

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.

## ACKNOWLEDGMENT

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

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## 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-

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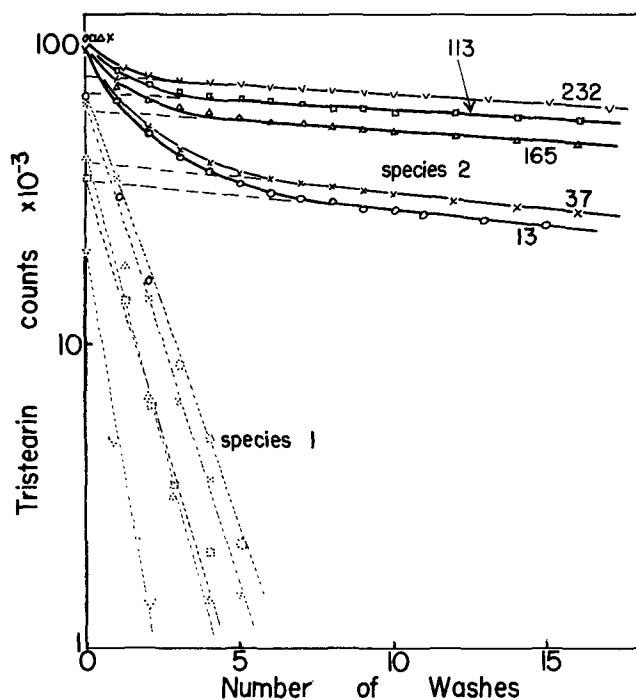


FIG. 1. Aging effect. Cleaning curves obtained 13, 37, 113, 165, and 232 hr after soiling. 0.03M NaOH, 65C, 10 sec cleaning treatments. Flow, 2 lb/sec.

tions of the two species present in the soil film. It seems logical that a study of each of these three variables could lead to more consistent results than studies that measure only overall detergency.

### Experimental

The experimental procedure was as described in Part I (detergent, .03M NaOH; soil, pure tristearin; surface, stainless steel) with the exceptions: a) in the aging studies the films were prepared as usual and allowed to age at room temperature for periods longer than 24 hr before cleaning treatments began; b) pure labelled tristearin was used without dilution with inactive tristearin in the studies with monomolecular layers, the soil load was reduced to 2 mg, and the soiled strips were given four 5-min immersions in  $\text{CCl}_4$  in order to remove all but the tightly held monomolecular layer (2).

### Results and Discussion

#### Effect of Age

It was observed in an earlier study (4) that aged films of tristearin were removed more slowly than fresh ones. A restudy of this aspect gave the results shown in Figure 1. It can be seen that each cleaning curve can be broken down into the sum of two semilog plots; the rate constants and proportions of species 2 obtained in this way are set out in Table I.

The dominant change in an aging film is an increase in the amount of species 2 and, since this is the slowly removed species, the overall rate of soil removal de-

TABLE I  
Effect of Age on Rate Constants and Species 2

Aging period (hr)	$k_1$	$k_2$	Species 2 (%)
13.....	3.9	.15	35
37.....	4.5	.14	39
113.....	5.0	.08	65
165.....	5.3	.10	58
232.....	8.3	.08	80

Conditions: .03M NaOH, 65C, 2.0 lb/sec flow rate.

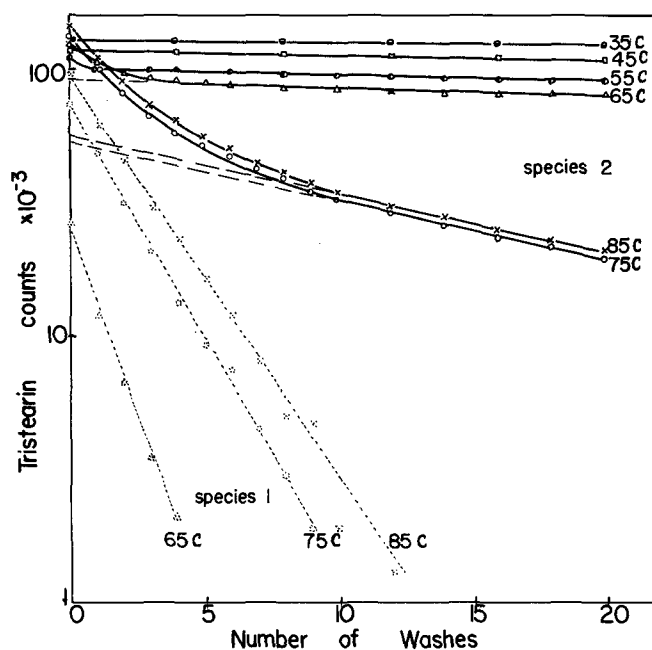


FIG. 2. Typical cleaning curves of various temperatures. 0.03M NaOH, 10 sec cleaning treatments. Flow, 0.8 lb/sec.

creases with age of the film. There is also a trend for the rate constant  $k_1$  to increase with age, and for rate constant  $k_2$  to decrease; but the increase in  $k_1$  is more than offset by the declining proportion of species 1. In a fresh film, species 1 represents ca. 65% of the soil load. After 232 hr  $k_1$  has doubled, but the amount of species 1 has declined to 20% of the soil load.

This aging effect appears to be independent of the state of the tristearin. In one experiment a strip was soiled but not baked immediately. This strip was first aged 5½ days, then baked (melted), and cleaned without further delay. This strip showed a marked increase in the amount of species 2; in overall cleaning it behaved the same as a strip that was aged 5½ days after baking. Evidently, the conversion from species 1 to species 2 is not affected by the melting and resolidifying of the tristearin.

