• *Technical*

Removal of Radio-Tagged Protein and Stearic Acid Soil from Glass

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Both algal protein and stearic acid soils are removed by water alone to near a 50% level; retained soil then becomes more difficult to remove. The bonding of protein soil to glass is stronger than that of tristearin, with indications that stearic acid soil is also slightly more adherent. The shape of the protein soil removal curves lacks the sigmoid shape of the tristearin or stearic acid soils, suggesting either the absence of sharp dependence upon critical micelle concentration, or the existence of adsorption largely at an essentially single energetic level. Both these soils are generally more effectively removed by anionic surfactants than was tristearin.

Sodium tripolyphosphate is quite effective for removal of both soils, but combination with surfactants failed to provide the synergistic combinations found in tristearin removal. Nevertheless surfactant soil removal was improved by STP combination.

PREVIOUS PAPERS (1,2,3) have dealt with the removal of radio-tagged tristearin or triolein from glass or quartz surfaces. This paper will present data for radio-tagged stearic acid and algal protein soil removal from glass to expand the possible application of the stripping or preferential displacement removal mechanism previously described. Differences in the bonding characteristics of these soils and shapes of the removal curves are to be compared with those of triglyceride fatty soils.

Experimental Procedures

The details of experimental procedure have been cited in previous papers (1,2,3), and only exceptions or additions will be mentioned. Each of the data points is the average of not less than three replicate measurements.

Materials Used

Ethylenediamine sodium tetraacetate (EDTA), commercial
Trisodium orthophosphate (TSP), commercial
Sodium tripolyphosphate (STP), commercial
Sodium metasilicate, commercial
Nonylphenol-10-EO (NP)
Dodecylphenol-10-EO (10 molar ethylene oxide adduct) (DDP)
Dodecylphenol-5-EO
Tridecanol- 5-EO(TDA)
Tridecanol-10-EO
Tridecanol-14-EO
Tridecanol-20-EO
Decanol-10-EO
n-Dodecanol-10-EO
Sodium dodecylbenzene sulfonate (NaDDBS)
Sodium tridecylbenzene sulfonate (NaTDBS)
Sodium pentadecylbenzene sulfonate (NaPDBS)
Sodium oleate, Fisher Scientific Company
Sodium lauryl sulfate (U.S.P.), Fisher Scientific Company

The nonionic surfactants were laboratory preparations from which the catalyst had been removed. The alkylbenzene sulfonates and the other anionics were essentially 100% active ingredients obtained by purification. The alkylbenzenes were cuts corresponding essentially to the carbon chain-lengths noted.

Soils

Tristearin (1.73 mcuries/mmole), Nuclear-Chicago
Triolein (0.12 mcuries/mmole), New England Nuclear
Algal protein (specific activity 0.234 μc/mg.), Nuclear-Chicago
Stearic acid (specific activity 2.52 mc./mmole), Nuclear-Chicago

Stearic acid soil was dissolved in carbon tetrachloride and diluted to a desired activity level and spot, or otherwise deposited.

The algal protein was dissolved in a tert-butanol-water mixture (49.5/49.5% by volume) and 1% (volume) of morpholine. A working solution (5500–6000 cpm./0.1 ml.) was tested, showing that the morpholine was volatilized from the spot-deposited film.

Monolayer Levels. Monolayer levels were obtainable for tristearin or -olein by after-washing with carbon tetrachloride (1,3). For stearic acid it was found that a 20-min. wash at 25°C. with absolute ethanol was needed to provide the monolayer level (Figure 5). Soil removal levels were the only data available for algal protein.

Data

Removal of Algal Protein. The proteinaceous soil was applied as a spotted application; the aging temperature variation was noted in Table I. It appeared that, with water removal, wash temperature, time, or aging temperature were not important variables, and the 80°C. aging temperature was adopted and used unless otherwise noted. For this work frosted glass was used, and polished substrate data are shown in Figure 2.

