curved for the

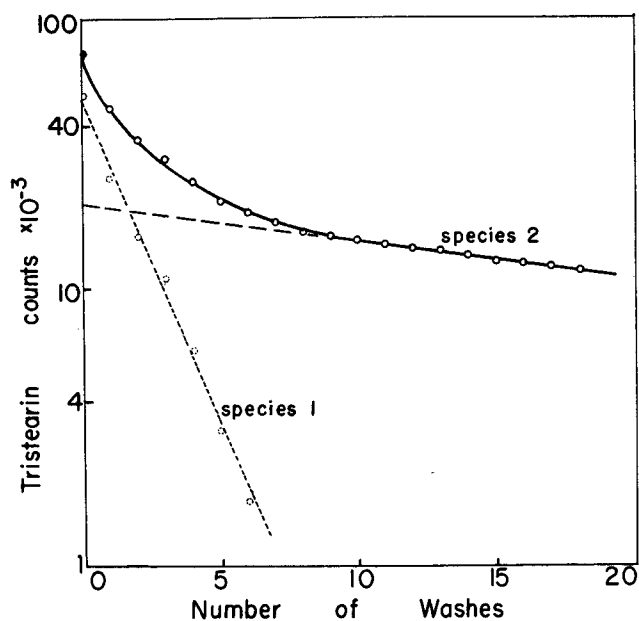


FIG. 1. Typical cleaning curve. 0.03 M NaOH, 65C, 10 sec cleaning treatments. Flow, 2 lb/sec.

first 7 washes and linear from the 8th to the 18th washes. In some experiments as many as 40 washes were given, and in every case the cleaning curve remained linear, once linearity was established. The linear portion of the graph cannot be attributed to a monomolecular layer of tristearin, because the soil remaining after the 18th wash (Fig. 1) represents approximately three molecular thicknesses, even when the rugosity of the steel surface is taken into account. Work of O'Connor and Uhlig (26) indicated that stainless steel of this type has a rugosity of ca. 4.

The shape of the cleaning curve is similar to that obtained for the sum of two independent first-order processes occurring at different rates (e.g., the overall decay of a mixture of two radioisotopes, one with a much longer half life than that of the other). When the linear portion of the cleaning curve is extrapolated back to zero washes, and the extrapolated line

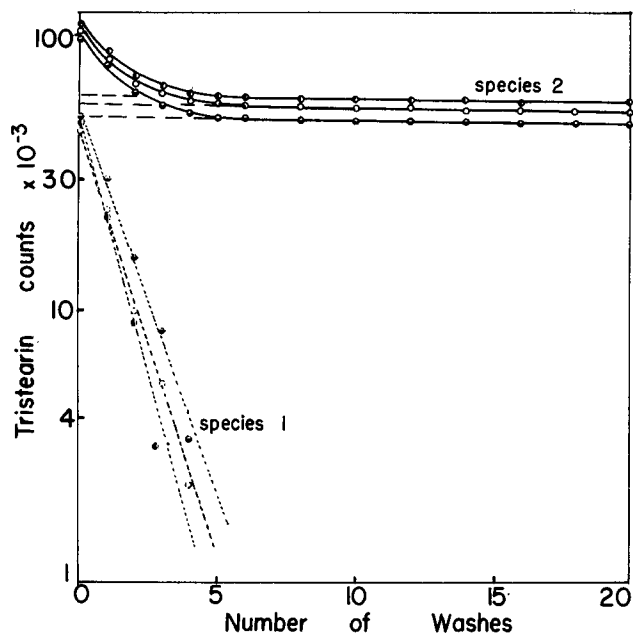


FIG. 2. Cleaning of three separate strips, given identical treatment. 0.03 M NaOH, 55C, 10 sec cleaning treatments. Flow, 0.2 lb/sec.

TABLE I  
Reproducibility of Data

Experiment	Rate constant $k_1$	Rate constant $k_2$	Species 2 (%)
1.....	4.7	.025	55
2.....	5.5	.025	56
3.....	4.0	.019	49

Conditions: .03M NaOH, 55C, 0.2/sec flow rate.

subtracted from the curve, the result is a second straight line with a much steeper slope. The line marked species 1 in Figure 1 was obtained in this way.

This result could be explained by assuming that two species of tristearin are present (herein called species 1 and species 2), that each is removed from the surface independently and simultaneously by a first-order process, and that species 1 is removed much faster than species 2. Using kinetic theory:

$$-d(A)/dt = k_1(A) \text{ and } -d(B)/dt = k_2(B)$$

where  $(A)$  and  $(B)$  are respectively the amounts of species 1 and 2 at any given time,  $k_1$  and  $k_2$  are the rate constants,  $k_1 > k_2$ ,  $t$  is the number of washes (constant time per wash).