An aging phenomenon appears to be of general occurrence. Anderson et al. (3), in studying the removal of tristearin from frosted glass, mentioned an aging effect; they suggested that it was due to a layer of moisture on their aged discs. Utermohlen and Wallace (15) studied the aging effect in mixtures of mineral oil, edible oils and fats, and lampblack and black ferric oxide, on cotton in soap solutions. They attributed aging effects to the presence of moisture and polymerization of unsaturated oils. Durham (5) commented on the well-known "aging factor" and suggested that it may be due to the slow penetration of the oil into the small capillaries of the textile fibers; once the oil has penetrated it becomes difficult to remove. In discussing the aging of sols, Overbeek (12) considered the mechanisms involved included partial flocculation, recrystallization, growth of large particles, and cementing or bridging together of particles. It is unlikely that any of the effects suggested by those workers applies to the model system being used in this study; tristearin is a fully saturated fat and does not polymerize, and stainless steel does not swell in water, nor does it have capillaries, as does cotton. It is possible that an increase in the proportion of species 2 soil is at least a partial explanation for the aging phenomenon found in other systems.

TABLE II  
% Species 2 vs. Temperature

Temp C	No of measurements	% Species 2 (mean)	Standard deviation
35.....	4	100	0
45.....	5	99.6	.07
50.....	1	100	.....
55.....	9	77	17.5
65.....	31	65	19.3
75.....	7	35	6.9
80.....	5	31	4.9
85.....	5	32	2.3
90.....	6	27	5.2

Conditions: .03M NaOH, 10 sec cleaning treatments, constant soil load, various flow rates.

#### Effect of Temperature

Figure 2 shows a set of cleaning curves obtained at different temperatures with other variables (initial soil load, detergent concentration, flow rate, cleaning time) held constant. The curves obtained at 80C and 90C have been omitted to avoid overcrowding the graph; they are similar to the 85C curve. The curves for 35C and 45C are linear from zero washes and have a low slope, indicating that the soil is 100% in the species 2 form. The 45C curve has a slope approximately double that at 35C, showing that the soil removal rate at 45C is almost double that at 35C. The slope (and rate constant) for species 1 soil cannot be obtained, since species 1 is absent. It should be noted that the experiments conducted at 35C and 45C removed so little soil that a linear plot of tristearin vs. number of cleaning treatments would give just as good a fit to the data as the semi-log plot. Taken alone, the 35C and 45C curves give no reason to postulate the existence of two species of soil or of first order processes. The existence of two species of soil and of first order processes is established by the cleaning curves obtained at 65C and higher. The cleaning curves at 35C and 45C are plotted on a semi-log graph to be consistent with the higher temperature curves.

At 55C a small curve appears. The slope for species 2 and the proportions of species 1 and 2 can be obtained; but the slope for species 1 cannot be obtained because the points are insufficient for construction of a line. In some cases there are sufficient points to obtain a rough estimate of the slope but insufficient points to obtain any accuracy. At 65C the curve is larger and the graph becomes linear by the 6th washing treatment. The rate constants  $k_1$  and  $k_2$  can be obtained from the slopes of the two lines, and the relative proportions of species 1 and 2 can be found. The rate constant  $k_1$  is ca. 100 times as great as the rate constant  $k_2$  at 55C. At 75C and 85C the curve becomes even more pronounced, the slope for species 2 is noticeably steeper than at 65C, but the slope for species 1 is not as steep as at 65C. The proportion of species 2 soil has declined considerably.

The relationship between the proportions of species 2 and temperature is shown in Figure 3 and tabulated in Table II. It can be seen that the species 2 constitutes 100% of the soil load at 35C, passes through a steep transition between 55C and 70C, and finally reaches about 25% of the soil load at 90C.

It is interesting that the standard deviation is small at both ends of the temperature range but becomes large at intermediate temperatures. It seems that some uncontrolled factor is involved in the large deviations at 65C and 55C, although this may be partly due to the number of measurements at these temperatures. The low mean values and the small standard deviations for species 2 for liquid tristearin contrast

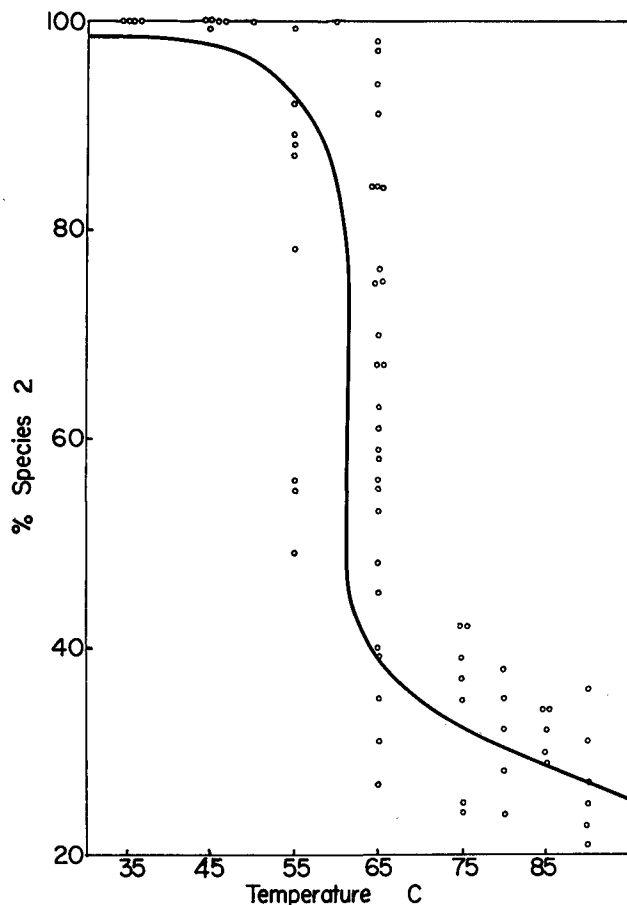


FIG. 3. Per cent species 2 vs. temperature. 0.03M NaOH, 10 sec cleaning treatments. Constant soil load, various flow rates.

with the higher mean values and large standard deviations for solid tristearin just below the melting point. This change could be related in some way to the melting of the tristearin.