Protein soil removal values from polished glass surfaces by anionic, nonionic, and surfactant-STP compositions are shown in Figures 2,3, and 4.

Stearic Acid Soil. Films of both spotted and continuous applications of stearic acid were applied to frosted glass. The continuous films were applied by immersion of the disks in solutions of the tagged soils. Since carbon tetrachloride failed to remove stearic acid soil to the monolayer level as with tristearin, other solvent washes were used as shown in Figure 5. Absolute ethanol proved capable of removing soil only to the monolayer level.

Figure 6 shows water removal and water removal values, followed by STP washing. Figure 7 is a comparison of glass and quartz surfaces. Soil removal values for anionic and nonionic surfactants are given in Figures 8 and 9, while builder removal and the detergency values of surfactant-builder mixtures are shown in Figures 10 and 11.

Discussion

Algal Soil. The data of Table I show that soil aging and the amount applied, as well as water wash tem-

TABLE I

Algal Protein Soil—Frosted Glass Substrate (Usual Preparation)

20-Min. soil aging temp. (°C.)	Initial count (cpm.)	20-Min. water wash temp. (°C.)	Removal (%)	Residual (cpm.)
50	*ca.* 5,500	50	60.8	....
50	*ca.* 5,500	50[a]	63.0	....
50	*ca.* 5,500	50[b]	67.0	....
50	*ca.* 5,500	75	60.8	....
80	*ca.* 5,500	75	57.7	....
138	*ca.* 5,500	75	59.7	2220
50	*ca.* 11,000	75	59.7	4350
50	*ca.* 11,000	23	57.2	....

[a] 40-min. wash.
[b] 100-min. wash.

perature and wash time, had little effect upon soil removal. Approximately 57 to 60% of the soil from frosted glass was removed in a 20-min. wash period even though the factors mentioned were markedly varied. This suggested that a portion of the tagged material probably consisted of water-soluble protein fragments and that some of the amino acids were preferentially retained at certain adsorption sites. In either event the retained soil, which was cured on the surface by heat treatment, in tenacity somewhat resembled heat-degraded egg protein on cooking surfaces, and both are very difficult to remove in the washing operation.

Figure 1 demonstrates the removal of this soil from frosted glass, quartz, and porcelain surfaces. Tri-

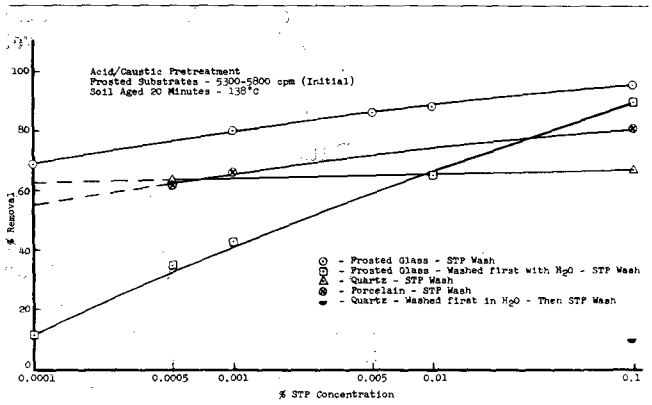

FIG. 1. Algal protein carbon-14 soil removal: tripolyphosphate concentration curves.

polyphosphate, when used in sufficient concentration (0.1% or greater), could approach complete removal, but quartz held the soil more tenaciously than did glass, suggesting greater affinity of the adsorption site for the soil, a greater number of adsorption sites, or a different type of adsorption, possibly the last.

It should be noted that the soil remaining after the water wash was much more resistant to removal than was the fresh surface washed with STP.

Initially polished glass had been used for tristearin work but had proved so easy to clean (few adsorption sites) that frosting to provide a greater number of sites had been resorted to. Since the frosted surface with protein soil had proved so retentive, experiments were made with polished glass. Here STP could achieve complete removal at concentration levels comparative with fatty soil, and a series of tests with nonionic surfactants was made (Figure 2).

