TABLE III

Determination of Percentage of Anionic Surfactant and Amine Oxide in Detergent Formulations

Ingredients	*Formulations (parts on 100% active basis)* I	II	III
Sodium alkyl benzene sulfonate[a]	....	20	20
Sodium alkyl ethoxy sulfate[b]	25	....	5
Lauryl dimethyl amine oxide[c]	5	5	5
Sodium xylene sulfonate	....	10	5
Tetrapotassium pyrophosphate	....	5	5
Analytical results			
Anionic, %	25.4	19.9	26.5
Amine oxide, %	4.6	5.2	5.9

[a] Ultrawet 60 K soft (Atlantic Refining Company).
[b] Tergitol Anionic 15-S-3S (Union Carbide Corporation).
[c] Ammonyx LO (Onyx Oil and Chemical Company).

as nonionic surfactants above pH 7, and as cationic surfactants below pH 3 the anionic surfactant was measured by alkaline methylene blue titration and acid methylene blue titration measured the anionic surfactant not complexed with amine oxide. The difference in the amt of anionic found by these two titrations was calculated as the amt of amine oxide in the formulation. The results given in Table III show that this technique is applicable to the analysis of detergent formulations containing amine oxides.

For the determination of anionic surfactant in alkaline media at concns of 100 ppm and less, a spectrophotometric method has been employed. The procedure is similar to that in *Standard Methods—Water and Waste-Water* (6). Measured amts of surfactant, chloroform, methylene blue and sodium hydroxide were shaken until all available methylene blue was oxidized to dimethylthionoline. These dyes are light sensitive and fade on prolonged exposure. Therefore, all measurements were carried out on a comparable time basis. Absorbances of solutions for various concns of sodium 2-ethylhexyl sulfate were taken at 547 mμ. The plot of absorbance versus concn was linear.

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Kinetic Studies of Detergency. III. Dependence of the Dupré Mechanism on Surface Tension

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Abstract

The kinetics of the removal of thin films of pure radioactive tristearin from a stainless steel surface by detergent solutions in a circulation cleaning system were used to study the effect of the surface tension of the detergent solution on the Dupré mechanism and the flow mechanism.

Lowering the surface tension reduced the effectiveness of the Dupré mechanism for both species 1 soil and species 2 soil, as expected. Lowering the surface tension increased the efficiency of the flow mechanism for both species of soil, but, at the present time, it is not known how much of the increase can be ascribed to the lowered surface tension, and how much is due to the increased concn of the surfactant that was used to lower surface tension.

Introduction

KINETIC ANALYSIS of the removal of tristearin from stainless steel indicates that two species of soil are present (2). The difference between the two species has not yet been resolved, but can probably be attributed to a difference in the attractive force(s) between the substrate and the two soil species. Both species are removed simultaneously and independently by two soil removal mechanisms: *a*) a time-dependent flow mechanism, and *b*) a time-independent interfacial mechanism (1,3) called the Dupré mechanism (4) in honor of the French scientist, M. Athanase Dupré (1869) who first developed the equations relating surface tension forces at a gas-solid-liquid interface. The force specifically associated with the air-solution interface is surface tension, which is probably responsible for this latter mechanism. The Dupré mechanism, in other words, might be visualized as tearing soil from the surface by the surface tension of the advancing or receding interface.

If this explanation is valid, the effectiveness of the Dupré mechanism should be related to surface tension; the mechanism should be most effective in solutions of high surface tension and diminish in solutions of lower surface tension. The experiment described below was designed to establish the relationship (if any) between surface tension and the Dupré mechanism.

Theoretical Aspects

Although the equations set up in an earlier paper (2) are correct, they do not allow separate consideration of the two cleaning mechanisms. This can be achieved by describing the cleaning process as:

$$-\mathrm{d(A)/dn} = \mathrm{K_1(A)}$$

where (A) represents the amount of species 1 soil remaining after n washes, K_1 is the rate constant for species 1 soil removal, and n the number of washes, each of constant time t^1.

