

Radiotagged Soils. Removal from Several Substrates and Adsorption Site Character

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Substrates investigated were glass, quartz, porcelain, steel, stainless steel, aluminum, polyethylene, methylmethacrylate, Nylon, and Teflon. Radiotagged (C-14) soils used were algal protein, stearic acid, and tristearin. Soil removal curves showed that Nylon, Teflon, methacrylate, and stainless steel had few soil-adsorption sites and that the adsorption was of an ion-exchange type. Algal protein and stearic acid soils appeared to adsorb through an ion-exchange type mechanism, with most substrates, while tristearin showed a van der Waals' type of adsorption with glass, quartz, steel, and aluminum. Conclusions as to adsorption type were based upon the shape of the soil-removal curves.

Adsorption studies showed that both anionic and nonionic surfactants were adsorbed by glass, porcelain, steel, and aluminum surfaces, apparently by an ion-exchange type of adsorption. The character of the surfactant adsorbed affected the degree of removal of subsequently applied soil; the more hydrophilic surfactants permitted easier soil-removal. Triphosphate, orthophosphate, and ethylenediamine tetraacetate anions and tetraethylammonium cations were adsorbed by these same substrates and influenced the ease of removal of subsequently applied soil. Pretreatment of substrate by alkali generally increased the ion or surfactant adsorption more than acid-pretreated surfaces, and rather marked similarities between the adsorption sites of glass and quartz were apparent from acid pretreatment.

Stearic acid soiled substrates were cleaned by a preferential displacement mechanism; the soil was rolled up into globules. Tristearin-soiled surfaces were cleaned by a similar mechanism.

REMOVAL of radiotagged tristearin, triolein, stearic acid, and algal protein soils from siliceous substrates has been reported (1,2,4,5). Quartz, glass, and porcelain surfaces have shown slight differences in adsorption-site characteristics but have served to demonstrate that the removal of soil is a preferential displacement mechanism. An object of this paper is to show the mechanism of soil removal from these and other substrates.

The previous reports have shown that sodium triphosphate (STP) appears to act by adsorbing on certain substrate sites so that subsequently deposited soil becomes much easier to remove. It would be suspected that this mechanism of STP adsorption would be one of ion-exchange, but only slightly polar soils, such as the triglycerides, might be expected to adsorb, not at ion-exchange sites, but at other primary sites, probably as a result of van der Waals' attractive forces. An attempt will therefore be made to describe more clearly these adsorption phenomena and to characterize the adsorption type with various soils and substrates.

Experimental Procedures. The details of experimental procedure have been cited in previous papers (1,2,4,5), and only exceptions or additions will be mentioned. Each of the data points or values is the average of not less than three replicate measurements.

Materials Used. Ethylenediamine sodium tetraacetate (EDTA), commercial
Trisodium orthophosphate (TSP), commercial
Sodium triphosphate (STP), commercial

Tetraethylammonium bromide, Eastman
Dodecylphenol-10-EO (10 molar ethylene oxide adduct) (DDP)
Dodecylphenol-5-EO
Tridecanol-10-EO (TDA)
n-Dodecanol-10-EO
Sodium dodecylbenzene sulfonate (NaDDBS)

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

Soils. Tristearin (1.73 meuries/mole), Nuclear Chicago
Triolein (0.12 meuries/mole), New England Nuclear
Algal protein (specific activity 0.234 $\mu\text{c}/\text{mg}.$), Nuclear Chicago
Stearic acid (specific activity 2.52 mc./mole), 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 (1:1 by volume), containing 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. The feature that makes the foregoing work feasible is the fact (1) that frosted glass slides, though soiled with excess radiotagged tristearin or triolein, retain a monomolecular layer of the tagged soil when washed in carbon tetrachloride. This characteristic effect was repeatedly demonstrated and was verified by measurements of actual surface areas of the slides by various procedures and other measurable adsorbate materials. For stearic acid a 20-min. wash at 25°C. with absolute ethanol resulted in the same phenomenon of removal only to the monolayer level. Soil-removal levels were the only data available for the algal protein soil.

Other Substrates. A porcelain surface was obtained through the courtesy of the Syracuse China Corporation. Metals used were stainless steel 304, 2B finish, SAE 1010 cold rolled steel; and 2024-T6 aluminum.

Plastic materials used were sheet stock of methylmethacrylate; Teflon; Nylon 101; and polyethylene of two types, low density-high pressure and high density-low pressure.

Disk Pretreatment. For glass the normal pretreatment is with acid followed by alkali (0.5% solutions for 5 min. at the boil), but, for following treatment by other materials, either an acid or alkali primary pretreatment was used. Secondary pretreatments followed the primary ones, at the solution temperatures noted, and were further followed by a 2-min. rinse at room temperature with distilled water.