The comparison of tridecanol-EO adducts for removal demonstrates also that, for this soil, the 10-mo-

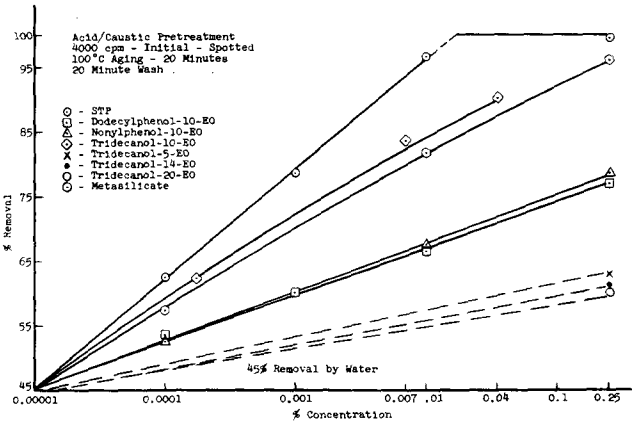

FIG. 2. Algal protein carbon-14 soil removal: nonionic surfactants with polished glass at 75°C.

lar ethylene oxide adduct is most effective of the 5,10, 14, and 20 EO levels. Little difference was apparent between the nonylphenol and dodecylphenol-10-EO products, and both were poorer than the tridecanol-10-EO adduct.

The considerably greater effectiveness of STP over sodium metasilicate is apparent as it was with tristearin soil.

Data for algal protein removal by anionic surfactants are given in Figure 3. Sodium oleate again was superior to the other anionics, as it was for fatty soil removal. Most important, the other anionics which, with fatty soil, were relatively ineffective, are with this soil as effective as the best nonionic. This would suggest a major difference, other than water removal, between the protein and fatty soils.

As with fatty soil, the combination of STP with surfactant (Figure 4) results in improvement in soil removal. The improvement is greatest for the surfactant least effective when used alone for removal. None of these mixtures was as effective as STP by itself when used at the same concentration.

The easy removal of a large portion of the protein soil by water may help to explain the lack of the sigmoid character of the removal curve. The shape of these curves does not appear to have any relation to critical micelle concentration, in contrast to oily soil, suggesting a difference in the type of soil adsorption or, expressed differently, a possible variation in the mechanism of soil removal as compared with oily soil.

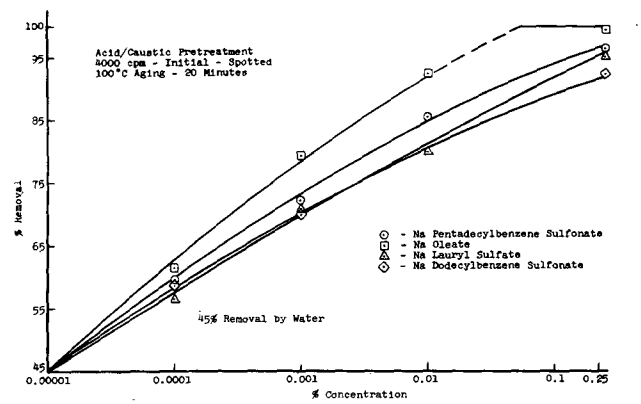

FIG. 3. Algal protein carbon-14 soil removal: anionic surfactants with polished glass at 75°C.