This can be integrated to give

$$\ln(\mathrm{A}) = \ln(\mathrm{Ao}) - \mathrm{K_1 n} \qquad (1)$$

where (Ao) represents the amount of species 1 soil at zero washes. K_1 represents the cumulative rate of soil removal by both the flow mechanism F and the Dupré mechanism D; i.e.

$$\mathrm{K_1} = \mathrm{F_1 t^1} + \mathrm{D_1}$$

where t^1 is the time duration of one washing treatment. By substitution in (1);

$$\ln(\mathrm{A}) = \ln(\mathrm{Ao}) - (\mathrm{nF_1 t^1} + \mathrm{nD_1}), \text{ or}$$

$$\ln(\mathrm{A}) = \ln(\mathrm{Ao}) - (\mathrm{F_1 t} + \mathrm{nD_1})$$

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where t = the total time of washing $= nt^1$
Similarly, the equation

$$\ln(B) = \ln(Bo) - (F_2t + nD_2)$$

can be derived for species 2.

Although the nature of the experiment restricts to integers the values of n, these equations possess an advantage in allowing separation of the constants for the two soil removal mechanisms.

The experiment is conducted by subjecting a soiled strip to a series of washes under standard conditions, each wash of constant time. From a plot of log soil vs. number of washes the rate constants K_1 and K_2 are found by a graphical method that has been described (2). Another soiled strip is then subjected to a series of washings under the same standard conditions as the first strip except that a constant washing time of different duration is used. Additional soiled strips are cleaned in a similar manner, using appropriate washing times of constant duration. In each case the rate constants K_1 and K_2 are obtained from each cleaning curve. The values of K_1 and K_2 thus obtained are then plotted against the time of a single washing treatment. Since $K_1 = F_1t^1 + D_1$ and $K_2 = F_2t^1 + D_2$, the slopes of these plots give the values of F_1 and F_2 (the respective flow mechanism constants for species 1 soil and species 2 soil) while the intercepts on the Y axis (at $t^1 = o$) give the values of D_1 and D_2 (the respective Dupré mechanism constants for species 1 soil and species 2 soil).

The steps required to obtain the desired data are shown in Figure 1. In graph A the log of the residual soil is plotted against the number of washes. The points on this graph are obtained by experiment. The slope of the linear portion of the cleaning curve gives K_2, which is the rate constant for removal of species 2 soil under a particular set of standard conditions including a standard washing time. The linear portion of the cleaning curve extrapolated back to zero washes is subtracted from the curve above it to give a second straight line of slope K_1 which is the rate constant for removal of species 1 soil under the same set of standard conditions. The values of K_1 and K_2 are obtained graphically from the cleaning curve and comprise the data for the second generation graphs, B and C.

In second-generation graph B the rate constant K_1 for species 1 soil is plotted against the duration in seconds of one washing treatment (t^1). The slope K_1 obtained from graph A gives one point on graph B. A series of graphs of type A are required to complete one graph of type B. The intercept on the ordinate of graph B gives the Dupré mechanism (time-independent) contribution D_1 to the rate constant K_1, while the slope of the line gives the flow mechanism (time-dependent) contribution F_1 to the rate constant K_1. The values for D_1 and F_1 are evaluated graphically. Curve C is another second generation graph, similar to curve B and separates the rate constant K_2 for species 2 soil into its two portions, D_2 and F_2. The values for F_1, F_2, D_1, D_2 comprise the basic data for the third generation of graphs, which are shown in Figure 2 and Figure 3.

Experimental

The experimental procedure was exactly as described previously (2), (detergent, 0.03*M* NaOH; soil, pure tristearin labeled with C^{14} on the carboxyl carbon; surface, stainless steel) except that under each set of conditions several strips were cleaned, each strip being subjected to a series of washes of constant duration, but of a different duration than for the other strips. Temp was kept constant at 65C (tristearin melts at 71.5C). Surface tension was controlled by adding different levels of a surfactant (commercial dimethylnaphthalensulfonate) that is noted for its very low power of detergency. Dimethylnaphthalensulfonate was selected because it most nearly approached the ideal requirement of high surface activity, zero detergency, and compatibility with hot dilute aqueous NaOH. The surfactant was added to the 0.03*M* aqueous NaOH at levels ranging from zero up to 0.1%, the level depending on the surface tension required. A DuNoüy ring tensiometer was used to measure surface tension. A sample was taken from the tank of hot circulating detergent solution and quickly placed in the DuNoüy tensiometer for measurement of surface tension before it could cool or age. This was done in order to measure the surface tension of the detergent solution as it existed in the circulation cleaning apparatus. A cool solution or a solution that has been allowed to rest until the surface reached an equilibrium condition does not have the same surface tension as a hot stirred solution. Because of the haste with which the measurements were necessarily made the surface tensions were measured to ±0.5 dyne/cm.