Primary pretreatment of aluminum, steel, and stainless steel disks consisted of degreasing with carbon tetrachloride, use of 0.1% HCl or NaOH at 50°C. for 1 min., and a water rinse. Aluminum disks appeared unchanged but apparently were coated with a thin layer of hydrous oxide. Steel surfaces rusted easily after treatment unless stored in a desiccator. No change in stainless steel surfaces was apparent.

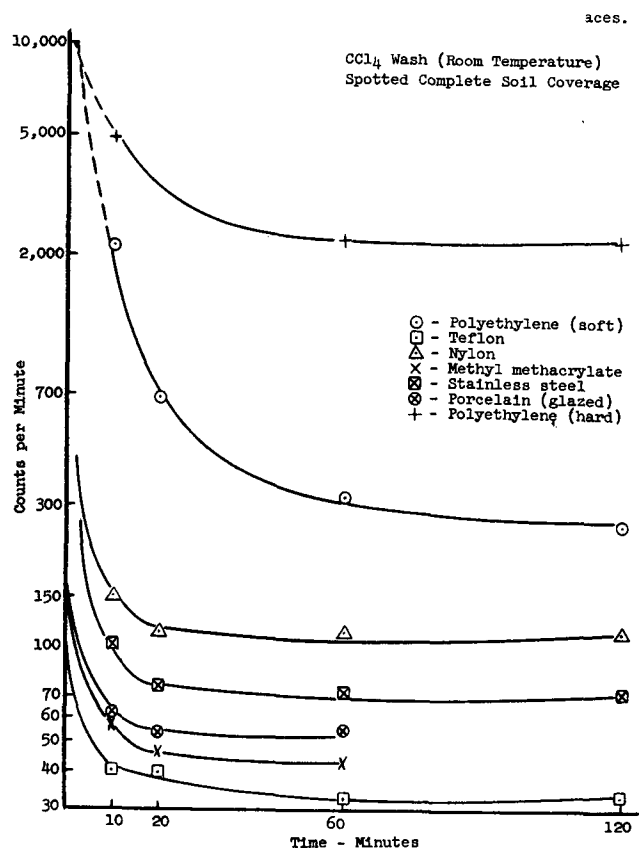


FIG. 1. Tristearin soil removal from various surfaces.

Data

Soil Removal from Other Substrates. Figure 1 provides carbon tetrachloride removal curves vs. wash time for a variety of substrates soiled with tristearin. Figure 2 shows removal value/concentration curves for the n-dodecanol-10-EO adduct, and Figure 3 the same for the dodecylphenol-10-EO adduct with other substrates.

Removal of algal protein soil by STP from a variety of substrates is shown in Figure 4.

Characterization of Substrate Surface. Attempts were made at characterization of the adsorption sites on glass and metal surfaces, using the primary and secondary pretreatment techniques described above. Only spotted soil applications were examined. Comparisons following soiling were made between the primary pretreated surface and those with secondary pretreatment, first by carbon tetrachloride washing to reveal the extent of true monolayer retained, followed by a surfactant wash, then another carbon tetrachloride wash to remove soil multilayers piled up by the surfactant through preferential displacement.

Table I shows the adsorption of surfactant on frosted glass surfaces and the effect of hydrophobe-hydrophil length of a poor detergent.

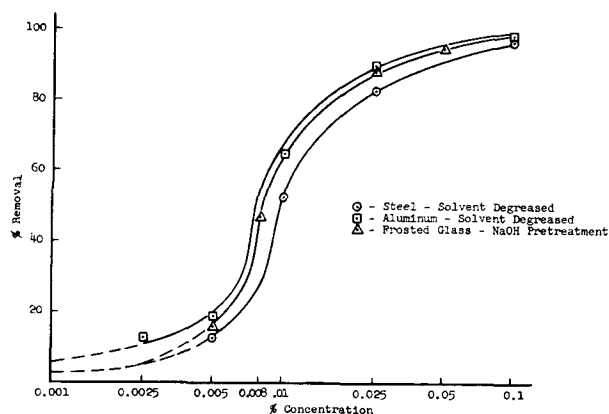


FIG. 2. Tristearin soil: surfaces washed with n-dodecanol-10-EO. Glass: 3500-4000 cpm spotted soil Metal: 4500-5000 cpm spotted soil Wash temperature, 75°C.

The effects upon soil retention by surfactant adsorption on glass, steel, aluminum, glazed and frosted porcelain are given in Table II.

The effects of pretreatment with various anions and cations upon soil adsorption are shown in Table III. Similar data for stearic acid soiled disks are shown in Table IV.