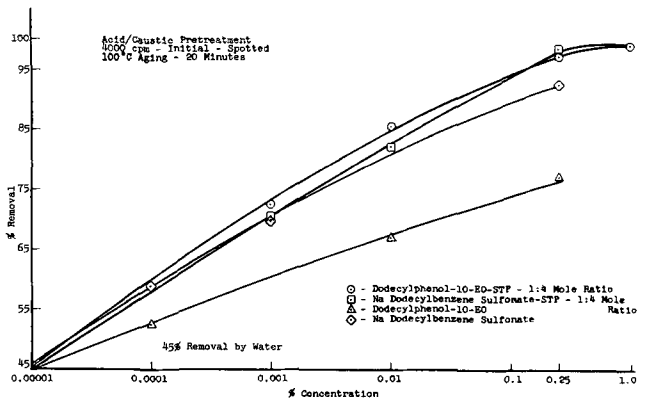

FIG. 4. Algal protein carbon-14 soil removal: surfactant-builder mixtures from polished glass at 75°C.

Stearic Acid Soil. Since a preliminary trial showed that a monolayer level was not approached for this soil by carbon tetrachloride washing, other solvents were investigated (Figure 5). It is apparent that only absolute ethanol provided the monolayer level of removal in the 20-min. wash interval. Longer washing time had no further influence on removal. These data suggest that cohesively bonded soil is removed only by a more polar solvent and that the cohesive bond energy for stearic acid is greater than for tristearin.

Figure 6 shows that water will remove 50% of the stearic acid soil (essentially zero for tristearin). Another curve shows that water-washing leaves an extremely energetically bound layer, which when washed at the higher STP solution concentrations approaches the monolayer. However, when the STP solution was used without prewashing with water, the soil removal was nearly complete. The explanation for these differences may lie in rearrangement of the soil either to cover more adsorption sites or to permit stronger or more effective bonding when the hot water wash is observed. Removal of half of the deposited soil may be through emulsification of the cohesively bound multilayer levels.

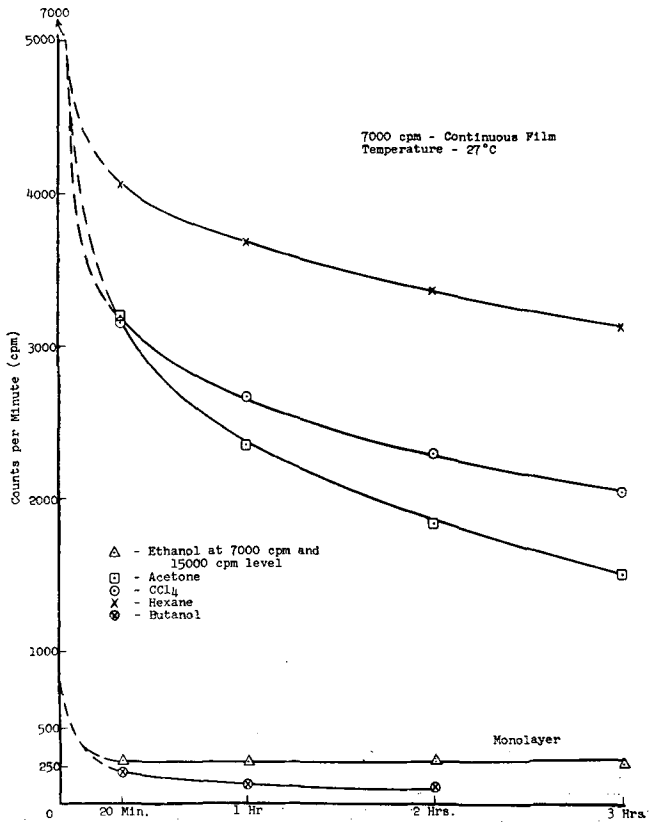

FIG. 5. Stearic acid carbon-14 soil: solvent wash/time study.

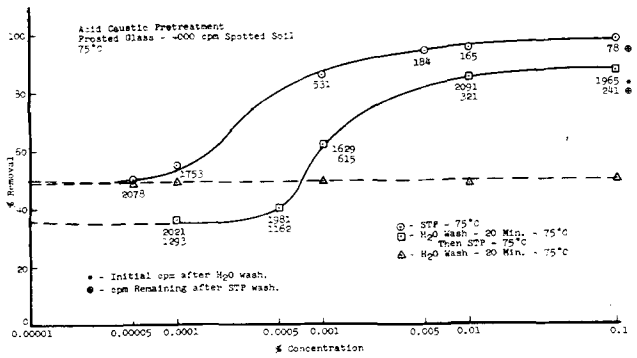

FIG. 6. Stearic acid carbon-14 soil: STP concentration curve.