Rearranging and integrating gives:

$$\ln(A) = \ln(A_0) - k_1 t \text{ and } \ln(B) = \ln(B_0) - k_2 t$$

where  $(A_0)$  and  $(B_0)$  are the amounts of species 1 and 2 at zero time. The total amount of tristearin present at a given time =  $(A) + (B)$ .

The experimental cleaning curve is described with a high degree of precision by the sum of the values of  $(A)$  and  $(B)$  for each value of  $t$ . From Figure 1, for example,  $A_0$ ,  $B_0$ ,  $k_1$ ,  $k_2$  can be evaluated, giving the equations:

$$\ln(A) = 10.88 - 0.574t \text{ and } \ln(B) = 9.99 - 0.0337t$$

It should be pointed out that the close agreement between the experimental cleaning curve and the sum of two independent simultaneous first-order processes is entirely empirical. No theory is yet in existence that would predict a relationship of this kind.

All the cleaning curves obtained in this study can be reduced to the sum of two semi-log plots as described above, a fact strongly suggesting that two species of tristearin are present. Both species are measured by radioactivity, but the loss of activity is not due to radiodecay, since the label in both instances is  $C^{14}$ , which has a half life of ca. 5,600 years. Species 1 is removed so rapidly that in 7 washes it is completely removed for all practical purposes, with the cleaning curve thereafter representing the removal of species 2 only.

This kinetic evidence for two species suggests the presence of an impurity in the tristearin. An infrared spectrum of the tristearin showed no evidence of impurity; specifically, the absence of monostearin, distearin, stearic acid, and glycerol were shown by the absence of a hydroxyl peak (note that species 1 accounts for ca. 30% of the sample). To test further for impurity, several soiled strips were cleaned until the linear portion of the cleaning curve was reached, the tristearin was removed from the strips by  $CCl_4$ , the  $CCl_4$  solution was concentrated, and a sufficient amount was applied to one strip to make a normal soil load. If the two species of soil were chemically different, this strip should have shown a linear cleaning relationship starting from zero washes, since species 1 would have been completely removed. Upon cleaning this strip, the usual cleaning curve was obtained, demonstrating that the two species do not arise from

TABLE II

Effect of Initial Soil Load on Rate Constants and Proportion of Species 2

Initial soil load (mg)	$k_1$	$k_2$	Species 2 %
1	3.1	.040	55
2.5	3.4	.048	58
5	3.1	.034	40
10	3.5	.039	33

Conditions: .03M NaOH, 65C, 0.2 lb/sec flow rate;  $k_1$  and  $k_2$  are the rate constants for species 1 and species 2 respectively.

an impurity. Other experiments have shown that the proportion of species 2 ranges from ca. 25% up to 100% of the total, although all tests were run with the same batch of pure tristearin. This leads to the conclusion that the two species arise from some kind of physical difference.

A possible explanation for the existence of two species is the polymorphism of tristearin. Ferguson and Lutton (6) showed that solid tristearin exists in three polymorphic forms, a  $\beta$  form (monoclinic, mp 71.5C), an  $\alpha$  form (orthorhombic, mp 65C) and a  $\gamma$  form (a glass mp 54.5C). Of these, the  $\beta$  form is thermodynamically the most stable; the  $\alpha$  and  $\gamma$  forms may change into the  $\beta$  form, but the  $\beta$  form does not convert into  $\alpha$  or  $\gamma$ . It is possible that in the preparation of the soiled strip the tristearin is formed as the  $\alpha$  or  $\gamma$  form and partly converts to the  $\beta$  form before cleaning begins. This possibility must be excluded because the two species appear in all cleaning curves conducted above the melting point of the  $\beta$  form.

Figure 2 shows the result of three experiments, run under identical conditions. The rate constants from Figure 2 are set out in Table I. Some of the variables in this model system are not fully controlled; in particular, the preparation of the thin tristearin film leaves something to be desired as far as uniformity is concerned. In addition, other unrecognized variables may be present. Taking this into consideration, the rate constants  $k_1$  and  $k_2$  may be considered as reproducible within the limits of experimental error.

Figure 3 shows the curves obtained with initial soil loads varied over a tenfold range, together with the derived species-1 plots. The data obtained from these plots are set out in Table II. The constancy of these rates within the limits of experimental error over a tenfold range of initial soil load establishes the validity of the kinetic treatment used in this study, and also the existence of the two species. The effect of initial soil load on the proportion of species 2 is also shown in Table II.