Discussion

Removal from Various Substrates. Since tristearin may be removed from glass to a monolayer level by a carbon tetrachloride wash, comparative values with other substrates were attempted (Figure 1). The wide disparity between removal levels is related to the character and number of adsorption sites present on a given surface. Further affecting soil adsorption (and ease of removal) are molecular density and character of surface, chemical reactivity of the substrate, and (implied) the free surface energy of the material. Teflon, a polymer of extremely low surface energy (3), is not easily wetted by the soils and exhibits a minimum of adsorption sites. Stainless steel is soiled to a less retentive level than is steel. The fewer the adsorption sites, the more readily is soil removed, and soil removal levels for Teflon, Nylon, methyl methacrylate, and stainless steel relative to glass, are extremely low. Polyethylene, though of relatively low surface energy, retains fatty soil through a dissolution process, recognized for a num-

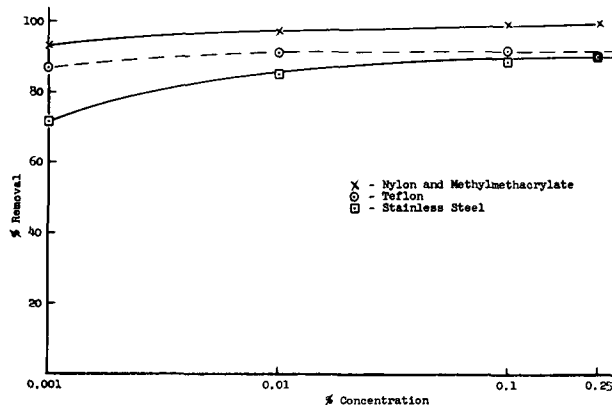


FIG. 3. Tristearin soil removal studies: various substrates. 3500-4000 cpm spotted soil 75°C. 20-min. wash with dodecylphenol-10-EO

ber of fatty cosmetic materials. The difference between the two polyethylene types may be attributed to differences in molecular weight and molecular packing. The decreasing order of soil retention was: polyethylene (hard); polyethylene (soft); Nylon; stainless steel; porcelain (glazed); methylmethacrylate; and Teflon.

Removal of tristearin from steel, aluminum, and glass substrates by *n*-dodecanol-10-EO solutions provided the curves of Figure 2. The several substrates gave the same type of sigmoid removal curve. Steel gave consistently lower removal values, attributable either to fewer or weaker adsorption sites. The aluminum and glass curves were almost identical in spite of their surface and chemical differences. In contrast, a normally less effective detergent for tristearin, dodecylphenol-10-EO, very easily removed soil at very low solution concentrations from Nylon, methyl methacrylate, Teflon, and stainless steel surfaces, confirming the scarcity of adsorption sites suggested by the solvent washes of Figure 1. Absence of the sigmoid type of removal curve should be noted.

The importance of the shape of the soil-removal curve frequently is overlooked. Comparison of Figures 2 and 3 shows the marked differences in these substrates for their retention of the soil. Obviously the number of adsorption sites affects apparent ease of removal, but the fact that complete removal is difficult to attain with otherwise easily cleaned substrate suggests a very strong soil bonding on a few sites.

The relatively sharp release of soil over a narrow concentration range for glass, steel, and aluminum (Figure 2), with their sigmoid shape of removal curves, compared with the low concentration dependence of the substrates of Figure 3, indicates a marked difference in adsorption-site character for these substrates. The relatively linear soil-removal curves suggest a type of ion-exchange, and the sigmoid shape suggests that for a given detergent concentration an energy barrier is lowered to release soil. This suggests a van der Waals' type of soil adsorption.

Algal protein soil (Figure 4) was removed from aluminum, polished glass, stainless steel, steel, and Teflon surfaces rather easily by STP; glass showed more complete removal and at a lower solution-concentration than for the other surfaces. The most retentive surface was the relatively porous aluminum substrate. The somewhat linear shape of these soil-removal curves more nearly resembles a type of ion-exchange adsorption. Increasing detergent concentration increments gradually and regularly release soil over a broad concentration range. This curve shows that the protein soil is adsorbed differently from the fatty soil, so that kind of substrate and soil affect type of adsorption. For example, glass gives a van der Waals' type of adsorption with tristearin, and an ion-exchange type with the protein soil. However adsorption of tristearin on Nylon or Teflon is not of the van der Waals' type but more nearly resembles an ion-exchange.

The comparative data of Figure 5 show the shape of the soil-removal curves by either STP or the tridecanol-10-EO adduct from glass for the several soils. The regular, almost linear shape of the protein and stearic acid soils, with high initial water removal, shows gradual soil release as a function of detergent concentration. (Curves for removal of these two soils by the tridecanol-10-EO product rather closely paralleled the STP curves and therefore are not shown.)