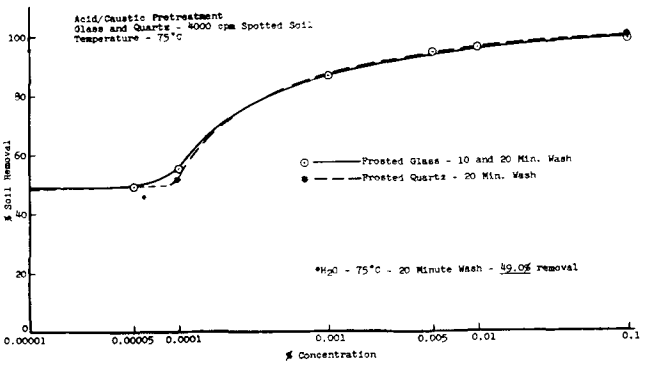

FIG. 7. Stearic acid soil: STP removal curve.

The STP removal curves (Figure 7) for glass and quartz are essentially identical, suggesting the same bonding mechanism.

The soil removal curves for both anionic and nonionic surfactants for stearic acid soil (Figures 8,9) resemble those for removal of tristearin. The sodium oleate curves for both soils are at a higher level than for the other anionics, and at 0.5% concentration the latter fall within a narrow range. The main excep-

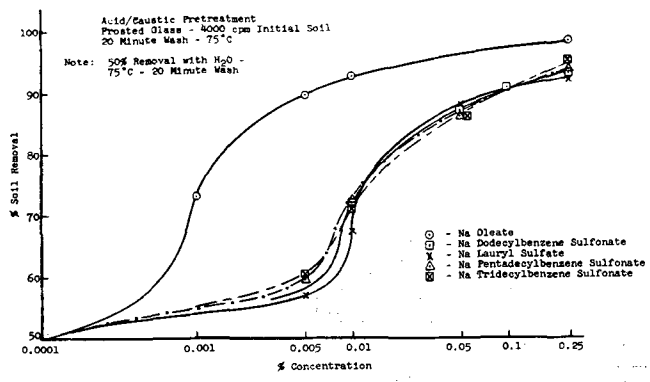

FIG. 8. Stearic acid carbon-14 soil: anionic surfactants.

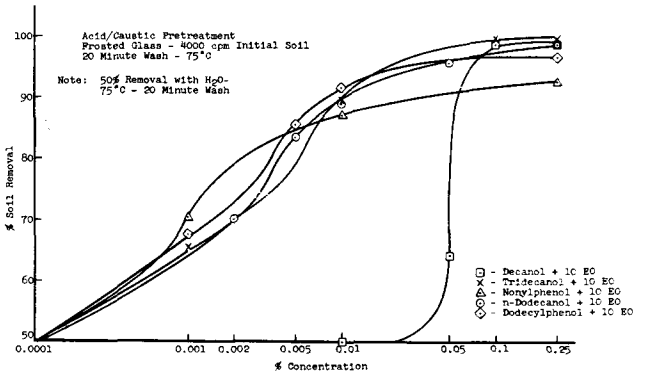

FIG. 9. Stearic acid carbon-14 soil: nonionic surfactant.

tion is sodium lauryl sulfate, which was ineffective with tristearin; but with stearic acid soil was as effective as the alkylbenzene sulfonates. Another difference is in level of removal, which is generally lower for tristearin soil.