Figure 4 plots  $k_1$  vs. temperature. No quantitative results can be obtained from this graph, because of the scatter in the values of  $k_1$  at high temperature and the uncertainty of the values of  $k_1$  for low temperature, due to the small amount of species 1 present (Fig. 2), but two trends are apparent. For solid tristearin,  $k_1$  is inversely related to the temperature and is roughly halved for each 10C rise in temperature. For liquid tristearin,  $k_1$  is only slightly temperature-sensitive, if at all.

A plot of  $k_2$  vs. temperature (Fig. 5) shows that the temperature dependence of  $k_2$  is entirely different from that of  $k_1$ . For solid tristearin,  $k_2$  is directly related to temperature; for liquid tristearin,  $k_1$  has only slight, if any, temperature dependence. The scatter in the data masks any trend present. The most interesting aspect of the temperature dependence of  $k_2$  is its sharp increase, about sixfold, at the melting point of tristearin. Note the uneven scale of the ordinate. The values of  $k_2$  for solid tristearin give a reasonable fit to Arrhenius plots. Activation energies ranging from 9.9 kcal/mole, at the lowest flow rate, up to 14.0 kcal/mole, at the highest flow rate, were calculated from the slopes of the Arrhenius plots.

The temperature dependence of cleaning in the system studied in this experiment is complex;  $k_1$  decreases,  $k_2$  increases, and the amount of species 2 decreases with rising temperature, the total effect being an overall increase in cleaning rate (Fig. 2). It is quite possible in another system, where the inter-

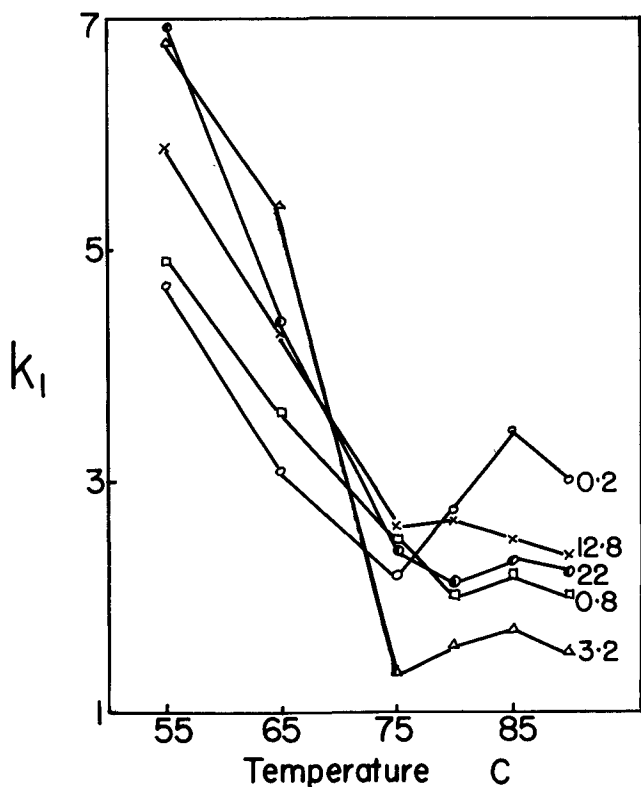


FIG. 4. Effect of temperature on rate constant  $k_1$  at flow rates of 0.2, 0.8, 3.2, 12.8, and 22 lb/sec. 0.03M NaOH, 10 sec cleaning treatments.

relations between  $k_1$  and  $k_2$  and amount of species 2 differ, that the effect of temperature on the overall cleaning rate may be different. Consider, for example, the effect of changing the species 2 temperature relationship while holding constant the temperature relationships of  $k_1$  and  $k_2$ . If species 2 decreased more slowly with rising temperature than it does in this study, the overall cleaning rate would be more or less insensitive to temperature, since the fall in  $k_1$

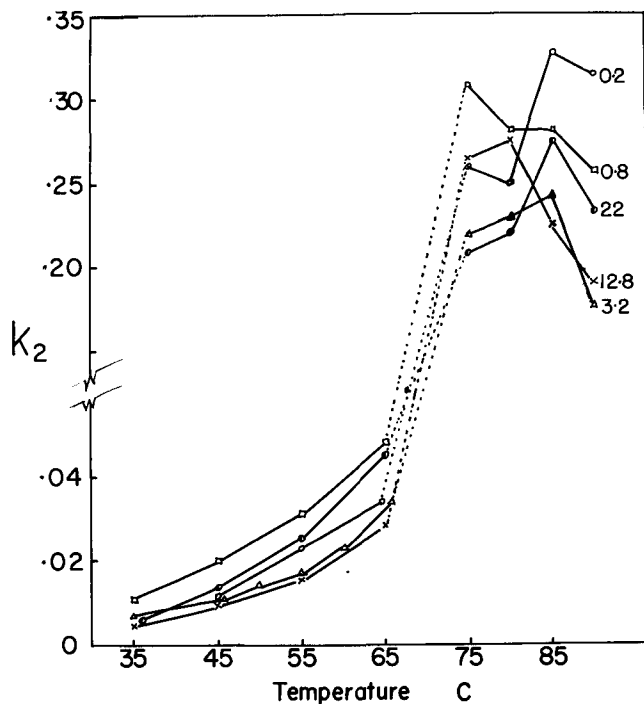


FIG. 5. Effect of temperature on rate constant  $k_2$  at flow rates of 0.2, 0.8, 3.2, 12.8, and 22 lb/sec. 0.03M NaOH, 10 sec cleaning treatments.