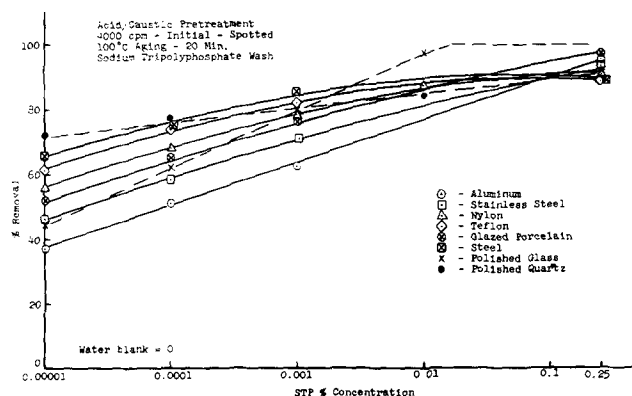


FIG. 4. Algal protein C-14 soil removal: various substrates at 75°C.

The sigmoid shape of tristearin soil-removal curves by the two detergents is more prominent with STP than with the tridecanol adduct. Differences between the curve shapes are attributable to differences in detergent ability to "neutralize" the attractive adsorptive soil energy forces.

Adsorption Site Character. It is generally considered that adsorbates are distributed over a surface as patches. These patches cover primary adsorption sites with possible over-run mechanically held or cohesively bound to the adsorbate at the primary site. Spotted soil as applied certainly does not cover all the primary sites, but free adsorption by exposure to a solution of the adsorbate should effectively cover them. An experiment (4) with stearic acid soil in which water-washing resulted in a more energetically bonded soil is a good example, for this soil must have been effectively redistributed and soil removal then became much more difficult. That soil patches leave apertures to the substrate surface where surfactant solutions can preferentially displace soil is evident by comparing spotted with continuous tristearin films (2). A continuous film of tristearin required 25-fold higher STP concentration for initial removal and never closely approached the final removal value for spotted soil. These findings strengthen the preferential displacement explanation of the removal mechanism for STP systems.

Experiments were designed to determine whether surfactants were adsorbed on glass or other substrates. These were carried out by exposure of the surface to the surfactant solution (then rinsing and drying), followed by soil deposition. The soil applied

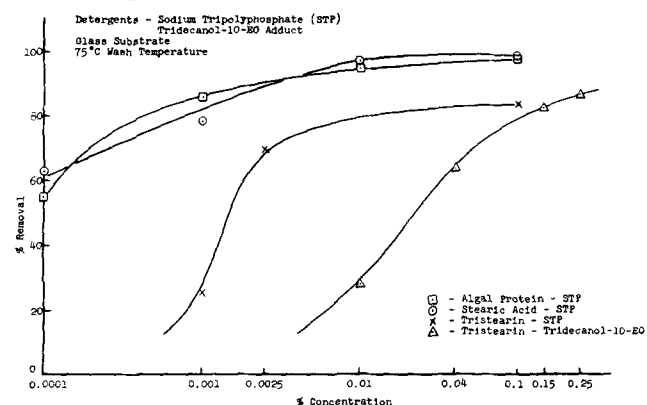


FIG. 5. Soil removal curves: three soils.

TABLE I

Surfactant-Pretreated Frosted Glass Surfaces

Tristearin soil, 251 cpm per monolayer

Spotted soil application

3500-4000 cpm radiotagged tristearin

(Secondary pretreatment comprising wash in 0.5% surfactant solution, rinsing, drying, before soiling)

Secondary treatment	Wash	% Soil removal	Remaining cpm
Dodecylphenol-10-EO			
Regular soil	CCl ₄	93.8	242
Pretreatment	CCl ₄	94.4	226
Regular soil	0.5% DDP-10-EO	77.9
Pretreatment	0.5% DDP-10-EO	87.2
Dodecylphenol-5-EO			
Regular soil	CCl ₄	93.8	242
Pretreatment	CCl ₄	95.2	99
Regular soil	0.5% DDP-5-EO	25.4
Pretreatment	0.5% DDP-5-EO	7.4
Sodium dodecylbenzenesulfonate			
Regular soil	CCl ₄	93.8	242
Pretreatment	CCl ₄	92.5	287
Regular soil	0.5% NaDDBS (pH 7)	11.8
Pretreatment	0.5% NaDDBS (low pH)	68.5
Pretreatment	0.5% NaDDBS (pH 7)	37.7