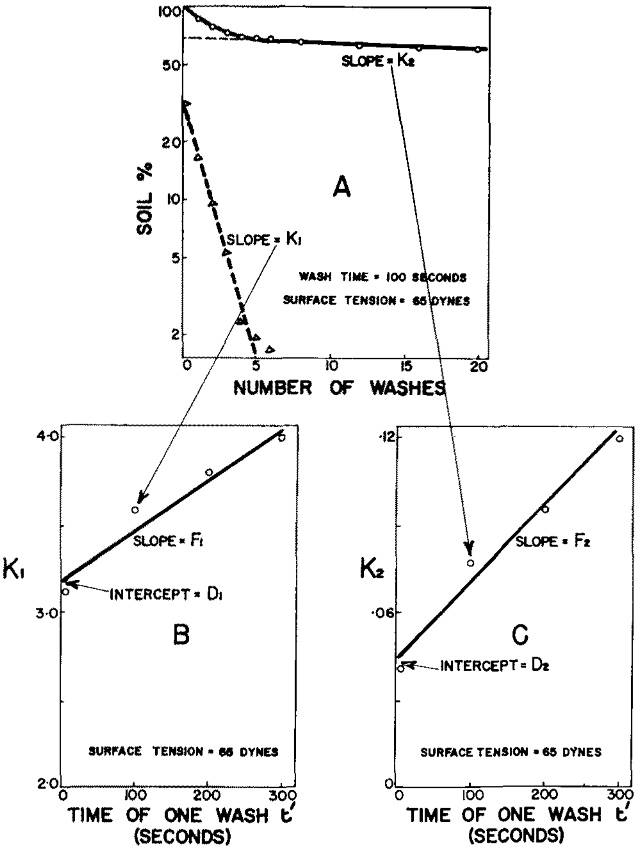

FIG. 1. Experimental cleaning curve is used to separate the two species of soil and evaluate the rate constants K_1 and K_2 from the slopes of the two lines. The rate constants provide one point on the second generation graphs (B and C), which separate the time-dependent mechanism (slope) from the time-independent mechanism (intercept).

Commercial saponin was used in one experiment to provide a contrast to the dimethylnaphthalensulfonate. Frequent additions of saponin were required to maintain surface tension because saponin is not stable to hot dilute sodium hydroxide. Consequently, the

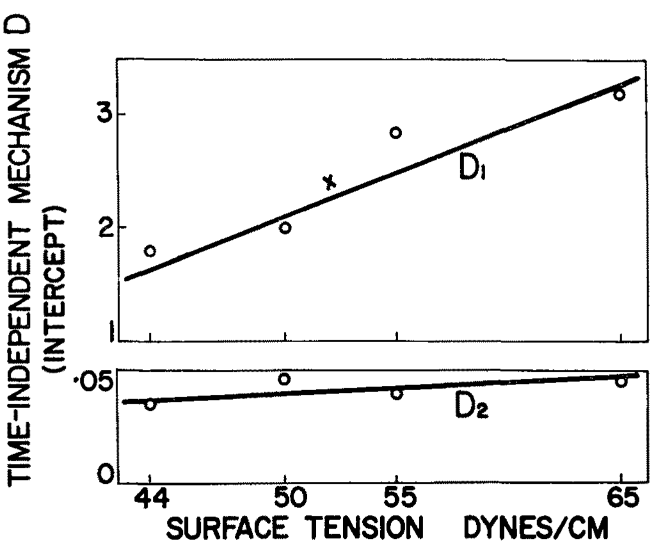

FIG. 2. Effect of surface tension on Dupré mechanism for species 1 soil (D_1) and species 2 soil (D_2). The point x is the D_1 value obtained with saponin used as surfactant.

surface tension was held at 52 ± 2 dynes/cm in the saponin experiment.