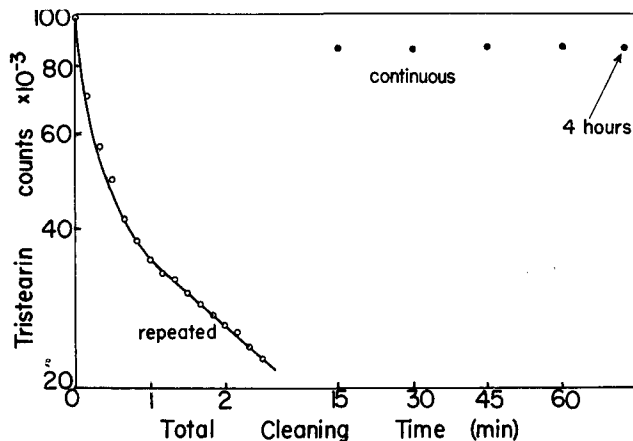


FIG. 6. Cleaning curves obtained by continuous cleaning and repeated cleanings. 0.03M NaOH, 65°C, flow 2 lb/sec.

would counterbalance the increase in species 1. If the amount of species 2 was small at low temperatures and if it decreased very slowly with rising temperature, the temperature relationship of  $k_1$  would become the dominant factor, and the overall cleaning rate would decrease with rising temperature.

The different temperature relationships of  $k_1$  and  $k_2$  and species 2 in different systems are probably the cause for the conflicting evidence found in the literature on the temperature relationship of the overall cleaning operation. Some workers, e.g. (9), found faster cleaning, whereas others, e.g. (10,13), reported little effect on cleaning with rising temperature. Jones did note that a decrease in efficiency is to be expected at temperatures below the melting point of oily material, an observation that agrees with results in this study. With surface-active types of detergents, the effect of temperature on micellization, solubilization, and cloud point may contribute to the temperature relationship of the cleaning rate, but these complicating factors are absent when NaOH is used as the detergent.

#### Effect of Cleaning Time

An earlier study (4) showed that two cleaning mechanisms must be present for what is now termed species 2 soil, one mechanism being time-dependent and the second more powerful mechanism being independent of time. The first effect was termed the "flow effect." The second effect was attributed to the movement of the air-detergent interface over the soiled strip and was termed the "Dupré effect" in view of equations derived by Dupré in 1869 (1) that related surface tension forces and contact angles at triple points.

To test whether the Dupré effect does arise from the movement of the air-detergent interface over the soiled strip, two strips were prepared in the usual manner and cleaned under the same conditions of temperature and flow rate. The first strip was placed in the test section and cleaned for 10 sec, the test section was drained for 10 sec, and the strip was given another 10 sec cleaning treatment without being removed. This was done 8 times before the strip was removed from the test section. This strip was in the section for 160 sec and in contact with moving detergent for 80 sec. During the period, an air-detergent interface moved over the strip 16 times and 75.3% of the soil was removed. The second strip was cleaned for 10 sec, and the pump was switched off for 10 sec while the strip remained in the pipe test section, sur-

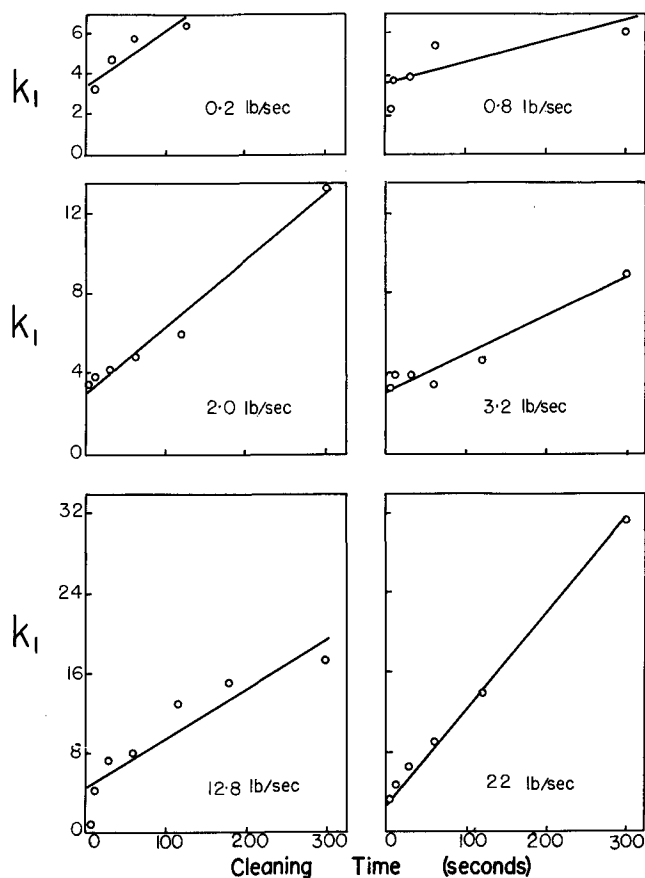


FIG. 7. Effect of duration of cleaning treatments on rate constant  $k_1$  at 0.2, 0.8, 2.0, 3.2, 12.8, and 22 lb/sec flow rates. 0.03M NaOH, 65C.

rounded by stationary detergent. This was done 8 times before the strip was removed; i.e., the strip was in the section for 160 sec: 80 sec in contact with moving detergent and 80 sec in contact with stationary detergent. An air-detergent interface moved over the strip two times, and 29.2% of the soil was removed, which is about the same as that removed by one 10 sec treatment. This experiment supports the hypothesis that the air-detergent interface is the source of the time-independent mechanism.