was sufficient, if evenly deposited, to provide about 15 monolayer levels over the surfactant-pretreated surface. In the absence of pretreatment a wash with carbon tetrachloride would lower the soil level to a single monolayer. Consequently, if surfactant adsorption had covered available soil-adsorption sites, more soil should thus be removed, and the residual soil level should be less than for the unpretreated surface. After-washing in aqueous solution with the same surfactant should show greater soil removal than a surface not pretreated with surfactant before soiling. This should follow since the soil had fewer primary sites to adhere to, and soil-to-surfactant bonds are much weaker than the soil-to-primary-site bonding. In preferential displacement the soil poorly bonded should be rolled up into globule form. Following this, a carbon tetrachloride wash would result in dissolution of the coherently-bonded soil in the globule, leaving only the partial monolayer of adhesively-bonded oil. Table I shows that both nonionic and anionic surfactants are adsorbed. Pretreatment with DDP-5 EO product indicated a considerable degree of adsorption as the remaining counts after a carbon tetrachloride wash indicate. Further, when this product was used to wash the soiled surfaces, it appeared either to redistribute the applied soil or to act as a bonding surface, or both. Sodium dodecylbenzene sulfonate was also adsorbed and, when used as a washing agent, acted in a manner similar to the DDP-5 EO adduct.

Table II expands the number of substrates tested and includes both an alkali and acid primary pretreatment. Values for the monolayer levels are shown; the carbon tetrachloride wash indicates the initial degree of adsorption of radiotagged tristearin. Values above or below that for the control (no secondary pretreatment) indicate the degree of adsorption of the secondary pretreating agent. Similar comparisons for the nonionic wash supplement the solvent wash data. The primary pretreatment had considerable effect upon both surfactant and soil adsorption. An increase in soil adsorption occurred with NaOH pretreatment for glass and aluminum while acid increased the adsorption for steel, suggesting activation of adsorption sites by such treatments. In general, the surface which adsorbed most surfactant gave the least soil adsorption and was most effectively cleaned.

After a demonstration of surfactant adsorptions and their effect upon soil removal, a series of adsorption tests was made with types of anions and cations.

The objective of these adsorption studies was to determine whether anion or cation adsorption occurred with various substrates, how it varied, and the effect upon soil removal or retention.

Table III shows the effect of preadsorption of anions and cations upon tristearin soil retention, and Table IV shows similar data for stearic acid soil. Effect of primary pretreatment may be shown by comparison of controls (no secondary pretreatment before soiling). Adsorption of anion or cation was shown by increase or decrease in the soil monolayer level over the control.

In general, all four pretreatment materials were adsorbed by the substrates, with a few exceptions, and to a greater extent after alkaline pretreatment. TEAB, the cation type of adsorbate, was slightly-to-moderately adsorbed, resulting in some cases in an increase in soil retention but more generally in a slight reduction.

The number of adsorption sites on NaOH pretreated glass were increased considerably over that treated with HCl. NaOH pretreatment of quartz slightly affected adsorption, the sites were of a different character, but the HCl pretreatment of both quartz and glass produced remarkably similar adsorption sites according to monolayer retention.

Acid pretreatment of aluminum generally reduced the number of adsorption sites, but this was the most adsorptive substrate of those tested. The stearic acid monolayer level for steel after the final ethanol wash (which removed cohesively-bound soil in the form of retracted globules) was much the same whether HCl or NaOH had been used for pretreatment even though initial monolayer levels varied. Acid pretreatment of stainless steel tended to cause increased retention of soil, but the values varied considerably. In general, the surfactant wash of the acid pretreated and soiled stainless steel surfaces tended to redistribute the soil while the NaOH pretreatment tended to cause more complete soil release.

TABLE II

Remaining Monolayer

Tristearin spotted soil, 3500-4000 cpm. Monolayer, 177 cpm for metal or glazed porcelain; 251 for frosted glass

Surface	Secondary pretreatment ^b	NaOH Primary ^a		HCl Primary ^a	
		CCl ₄ wash ^c	Nonionic wash ^d	CCl ₄ wash	Nonionic wash
Frosted glass	None	1.12	0.25	0.79	0.08
	DDP-10-EO	0.67	0.18	0.57	0.06
	DDP-5-EO	0.65	0.12	0.36	0.04
	NaDDBS pH 7	0.80	0.20	0.67	0.08
Steel	None	1.12	0.22	2.92	0.53
	DDP-10-EO	1.29	0.37	1.54	0.62
	DDP-5-EO	0.98	0.38	1.04	0.31
	NaDDBS pH 7	1.35	0.27	1.02	0.80
Aluminum	None	9.1	3.64	1.16	1.36
	DDP-10-EO	8.5	3.26	1.70	0.55
	DDP-5-EO	2.38	0.92	1.37	0.45
	NaDDBS pH 7	3.02	2.12	2.13	1.01
Glazed porcelain	None	0.39	0.15	0.27	0.18
	DDP-10-EO	0.33	0.14	0.26	0.22
	DDP-5-EO	0.27	0.17	0.22	0.18
	NaDDBS pH 7	0.29	0.21	0.32	0.19
Frosted porcelain	None	0.27
	DDP-10-EO	0.35
	DDP-5-EO	0.26
	NaDDBS pH 7	0.27