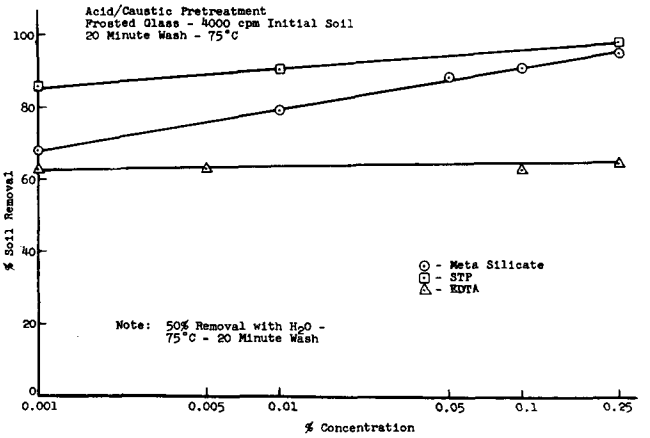

FIG. 10. Stearic acid carbon-14 soil: removal by builders.

Increase in soil removal level of anionics for protein and stearic acid soils may be at least partially ascribed to an ion-exchange mechanism.

Similarities also exist between the two soils when washed with nonionic surfactants. Though higher solution concentrations are required for tristearin removal, the shapes of the decanol-10-EO, nonylphenol-10-EO, and tridecanol-10-EO product curves are rather similar. The decanol product exhibits a similar sharp increase in effectiveness over a narrow, but higher concentration range.

Removal by builders, Figure 10, shows ethylenediamine sodium tetraacetate as relatively ineffective; and, at sufficiently high concentration, sodium metasilicate approached STP effectiveness. The shape of the EDTA and STP curves suggests that sequestration is not the controlling factor in stearic acid soil removal. STP has an additional unspecified quality.

Surfactant-STP built compositions, in general, were superior to the pure surfactant, and high removal levels were achieved at lower solution concentrations. Synergism was particularly notable at low solution concentration levels (Figure 11).

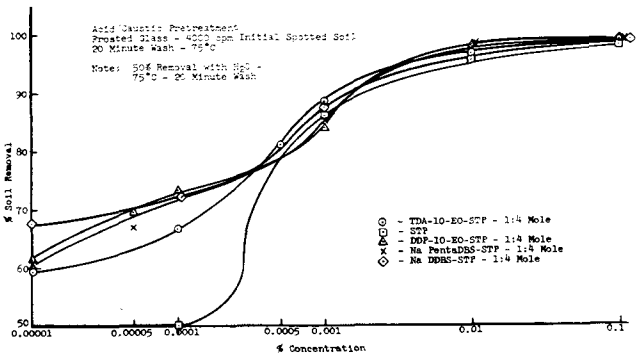

FIG. 11. Stearic acid carbon-14 soil: STP built compositions.

Effect of nonionic use at cloud-point temperatures closely duplicated the findings with triolein soil (3). Optimum removal for a given surfactant occurred at its cloud-point temperature, and, as before, only certain nonionics could be used most satisfactorily over a broad temperature range.

Decrease in deflection of the sigmoid portion of the stearic acid soil removal curves, as compared with tristearin, may be attributed to the influence of an ion-exchange mechanism.

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Determining Refining Loss by the Sodium Balance Method[1]

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The Sodium Balance Method is a rapid and reliable procedure for determining plant refining loss. By sodium analysis of each stream flow, treated crude, refined oil, and soap, the refining loss is calculated through substitution of sodium values for each component in an equation. The accuracy of this Sodium Balance Method for refining loss equals that of conventionally accepted methods, such as weight and total fat loss.

[1] Presented at the 34th Fall Meeting, American Oil Chemists' Society, New York, October 17–19, 1960.

REFINING LOSS is a measure of the efficiency of a refining operation. To the refiner this value is important for determining how effectively his plant is operating and for compliance with negotiated contract agreements under the accepted trading rules.

In either a batch- or continuous-refining operation the loss occurs in the soap phase. As a result of the chemical reaction and processing procedure the soap