The data show no trend relating the proportion of species 2 to the flow rate of the detergent solution. Other studies (reported in Part II) show that the proportion of species 2 increases with age of films and decreases with rising temperature.

Our knowledge of the two species is summarized below.

- 1) There is good empirical evidence for the existence of two different species of tristearin, species 1 and species 2. There is no evidence for a graduated change in properties from species 1 to species 2.
- 2) The two species are chemically identical.
- 3) The two species are not polymorphs.
- 4) Species 2 appears to be more closely associated with the surface than species 1; the amount of species 2 is variable but is more or less independent of the initial soil load; it is not a monomolecular layer and it is removed simultaneously with species 1.

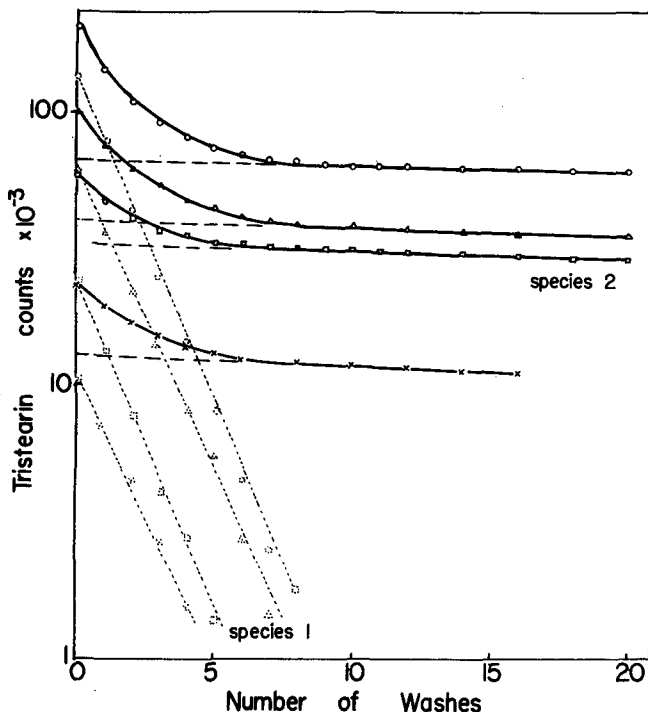


FIG. 3. Effect of initial soil load on cleaning. 0.03 M NaOH, 65C, 10 sec cleaning treatments. Flow, 0.2 lb/sec.

- 5) The proportion of species 2 decreases from 100% of the total soil load at 35C to ca. 25% at 90C (at constant soil load).
- 6) The proportion of species 2 increases with age (at constant soil load).
- 7) Variation of the flow-rate over a 110-fold range does not affect the proportion of species 2.
- 8) Species 2 is removed from 10-100 times as slowly as species 1; evidently it is bound more strongly than species 1.
- 9) The amount of species 2 can be measured, but the scatter shows that its proportion is not under experimental control.

When the work of other investigators is examined in

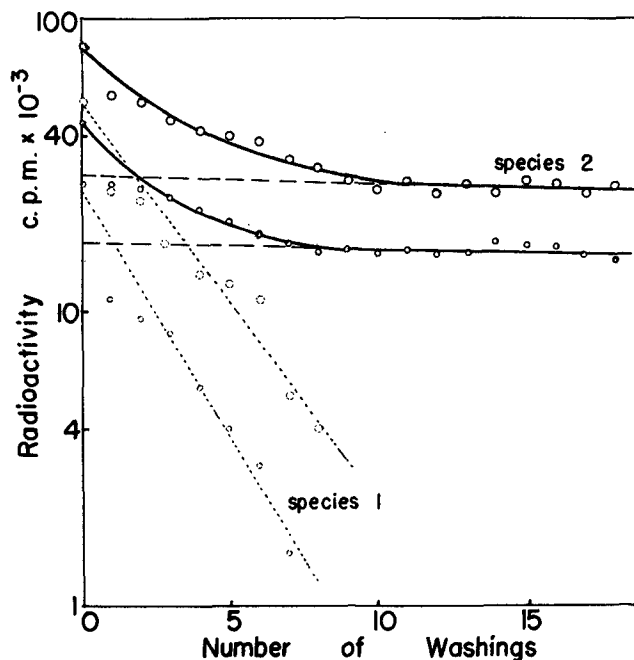


FIG. 4. Cleaning curve for skim milk solids on stainless steel, showing two soil species. From data of Pflug et al. (29).