^a Primary pretreatment: Glass—NaOH, 0.5%, 100°C., 5 min.; HCl, 0.5%, 100°C., 5 min. Metal—degrease with CCl₄; NaOH or HCl, 0.1%, 50°C., 2 min.; degrease with CCl₄.

^b Secondary pretreatment: 0.5% surfactant, 5 min., 75°C., rinse 2 min. with distilled water, room temp.; DDP-5 or -10-EO, dodecylphenol; NaDDBS, sodium dodecylbenzenesulfonate.

^c 20-min. wash at room temperature.

^d 20-min. wash, 0.25% dodecylphenol DDP-10-EO at 75°C.

TABLE III

Effect of Pretreatment, Tristearin-Spotted Soil
Tristearin spotted soil, 3500-4000 cpm initial. Monolayer, 177 cpm for metal; 251 for glass

Surface	Secondary pretreatment ^c		NaOH Primary ^b		HCl Primary ^b	
			Initial mono-layer	After nonionic wash ^d	Initial mono-layer	After nonionic wash ^d
Frosted glass	None	0.88	0.25	0.41	0.06
	TEAB ^a	0.5	0.53	0.16	0.35	0.12
	STP	0.5	0.65	0.16	0.79	0.08
	EDTA	0.5	0.69	0.08	0.72	0.20
	TSP	0.5	0.71	0.16
Aluminum	None	2.27	2.24	0.94	0.19
	TEAB	0.5	6.38	9.20	8.15	4.01
	STP	0.5	1.89	0.55	1.39	0.24
	EDTA	0.5	0.80	0.20	0.88	1.13
	TSP	0.5	1.75	0.28	0.85	0.25
Steel	None	0.67	0.40	1.14	0.16
	TEAB	0.5	1.26	0.59	5.79	0.43
	STP	0.5	0.42	0.19	0.79	0.22
	EDTA	0.5	0.83	0.22	1.18	0.24
	TSP	0.5	0.39	0.16	1.57	0.13

^a TEAB—tetraethylammonium bromide
^b STP—sodium tripolyphosphate
^c EDTA—ethylenediamine sodium tetraacetate
^d TSP—trisodium orthophosphate.

^b Glass pretreated with 0.5% NaOH or HCl, 5 min. at boil. Metals pretreated with 0.1% NaOH or HCl for 1 min. at 50°C.; degrease with CCl₄.

^c At concentration noted at 100°C. for 5 min., rinse 2 min. with distilled water at room temperature.

^d 0.25% solution at 75°C.: glass with DDP-10-EO; metals with n-decanol-10-EO.

As might be expected, differences in the magnitude of the monolayer between comparable primary and secondary pretreatments for the two soils was apparent, but the trends appeared to be the same.

The ethanol wash for stearic acid soil, following the nonionic surfactant wash, indicated that in most instances the surfactant had caused lowered surface coverage by rolling the soil up into multilayered globules though in a few instances the removal had proceeded to the monolayer stage. Consequently, though the removal count after the surfactant wash was nearly identical with the initial monolayer, the fact that cohesively-bound globular soil could be removed by ethanol indicated that preferential soil displacement on the surface had occurred (apparently sufficiently high concentration for soil removal to occur had not been reached).

Summary and Conclusions

Tristearin may be removed by carbon tetrachloride to different levels, dependent upon substrate adsorption-site level. With glass retaining a monolayer level, the decreasing order of soil retention was: polyethylene (hard); polyethylene (soft); glass; Nylon; stainless steel; porcelain (glazed); methylmethacrylate; Teflon. The low surface energy of several of these substrates may be correlated with the scarcity of adsorption site for this soil. Polyethylene, though a low surface energy substrate, retained soil through a dissolution mechanism.

Tristearin removal curves by aqueous solutions of surfactants for steel, aluminum, and glass were entirely different in character from the almost linear curves of the low energy Nylon, methacrylate, and Teflon substrates. This suggested a difference in the type of adsorption between these classes of substrate.