Figure 6 also shows the effect of the air-detergent interface. The open circles represent one strip that was given a series of 10 sec treatments. Two min of cleaning (representing 12 treatments) removed 75% of the soil. The full circles represent separate strips that were given one treatment only. One cleaning treatment of 15 min duration removed only 15% of the soil. The small amount of cleaning associated with long continuous cleaning times has been shown (4) to coincide with the rolling up of the soil into lumps that are very resistant to removal by the detergent.

The question now arises whether the advancing or receding air-detergent interface is responsible for the time-independent cleaning mechanism. Figure 6 shows that one prolonged treatment of 15 min or more removed about half as much tristearin as one 10 sec treatment. This anomaly of better cleaning with shorter cleaning times can be explained: the advancing air-detergent interface removes about 15% of the tristearin; 10 sec later the receding air-detergent interface removes another 10%; but 15 min later, when the tristearin has rolled into lumps, the receding air-detergent interface removes almost no tristearin. This evidence leads to the conclusion that both the advanc-

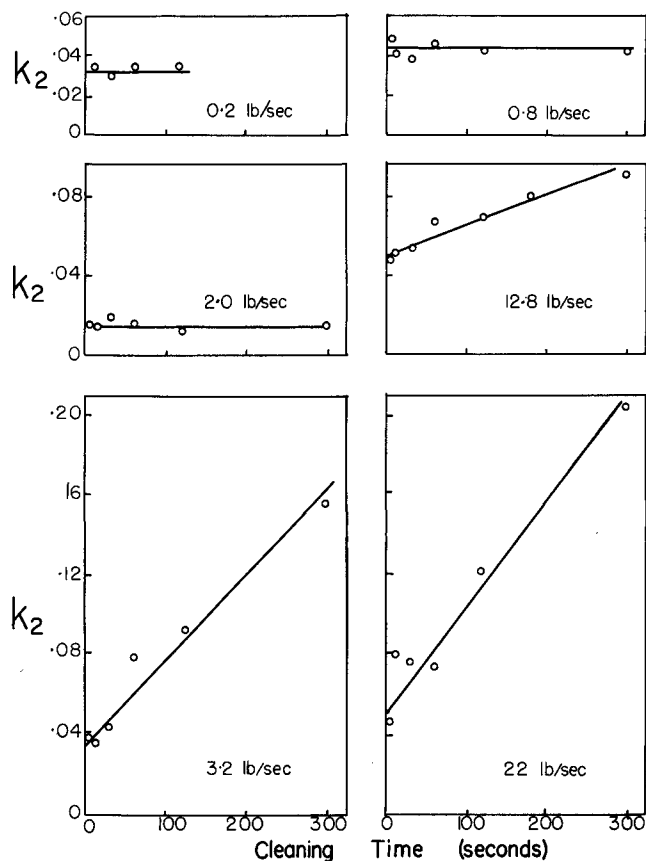


FIG. 8. Effect of duration of cleaning treatments on rate constant  $k_2$  at 0.2, 0.8, 2.0, 3.2, 12.8 and 22 lb/sec flow rates. 0.03M NaOH, 65C.

ing and receding interfaces are effective.

The hypothesis that both the advancing and receding air-detergent interfaces are responsible for the time-independent process was substantiated by visual observation. A strip was soiled with four times the normal tristearin load (20 mg), and cleaned at 65C with the flow rate slowed to a linear velocity of less than 1 cm/sec. As the advancing air-detergent interface moved up the soiled strip, the tristearin could be clearly seen coming off the strip at the moving interface and floating on the surface. As the receding air-detergent interface moved downward over the soiled strip, the tristearin could again be seen coming off the strip and floating on the surface.

To measure the contributions of the Dupré and flow mechanisms, a series of experiments was run at a constant temperature of 65C. Complete cleaning curves were obtained at each flow rate with treatments of 2, 10, 30, 60, 120, and 300 sec, and the rate constants were obtained. These are plotted in Figures 7 and 8, and lines of best fit were calculated by the method of least squares. The results indicate that a linear relationship exists between the rate constant and the time of cleaning treatments, although there are some marked deviations from the line of best fit. The tests using a flow rate of 2 lb/sec were conducted in a horizontal test section. This experiment established the existence of the two mechanisms of soil removal, and the test section was then changed to a vertical position to give a more uniform and reproducible movement of the air-detergent interface over the strip.