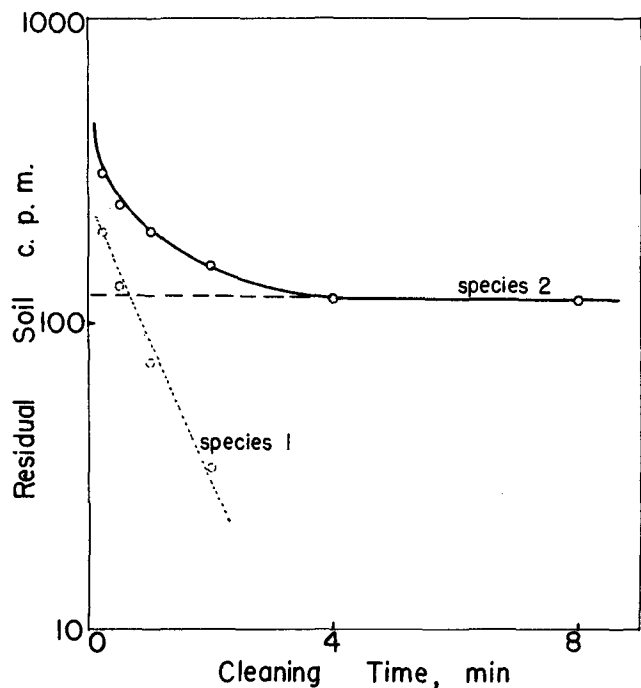


FIG. 5. Electrocleaning curve for stearic acid on steel showing two species of soil. From data of Hensley (14).

this light, it appears that this is not an isolated phenomenon restricted to tristearin, but that many soils exist in two forms, although the existence of two distinct species as such does not appear to have been recognized explicitly. Pflug et al. (29) studied the removal of dried skim milk films from stainless steel with a commercial detergent mixture. When the logarithm of the milk solids remaining on the steel surface was plotted vs. the number of washings, they obtained curves that became linear after ca. 10 washings. These curves can be shown to be the sum of two first-order processes acting on two soil species by the technique of extrapolation of the linear part of the curve and subtraction from the curved portion. Figure 4, drawn from the data of Figure 6 in the paper by Pflug et al., shows a reasonable fit, considering that the experiment was not designed for highly accurate results.

Hensley (13) studied the removal of a thin film of stearic acid from a metal surface by electrocleaning in a sodium metasilicate bath. Figure 5, derived from his data, shows the presence of two species in his system.

A number of other workers showed cleaning curves as a function of time, and in each case the curves follow the same general shape shown in Figure 1. These papers do not show enough points to derive a slope for species 1 soil, but the curves suggest that the cleaning process could be represented by the sum of two linear semi-log plots; one plot, with a steep slope, representing species 1; the other, with a lesser slope, representing species 2. Examples of such curves are given by Hensley et al. (14), who studied the removal of stearic acid from steel in hot unagitated solutions of NaOH, Na metasilicate,  $\text{Na}_3\text{PO}_4$ , tetrasodium pyrophosphate,  $\text{Na}_2\text{CO}_3$ , and Kreelon; Anderson et al. (3), who studied the removal of tristearin from frosted glass using sodium tripolyphosphate in a modified Terg-O-Tometer; Utermohlen and Ryan (34) and Utermohlen and Wallace (35), who studied mixtures of mineral oil, edible fat, lampblack, and black ferric oxide on cotton cloth

using soap and detergents in a Launder-Ometer; Romero and Stern (32) who studied the removal of stearic acid from stainless steel and nickel using a nonionic commercial detergent in an ultrasonic cleaning machine; Mankowich (22) who removed triolein and oleic acid from cold-rolled steel with several nonionic and anionic detergents by immersion without agitation in hot solutions; Rhodes and Brainard (31), who used soiled cotton and soap solutions; Bacon and Smith (4), who used a soil mixture on cotton cloth, and commercial soap and 3 different anionic detergents in a Launder-Ometer; Jennings (16), who studied the removal of dried whole-milk films on stainless steel, using NaOH solutions in a circulation cleaning apparatus; and Wagg and Britt (38), who studied the removal of  $\text{C}^{14}$ -labelled stearic acid from chopped cotton fibers, using various detergents.