Results and Discussion

Effect of Surface Tension on Dupré Mechanism

The Dupré mechanism rate constants for species 1 soil and species 2 soil (respectively D_1 and D_2) are plotted against surface tension in Figure 2. The Dupré mechanism rate constants for both species 1 soil and species 2 soil are directly proportional to the surface tension of the detergent solution. It might be argued that the surfactant has caused a number of changes in the detergent solution and that this result does not necessarily relate the Dupré mechanism to the surface tension. It must be remembered, however, that the Dupré mechanism arises from the air-detergent interface moving across the soiled metal strip, and it is difficult to think of any effect that the surfactant can produce in the surface other than lowered surface tension. The saponin solution exerts a similar effect upon the Dupré mechanism even though it has different properties from those of dimethylnaphthalensulfonate. Figure 2 would have a negative slope if the surfactant exerted some power of detergency through the Dupré mechanism, because the lower surface tension corresponds to the higher surfactant concn and stronger cleaning power. The absence of such a relation points clearly to a direct relation between surface tension and Dupré mechanism.

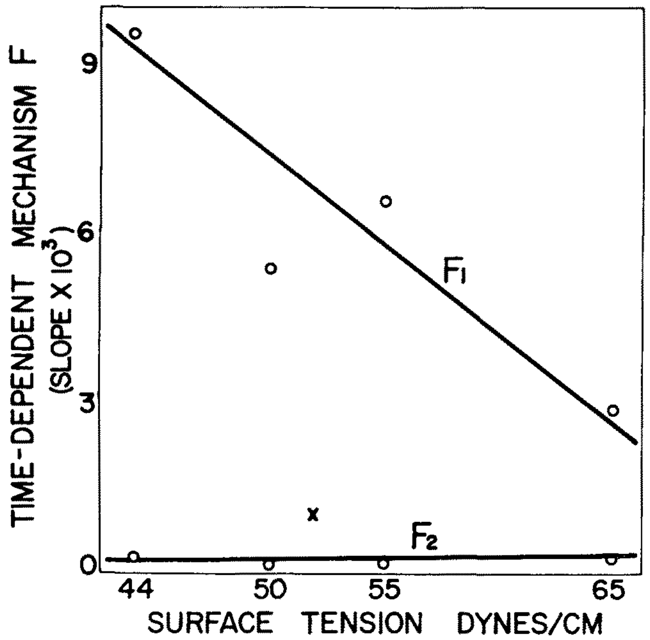

FIG. 3. Effect of surface tension on flow mechanism for species 1 soil (F_1) and species 2 soil (F_2). The point x is the F_1 value obtained with saponin used as surfactant.

It is possible to make two interesting extrapolations to the field of practical cleaning if we assume that the results of decreasing Dupré mechanism rate constant with decreasing surface tension are not restricted to the model system used in this study but are of general occurrence. First, most commercial detergents are designed to produce a low surface tension for the sake of easy wetting, and, therefore, would be expected to minimize this mechanism. Conventional methods of cleaning (immersion of the article to be cleaned in the detergent solution until completion of the cleaning operation) give this weakened mechanism only one chance to operate; viz. when the article is immersed in the detergent solution. There is little soil left for the Dupré mechanism to work on at the time of removal of the clean article from the detergent solution. Under these conditions the contributions of this mechanism would be minor, and, therefore, it is not surprising that it has not been recognized. Second, it is possible that some cleaning operations could be designed to utilize this mechanism more fully and thereby obtain more rapid cleaning than with conventional methods. The Dupré mechanism should be effective in a system in which multiple air-detergent interfaces pass over the article to be cleaned, and which utilize a detergent solution with a *high* surface tension.

Effect of Surface Tension on Flow Mechanism

Species 1 soil shows a higher flow mechanism rate constant at lower surface tensions while that for species 2 soil remains fairly constant (Fig. 3). The flow mechanism is related to the properties in bulk of the detergent solution because it takes place *in* the detergent solution and not at the surface. Since the lower surface tensions result from higher concns of surfactant, it is not possible to determine whether the improvement in the flow mechanism rate constant is caused by the lowering of the surface tension or by the detergency power or some other additive property of the surfactant. The flow-mechanism rate constant is considerably less with saponin as a surfactant than with dimethylnaphthalensulfonate at the same surface tension. Although not conclusive, this supports the hypothesis that at least a portion of the increase in the flow mechanism rate constant at higher surfactant concentrations is related to the detergency properties of the surfactant rather than the reduced surface tension. At present, it is not known to what extent the surface tension of the detergent solution affects the flow mechanism rate constant.

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