The contribution of the Dupré mechanism is obtained by extrapolating the rate constant-time curves back to zero time. The contribution of the flow mecha-

TABLE III  
Effect of Cleaning Time on Rate Constants

Flow rate lb/sec	$k_1 = Ft + D$	$k_2 = Ft + D$
0.2	$k_1 = .028 t + 3.5$	$k_2 = 0 + .033$
0.8	$.008 t + 3.5$	$0 + .042$
2.0 <sup>a</sup>	$.033 t + 3.1$	$0 + .015$
3.2	$.017 t + 3.1$	$.00039 t + .041$
12.8	$.050 t + 4.6$	$.00012 t + .052$
22.0	$.092 t + 3.4$	$.00049 t + .058$

Conditions: .03M NaOH 65C.

<sup>a</sup> This experiment was performed in a horizontal pipe.

nism is obtained from the slopes of the lines. Both rate constants,  $k_1$  and  $k_2$ , can be expressed in terms of an equation of the type

$$\text{rate constant} = Ft + D$$

where  $F$  = flow-mechanism constant

$t$  = time in seconds

$D$  = Dupré-mechanism constant

Table III contains the  $F$  and  $D$  values obtained from Figures 7 and 8. It should be noted that the range of flow rates studied is in excess of two orders of magnitude. The scatter in the values of  $F$  and  $D$  prevents useful mathematical treatment of the data of Table III, but some important conclusions can nevertheless be drawn. The Dupré mechanism is effective in the removal of both species of tristearin but is about two orders of magnitude greater for species 1 than for species 2. Also, the Dupré mechanism is independent of the flow rate for both species, a result that is not surprising since the forces arising at the air-detergent-soiled steel junction are not dependent upon flow rate. A 10 sec cleaning time was used in all other experiments of this study. If the value of 10 sec is substituted for  $t$  in the equations of Table III, it will be found that the Dupré mechanism is responsible for about 90% of the soil removal in these experiments.

The flow mechanism for species 1 shows a minimum at a rate of 3.2 lb/sec. Since all flow rates are in the turbulent region, the minimum cannot be associated with a change from laminar to turbulent flow. No explanation can yet be given for this minimum. The flow mechanism for species 2 is absent at flow rates of 2 lb/sec and less, but present at flow rate of 3.2 lb/sec and higher. The existence of a threshold flow rate, below which the flow mechanism is absent for species 2, is interesting. It could be interpreted as an example of the Kling and Lange (11) energy barrier, which must be overcome before soil is removed from a surface. If this is the correct interpretation, it again shows that species 2 is bound more strongly than species 1, since species 1 shows no such threshold over the range of flow rates studied. Jennings et al. (8) studied the removal of thick milk films from stainless steel in a circulation cleaning system and found a threshold flow rate equivalent to a Reynolds number of ca. 25,000; soil removal was independent of flow rate below this threshold, and directly proportional to flow rate above this threshold value. It is possible that a threshold level exists for the mechanical-energy requirement of detergency.

#### Comparison with Monomolecular Layers

Only polymolecular films have been studied up to this point in these experiments. Even after prolonged cleaning, the tristearin level never reached the equivalent of a monomolecular layer. There is evidence to indicate that a monomolecular layer of tristearin is bonded more strongly to the steel than to itself (2); hence it was predicted that a monomolecular layer

would be removed more slowly than a polymolecular layer. It is not intended to make a thorough study of the kinetics of removal of monomolecular layers in this model system but, for comparative purposes, two strips were soiled with a monomolecular layer of tristearin and cleaned in the usual way. The results are shown in Figure 9, together with the curve of a polymolecular layer cleaned under the same conditions.

Although there is no evidence for assuming first-order kinetics for the removal of monomolecular layers, a semi-log plot has been used for comparison. Actually, the points fit a semi-log plot for the first 7 or 8 cleaning treatments, and then diverge. The slopes obtained from Figure 9 are shown in Table IV, together with the slopes obtained for polymolecular layers given the same cleaning treatment.

In comparing the monomolecular layers, it will be seen that 60 sec cleaning treatments give an initial slope which is twice that for 2 sec cleaning treatments. This indicates that two mechanisms, one time-dependent, and the other time-independent, must be effective in monomolecular layers also, since a time-dependent mechanism alone would give the 60 sec plot an initial slope 30 times as great as that for the 2 sec plot.

The initial slope of the monomolecular layer given the 2 sec treatments is double that for the species 2 slope for the same experimental conditions. For the 60 sec treatment, the initial slope of the monomolecular layer is four times as great since  $k_2$  is independent of the flow rate at 2 lb/sec (see Table III) and the monomolecular layer rate is not. The more rapid removal of the monomolecular layers indicates that the forces holding species 2 to the surface are even greater than the strong force of adhesion between the monomolecular layer and the surface. The partial time-dependence of removal of the monomolecular layers is in contrast to the time-independence of species 2 at this flow rate and shows that species 2 is physically different from a monomolecular layer.

The rate constants  $k_1$  are about one order of magnitude greater than the initial slopes for the monomolecular layers. The time-dependent mechanism in the monomolecular layers must be proportionately more dominant than in the rate constant  $k_1$  since a 30-fold increase in cleaning time increases  $k_1$  by 25%, but increases the initial slope of the monomolecular layers by 100%. This comparison between a monomolecular soil film and a polymolecular soil film indicates that the two mechanisms are still present in the monomolecular film, but that it has different properties than either species 1 or species 2 soils. To save confusion a monomolecular layer might be designated as species 3 soil, but this is a minor point since practical detergency is seldom concerned with removing the last monomolecular soil layer.

#### The Mechanism of the Cleaning Action

The mechanism of detergent action has been attributed to many factors, including surface tension, interfacial tension, contact angle, surface viscosity, lather, electrostatic properties, solubilization, adsorption, cryoscopy, wetting, suspending action, emulsification, saponification, and lubrication. In this study only NaOH was used as detergent, to eliminate such factors as solubilization, lather, and surface tension (NaOH raises surface tension slightly).