The concept of two distinct soil species agrees with the findings of other workers: Harris (9), who commented on the slow rate of cleaning at low soil levels; Vaeck et al. (36), who studied the cleaning of artificially soiled fibers and divided their soil into two classes, a "coarse" fraction that is removed completely or nearly so, and a "fine" fraction that is removed slowly; Jones (18), who noted that it is contrary to experience for all dirt to be eventually removed from a surface; Ackley (1), who wrote that "It is entirely possible that the forces responsible for holding the last small amount of soil to the fabric may be somewhat different from those holding the more easily removed superficial soil"; Lawrence (21), who noted the persistent adhesion of soil responsible for the graying of whites; Fineman and Kline (7), who found a layer of irremovable soil on the surface of pickled steel; and Norris and Ruchhoft (25), who studied the removal of oily soil from glass and found that a higher proportion of soil was removed when the initial soil load was increased. Powe (30) made a special study of the soil tenaciously bound to cotton and found that it consisted of clay minerals, 0.02-1 in. diameter, mixed with a large amount of organic material. Powe concluded that the tenaciously bound soil is a surface phenomenon since the particulate matter did not penetrate the fibers.

These results cover a wide range of soils, surfaces, detergents, and conditions of cleaning; yet all are consistent with the existence of two species of soil.

Many workers show that increasing detergent concentration increases detergency up to some limit that is below 100% (e.g. 10,11,12,17,22). It is possible that such detergency concentration curves represent the increasing removal of species 1 with increasing detergent concentration, and that species 2 is relatively unaffected by increasing detergent concentration.

One of the problems in practical detergency is the gradual accumulation of a residual soil layer with repeated soilings and washings (15,23). It is possible that species 1 soil is completely removed in these cases, but that little of species 2 is removed, in which case species 2 soil would accumulate with each soiling-cleaning cycle and cause the build-up of a more resistant soil.

The nature of species 1 is fairly easy to visualize as the soil that is removed in most detergency studies and can be considered as "normal" soil. The nature of species 2 is difficult to understand; most suggestions that come to mind fail to account for all aspects of its behavior. It is possible that species 2 may be

occluded or semi-occluded at irregularities in the surface, but this is not a satisfactory explanation for points 5, 6, and 9 in the summary above. Further, Shuttleworth and Jones (33) used an electron microscope to study the retention of small-particle-size carbon black on fibers and concluded that micro-occlusion is not the dominant mechanism of soil retention on fibers. Another possibility is that species 2 is a strongly adsorbed multimolecular layer on the surface, but it is difficult to imagine this adsorption being effective through many molecular thicknesses of tristearin. Fineman and Kline (7), from study of the role of substrate in detergency, suggested that the electrical characteristics of the substrate influence the mode of removal of the soil, and that with a steel substrate these forces extend to the outermost soil layer. It is possible that some kind of long-range force of this kind is responsible for the difference between species 1 and species 2. It has long been known that thin films often exhibit extraordinarily high mechanical strength. It is possible that species 2 may be related in some way to the same factors that are responsible for the high mechanical strength of thin films. At present, however, it is not possible to draw definite conclusions concerning the nature of species 2, although the presence of species 2 in soil films must become an important consideration in the interpretation of detergency tests.

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## Kinetic Studies of Detergency. II. Effect of Age, Temperature, and Cleaning Time on Rates of Soil Removal

M. C. BOURNE<sup>1</sup> and W. G. JENNINGS, Department of Food Science and Technology, University of California, Davis, California

## Abstract

The effects of variation in temperature, flow rate, cleaning time, and age were studied in a model circulation system. The results are recorded as changes in the rate constants  $k_1$  and  $k_2$  and changes in the relative proportions of the two soil species. The removal of tristearin in this simple system was found to proceed by two independent mechanisms, acting simultaneously. The first, named the "flow mechanism," is dependent on time, and its rate increases with flow rate. The second, which the authors term the "Duprè mechanism," is not dependent upon time and arises from the air-detergent interface that moves over the surface. The Duprè effect is independent of flow rate at all rates of flow. In most of the experiments the Duprè mechanism accounted for about 90% of the removal of tristearin. A comparison is made between the removal of mono-

molecular films and thin polymolecular films. It is shown that the empirical finding of apparently simple first-order kinetics is not inconsistent with the complex processes that remove tristearin from the surface.

## Introduction

A MAJOR OBSTACLE in detergent testing and detergency research is the frequently poor reproducibility, and sometimes contradictory results, obtained from detergency tests, as emphasized by Weatherburn and Bayley (17). This variability suggests that one or more uncontrolled factors are present.

In the first paper of this two-part presentation, the authors showed that the chemically pure soil used in a model circulation cleaning system consisted of two soil species independently and simultaneously removed at two different rate constants,  $k_1$  and  $k_2$ . It therefore seemed appropriate to restudy some of the variables in detergency, and see how they affected the rate constants,  $k_1$  and  $k_2$ , and the relative propor-

<sup>1</sup> Present address: Dept. of Food Science and Technology, New York State Agricultural Experiment Station, Cornell University, Geneva, N. Y.