The sigmoid-shaped tristearin-removal curves from glass and certain other substrates were replaced by nearly linear curves with algal protein soil and stearic acid soil. This suggested for the linear concentration-dependent curves for substrates or soils that

these were ion-exchange type of adsorptions, being only slowly removed at increasing detergent concentration. In contrast, the polar but essentially nonionic tristearin was removed from glass, aluminum, and steel in sigmoid-shaped curves, suggesting a soil adsorption energy potential level satisfied over a comparatively narrow detergent concentration range, *i.e.*, that the soil adsorption was of the van der Waals' attractive type.

It was demonstrated that both nonionic and anionic surfactants were adsorbed by glass, steel, aluminum, and porcelain surfaces. The primary pretreatment of the substrate with NaOH increased surfactant adsorption for glass and aluminum while HCl pretreatment increased the surfactant adsorption for steel, suggesting activation of adsorption sites by such treatment.

Alkaline substrate (glass, aluminum, quartz, steel, and stainless steel) pretreatment generally increased the adsorption of tripolyphosphate, orthophosphate, and ethylenediamine tetraacetate anions and tetraethylammonium cations as compared with the acid pretreatment. Pretreatment of glass with NaOH considerably increased the number of adsorption sites over the acid pretreatment, and both glass and quartz adsorption sites were remarkably similar after the acid pretreatment. Acid pretreatment of stainless steel tended to increase the number of adsorption sites.

The various primary and secondary pretreated stearic acid soiled disks, when surfactant-solution washed, showed that the soil had been rolled up into multilayered globules, demonstrating the preferential soil displacement phenomenon.

TABLE IV
Effect of Pretreatment, Stearic Acid-Spotted Soil

253 cpm for glass 133 cpm for metal		Initial Count 3500-4000 cpm					
		NaOH—Primary Pretreatment ^a			HCl—Primary Pretreatment		
Surface	Secondary pretreatment ^b	Initial mono-layer ^c	After DDP-10 EO Wash ^d	EtOH wash ^e	Initial mono-layer	DDP-10 EO wash	EtOH wash
Frosted glass	None	1.25	1.29	0.94	0.29	0.20	0.12
	TEAB ^f	1.24	1.28	0.90	0.36	0.29	0.24
	STP	0.30	0.20	0.17	0.34	0.41	0.15
	EDTA	0.37	0.14	0.11	0.32	0.20	0.20
	TSP	0.22	0.51	0.27	0.33	0.42	0.22
Frosted quartz	None	0.99	0.17	0.13	0.38	0.30	0.19
	TEAB	0.23	0.17	0.13	0.34	0.32	0.17
	STP	0.30	0.15	0.13	0.52	0.25	0.20
	EDTA	0.27	0.21	0.18	0.31	0.31	0.21
	TSP	0.23	0.28	0.27	0.30	0.46	0.31
Aluminum	None	6.4	13.3	8.6	1.67	5.3	1.04
	TEAB	5.6	10.6	7.2	3.34	8.1	6.2
	STP	8.8	7.6	5.8	7.8	6.2	4.2
	EDTA	4.3	10.0	7.5	1.49	3.5	4.4
	TSP	9.4	9.8	7.0	8.0	5.3	2.24
Steel	None	1.36	1.49	0.87	2.08	1.54	0.89
	TEAB	2.22	1.73	1.33	2.16	2.06	1.39
	STP	1.07	1.68	1.06	2.22	1.12	1.10
	EDTA	1.75	1.17	0.87	1.77	1.39	0.96
	TSP	0.48	2.10	1.28	1.15	1.71	1.28
Stainless steel	None	2.22	1.38	0.57	1.64	1.56	0.79
	TEAB	0.81	0.61	0.54	0.55	2.67	0.77
	STP	0.64	0.34	0.32	1.10	2.72	0.74
	EDTA	1.02	0.80	0.45	1.22	0.66	0.49
	TSP	0.62	0.30	0.57	0.57	1.63	0.70

^a Primary pretreatment, glass—0.5% HCl or NaOH, 5 min., 100°C.; metal—0.1% HCl or NaOH, 1 min., 50°C., degreased

^b Secondary pretreatment, 0.5% at 100°C., 5 min. Rinse 2 min. with distilled water, dry.

^c Initial monolayer by EtOH, 20-min. wash at 25°C.; 253 cpm.

^d Dodecylphenol—10 EO wash, 0.25%, 75°C., 20 min.

^e EtOH was as in "c," following DDP, 10 EO wash and count.

^f TEAB—tetraethylammonium bromide
STP—sodium tripolyphosphate
EDTA—ethylenediamine sodium tetraacetate
TSP—trisodium orthophosphate.