The strong tristearin-substrate bond and weak tristearin-tristearin bond present in this model system

(2) suggests a three-step mechanism of tristearin removal.

Step 1) Since each layer is held by the same strength bonds the tristearin is removed at a constant rate until only two layers remain on the surface, (zero order kinetics):

$$-dS/dt = k$$

where  $S$  is the amount of tristearin removed.

Step 2) As the second layer of tristearin is removed the strongly held monomolecular layer is exposed. The amount of the second layer removed will be proportional to the amount present (first order kinetics):

$$-dS/dt = k\theta$$

where  $\theta$  is the fraction coverage of the second layer.

Step 3) The removal of the monomolecular layer commences as soon as a part of it is exposed. The rate constant will be small since stronger bonds must be broken. The amount removed will be proportional to the amount of the monomolecular layer exposed, (another first order process):

$$-dS/dt = k_2\phi$$

where  $\phi$  is the fraction of exposed monomolecular layer.

This three-step mechanism must be excluded because the experimental results show that the first step does not follow zero order kinetics.

The most probable mechanism would seem to be the rolling up of the tristearin by preferential wetting (1,6,7,11,14,16). Bourne and Jennings (4) showed that the solid tristearin on stainless steel is rolled up into lumps after long exposure to aqueous NaOH.

There is good evidence to believe that immersion in  $\text{CCl}_4$  removes all but a monomolecular layer of tristearin from stainless steel and frosted glass (2). In this study, it was found that immersion of the soiled strips in  $\text{CCl}_4$  consistently gave residual counts in the range of 3,500–4,500 (10 min counts), but after a series of cleaning treatments immersion in  $\text{CCl}_4$  gave much lower residual counts. For example, a strip with an initial count of 106,750 gave a residual count of 4,213 after immersion in  $\text{CCl}_4$ . In another experiment the same strip gave an initial count of 117,389; after twelve 10 sec treatments in .03M NaOH at 65C the count had fallen to 33,668; immersion in  $\text{CCl}_4$  reduced the count to 1,414. This result indicates that the detergent not only cause the continuous tristearin film to roll up but also protects the exposed stainless steel surface against redeposition of tristearin from the  $\text{CCl}_4$ . From this evidence it seems probable that preferential displacement and rolling up of the tristearin is the mechanism of removal in the model system used in this study.

On the other hand, the Dupré mechanism, which is the dominant mechanism of this system, arises from the air-detergent interface which moves across the strip very rapidly, especially at high flow rates. It is therefore unlikely that the tristearin would have time to be rolled up for the Dupré mechanism. It seems, therefore, that the rolling up process is a phenomenon that is unrelated to the Dupré mechanism, but may be associated with the flow mechanism.

In view of the variable proportion of species 2 in this system, there must be a process for converting species 1 into species 2 and vice versa. Hence, each species may be lost by three processes: the Dupré

TABLE IV  
Comparison of Monomolecular layer and Polymolecular layer

Nature of film	Factor	Cleaning time	
		2 sec	60 sec
Polymolecular layer.....	Rate constant $k_1$	3.5	4.8
Polymolecular layer.....	Rate constant $k_2$	.15	.16
Monomolecular layer.....	Initial slope	.33	.63

Conditions: .03M NaOH, 65C, 2lb/sec.

mechanism, the flow mechanism, and conversion to the other species. In view of the complex kinetics it seems remarkable at first sight that the overall rate of removal of each species can be empirically described to a high degree of precision by a simple first-order process.

This complexity presents no problem if we postulate that each process is a first-order process. For example, there are four processes affecting the amount of species 1, and if these are all first-order we have:

$$1) \text{ loss by flow mechanism: } -d(A)/dt = k_F(A)$$

$$2) \text{ loss by Dupré mechanism: } -d(A)/dt = k_D(A)$$

$$3) \text{ loss by conversion to species 2:}$$

$$-d(A)/dt = kc_1(A)$$

$$4) \text{ gain by conversion of species 2 into species 1:}$$

$$+d(A)/dt = kc_2(B)$$

where  $k_F$ ,  $k_D$ ,  $kc_1$ , and  $kc_2$  are first order rate constants, (A) is the amount of species 1 present at time  $t$  and (B) is the amount of species 2 present at time  $t$ . Summing the four processes gives:

$$-d(A)/dt = (k_F + k_D + kc_1)(A) - kc_2(B)$$

$$\text{or}$$

$$-d(A)/dt = k_1(A) - kc_2(B)$$

$$\text{where } k_1 = (k_F + k_D + kc_1)$$

The conversion of species 1 into species 2 is slow during the aging process (Table I) and the inter-conversion of the species is probably slow or non-existent, during the course of a cleaning experiment. If this is so, the term  $kc_2(B)$  becomes very small relative to the term  $k_1(A)$ , and it can therefore be dropped from the equation. The overall loss of species 1 then becomes:

$$-d(A)/dt = k_1(A)$$

which is the equation of a simple first order process.