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The Comparative Value of Heated Ground Unextracted Soybeans and Heated Dehulled Soybean Flakes as a Source of Soybean Oil and Energy for the Chick

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Experiments were conducted to evaluate heated unextracted soybean fractions as sources of soybean oil and protein for the growing chick. Heated dehulled unextracted soybean flakes produced growth rate and feed efficiency equal to that obtained with the combination of soybean oil meal and degummed soybean oil while heated ground unextracted soybeans were less satisfactory in this respect. The poorer results obtained with ground unextracted soybeans were shown to be related to a poorer absorbability of the oil in them. Flaking the soybeans markedly improved the absorbability of the oil by the chick, probably by causing a greater disruption of cellular structure than was obtained by the grinding of the soybeans. The metabolizable energy of ground unextracted soybeans was substantially less than that of unextracted soybean flakes. Most of the differences in metabolizable energy were accounted for by differences in absorbability of the oil.

Soybean hulls at a level equivalent to that contained in soybeans were found to have no effect on growth rate and only a slight effect on feed efficiency. Autoclaving soybean oil did not lower its value for the chick. The relationship between the poorer growth obtained with ground unextracted soybeans and the low absorbability of the oil in them was discussed.

To obtain maximum efficiency in the use of unextracted soybean products in chick rations, some such means as flaking must first be employed to increase the availability of the oil.

HIGHLY unsaturated vegetable oils are excellent sources of energy for the chick and have also been shown to increase rate of growth in chicks (1,2). Low dietary levels of soybean oil have been reported to improve growth rate by several workers, using practical or semipurified diets (3,4,5,6), while studies with purified diets have shown that approximately 10% soybean oil is needed for maximum growth response (2).

The work to be described was undertaken to determine the ability of unextracted soybean products to serve as a source of both soybean oil and protein for the chick. In a preliminary report (7) heated dehulled unextracted soybean flakes were shown to be as effective as the combination of soybean oil meal and degummed soybean oil in semipurified chick diets, based on measurements of growth rate of chicks and efficiency of feed utilization. Renner and Hill (8) reported a lower metabolizable energy value for heated

ground unextracted soybeans than expected from the energy values that were previously determined for soybean oil and soybean oil meal. This was shown to result from incomplete utilization of the oil in the soybeans and provided an explanation of the failure of heated ground soybeans to stimulate growth in earlier studies in this laboratory.

Further studies on the growth-stimulating effect and metabolizable energy values of unextracted soybean products in chick diets are presented in this paper.

Materials and Diets

The two semipurified reference diets used in these experiments are shown in Table I. One (I) is the low-fat basal diet (1.5% fat) used as the negative control, and the second (II) is the soybean oil-supplemented diet (14.3% fat), which served as the positive control. The diets were based largely on glucose and soybean oil meal and were supplemented with adequate amounts of all vitamins and minerals known

TABLE I
Composition of Low-Fat Basal and Soybean Oil Reference Diets

Ingredients	Diet I	Diet II
	Low-fat basal diet ^a	Soybean oil diet ^a
	%	%
Glucose (Cerelese).....	46.6	23.8
Soybean oil meal (50% protein).....	41.0	48.7
Soybean oil, degummed.....	12.8
Constant ingredients.....	12.4	14.7
Dried fish solubles.....	0.50	0.60
Corn distillers dried solubles.....	2.00	2.38
Dried whey.....	2.00	2.38
Corn oil or soybean oil.....	0.50	0.60
DL-Methionine.....	0.15	0.18
Glycine.....	0.50	0.60
Limestone.....	1.83	2.18
Dicalcium phosphate.....	1.30	1.55
Iodized salt.....	0.60	0.71
Manganese sulfate.....	0.03	0.04
Chromium oxide mix (30% Cr ₂ O ₃).....	1.00	1.19
Mineral mixture ^b	1.15	1.37
Vitamin mixture ^b	0.82	0.95
Diphenyl-p-phenylenediamine.....	0.01	0.01
Butylated hydroxytoluene.....	0.01	0.01

^a All proportions are on a dry-matter basis.

^b Mineral and vitamin mixtures supply, in mg./100 g. of basal diet: 870 KH₂PO₄, 240 MgSO₄, 0.3 NaI, 28 FeSO₄·7H₂O, 0.8 CuSO₄·5H₂O, 6.3 ZnO, 0.17 CoCl₂·6H₂O, 0.83 Na₂MoO₄·2H₂O, 0.022 Na₂SeO₃, 1.0 thiamine, 1.0 riboflavin, 4.0 calcium D-pantothenate, 2.0 pyridoxine HCl, 8.0 niacin, 0.3 folacin, 0.3 menadione, 0.04 biotin, 0.005 vitamin B₁₂, 1.0 chlortetracycline, 147 choline chloride; 3.3 I.U. alpha-tocopheryl acetate, 1,000 I.U. vitamin A, 150 I.C.U. vitamin D₃.

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