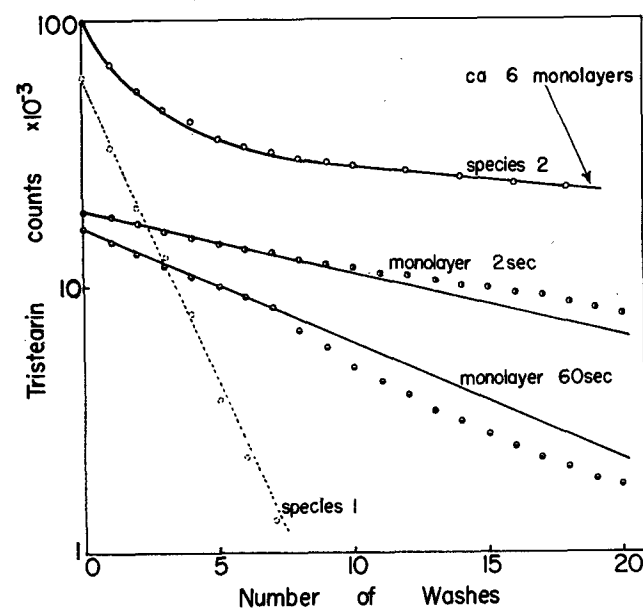


FIG. 9. Cleaning curves obtained on polylayer and monolayers. 0.03M NaOH, 65C. Flow, 2 lb/sec.

The same reasoning can be applied to produce the simple first order equation:

$$-d(B)/dt = k_2(B) \text{ for species 2.}$$

The removal of the rolled-up films of tristearin that are obtained after a long continuous treatment is very slow and similar to that for species 2. This leads to the speculation that some feature of the rolling-up process is responsible for the formation of species 2.

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# Quantitative Gas Liquid Chromatographic Analysis of Butterfat Triglycerides<sup>1</sup>

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#### Abstract

Gas liquid chromatographic triglyceride separation by carbon number, and integration of the area response obtained in the hydrogen flame ionization detector, has permitted the calculation of the following molar proportions for the various triglyceride types in a blended butterfat sample: C<sub>24</sub> 0.5, C<sub>25</sub> 0.08, C<sub>26</sub> 0.57, C<sub>27</sub> 0.18, C<sub>28</sub> 0.81, C<sub>29</sub> 0.17, C<sub>30</sub> 1.15, C<sub>31</sub> 0.2, C<sub>32</sub> 3.1, C<sub>33</sub> 0.34, C<sub>34</sub> 5.41, C<sub>35</sub> 1.0, C<sub>36</sub> 10.6, C<sub>37</sub> 1.2, C<sub>38</sub> 12.8, C<sub>39</sub> 1.15, C<sub>40</sub> 10.7, C<sub>41</sub> 1.0, C<sub>42</sub> 6.1, C<sub>43</sub> 0.58, C<sub>44</sub> 5.15, C<sub>45</sub> 0.6, C<sub>46</sub> 5.8, C<sub>47</sub> 1.0, C<sub>48</sub> 6.45, C<sub>49</sub> 1.47, C<sub>50</sub> 8.5, C<sub>51</sub> 1.43, C<sub>52</sub> 6.95, C<sub>53</sub> 1.05, C<sub>54</sub> 4.0. The validity of these estimates was verified by similar determinations performed on molecular distillates of butterfat and on butterfats with known amounts of added saturated and unsaturated long chain triglycerides. The fatty acid carbon recoveries estimated on the basis of the observed triglyceride peak proportions were of the order of 95% or better.

A comparison of the experimentally determined triglyceride type distributions with those calculated on the basis of a completely random fatty acid arrangement for the blended and the molecularly distilled samples showed considerable differences, the most apparent of which was the greater proportion of both short and long chain triglycerides consistently predicted for the random population. On the basis of these studies, it is suggested that butterfat possesses a non-random fatty acid distribution which is reflected in its triglyceride type distribution.

#### Introduction

THE COMPOSITION OF BUTTERFAT has been the subject of many investigations in the past. While the identification and elucidation of the structure of the constituent fatty acids of butterfat has now been almost completed (1,2) virtually nothing is known

about the triglyceride structure of this fat.

The large number of fatty acids in butter gives rise to an extremely high number of combinations as glycerides, which differ little in their physical properties when adjacent triglycerides of the series are compared. As a result, quantitative separations of individual triglycerides have proved extremely difficult. Such relatively successful techniques of glyceride fractionation as low temperature crystallization and countercurrent distribution have failed to effect any butterfat separations useful in structural studies (3).

Analyses of the butterfat triglyceride structure by use of pancreatic lipase for cleaving the fatty acids esterified on the 1 and 3 positions of the glycerol have revealed an increased concentration of the C<sub>10</sub>, C<sub>12</sub>, and C<sub>14</sub> saturated acids in the monoglycerides resulting from the action of the enzyme on the intact fat (4,5). On the basis of a mathematical evaluation of the distributions of triglyceride types and isomeric forms in terms of saturation and unsaturation, however, it has been concluded (5), that in butterfat the fatty acyl groups, classified only as saturated and unsaturated, have been brought together in groups of three at random, or nearly so. Accordingly, butterfat has been described as another of the group of fats in which saturated and unsaturated fatty acids are associated as S<sub>3</sub>, S<sub>2</sub>U, SU<sub>2</sub>, and U<sub>3</sub> in proportions which can be specified, at least approximately, by application of the laws of probability operating freely or with some restriction. These conclusions are supported by analyses of the trisaturated glycerides of milk fat by the mercaptoacetic acid method (6).

It is obvious that comparisons of fatty acid positioning on the basis of saturated and unsaturated acids as classes is not an ideal manner of determining triglyceride structure, in that it obscures patterns in the placement of the individual fatty acids. Neither is an enzymatic positional analysis, when performed on a complex mixture of triglycerides. Before such studies become meaningful, an effective preliminary segregation of the fat either on the basis of unsaturation or molecular weight, or both, is obligatory.

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