Studies of Soiling and Detergency

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Abstract

A study was made of the desorption of carbon-14 labeled fatty acid, fatty alcohol, hydrocarbon, triglyceride, and hydrophobic and hydrophilic particulate carbon from cellulose, Nylon, and polyethylene terephthalate films into aqueous solutions of cationic, anionic, and nonionic detergents. Use of the polymers in film form as end-windows of a Geiger counter and labeling of the soils with radioactive carbon-14 allowed continuous monitoring of the amount of sorbed material and normalized the usual complication of fiber and fabric geometry so that results obtained with different polymers could be directly compared.

An excellent correlation was established between fatty soil removal from polyethylene terephthalate film and fabric surfaces; thus results obtained with film substrates have practical significance. Wash variables were carefully controlled and were altered one at a time to learn their effect on the soil-removal process. Results are discussed in terms of the possible mechanisms of soil removal.

Introduction

KEEPING CLEAN is an old problem, and soiling and detergency are much studied subjects. Yet there are still unanswered questions. How does the chemical make-up of a soiled surface affect the nature of the soil which deposits on it, and the rate at which this soil is removed in a detergency process? Are optimum conditions for removing soil from one kind of substrate also optimum for removing soil from other substrates? Which of the proposed mechanisms of detergency are kinetically important, and is this importance affected by changes in substrate, soil, and wash conditions? One can think of others.

These questions are of great practical as well as theoretical interest. Nearly all studies of textile detergency have been focused on cellulose, yet the problem of keeping cotton fabrics clean has not been completely solved. Bluing agents were used to hide residual soil on cellulose for many years. Now substantive optical whiteners are necessary to hide the gray-yellow color left on cottons after repeated wear-wash treatments. Lack of knowledge of soiling and detergency mechanisms, optimum detergents, and laundry conditions, also of good substantive optical whiteners, leave discoloration of the more hydrophobic synthetics as a problem to be alleviated. This work is the beginning of an attempt to develop the basic understanding necessary for a practical solution to this problem.

Materials and Methods

Polymer Films

Three different polymer substrates were studied: cellulose, Nylon, and polyethylene terephthalate. The films were 0.25 to 1.5 mils in thickness and were cleaned by Soxhlet extraction prior to use.

Fabrics

A few experiments were performed on a sample of taffeta fabric of 100% Dacron polyester fiber. This was freed from size and/or finish by Soxhlet extraction with carbon tetrachloride prior to the application of model soil.

Detergents

Representative cationic, anionic, and nonionic surfactants were tested: sodium lauryl sulfate (SLS), cetyl trimethyl-ammonium bromide (CTAB), and nonylphenyl polyethylene glycol (NPPG), a commercial sample of Igepal CO–630 (0.01M solution has a cloud point at 53C).

Soils

Fatty Soils. Samples of high purity C-14 labeled stearic acid, octadecyl alcohol, glyceryl tristearate, and octadecane were diluted to a specific activity of ca. 1 millicurie/millimole with purified samples of the nonradioactive chemicals. The diluted samples were dissolved in distilled carbon tetrachloride to make solutions of approximate concentration 0.1 mg/ml, which were applied to the polymer film surfaces as described below.

Three solutions of mixed soils were also prepared, in each of which the total soil concentration was 0.3 mg/ml and the composition of the soil mixture approximately 30% glyceryl tristearate, 30% stearic acid, 20% octadecyl alcohol, and 20% octadecane (proportions nearly like those of acid, ester, alcohol, and hydrocarbon in human sebum). One soil constituent in each mixture was labeled with C-14.

Particulate Carbon Soils. Twenty milligrams of a sample of hydrophobic C-14 labeled amorphous carbon, with an activity of 0.005 mc/mg, was suspended in 50 ml of carbon tetrachloride. Electron and light micrographs of the particulate carbon showed that the particle size ranged from 10 to 0.2 μ. Hydrophilic carbon was produced by treating hydrophobic carbon with wet air containing 1.5% ozone at 90C for 6 hr. (1).

Other Reagents

Water was distilled from an all-glass apparatus and stored in polyethylene bottles. Carbon tetrachloride was fractionated from a 4-ft column rated at about six theoretical plates.

Apparatus

The apparatus used in this study is similar in principle to that described by Cook and Ries (2). It monitors continuously the amount of C-14 labeled fatty soil sorbed on the window of a sensitive Geiger tube from or into an aqueous detergent solution which surrounds the tube. A complete sorption isotherm can thus be developed in one experiment.

The equipment consists of a Nuclear-Chicago Model D-47 Gas Flow Detector, coupled to a Nuclear-Chicago Model 1620 BS Analytical Count Ratemeter and a Brown Recorder. Heat and agitation in the detergent solutions are achieved by a Cole-Parmer "Mark I" combination magnetic stirred and hot plate and placing of the detergent solution under the Geiger counter by a Central Scientific "Lab-Jack."

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The counter was used with the standard "Micromil" window in place. However the Geiger tube adapter ring was modified to permit easy attachment and detachment of a special film cylinder sleeve, on which the polymer test surfaces were mounted.

Procedure for Polymer Films

A piece of 0.25-mil Mylar was centered over the open end of a film cylinder, resting on a level table top. The Mylar was covered by a sheet of the polymer film to be studied. A Teflon ring gasket was pressed down onto the films and around the film cylinder. This smoothed the film in "drumhead" fashion over the open cylinder end. Use of the double drumhead was necessary to prevent the diffusion of helium Geiger tube quench gas through the test film to the polymer water interface, where it interfered with the kinetics experiments.

Soils were applied by pipetting 1-ml aliquots of their carbon tetrachloride solutions onto the outer surface of the test films. After the solvent had completely evaporated, the film-mounting cylinders were placed over the Geiger tube and the soiled films were counted. The cylinders were then removed from the counter, and the soiled surfaces were hand-polished with a soft, grease-free tissue pad. The counting and polishing treatment was repeated three times, then a near-equilibrium distribution of soil was established betweeen the polymer and pad surfaces. Polishing, as described, normalized the distribution of soil on the film and markedly increased the precision of the experimental results.

Film samples were soiled for experiments involving the removal of particulate carbon in the presence of fatty soil as follows. a) One ml of carbon tetrachloride containing 8 mg of fatty soil was deposited on the film, the solvent was allowed to evaporate, and the soiled film was polished lightly with a clean tissue. b) A suspension of 20 mg of tagged particulate carbon in 50 ml of carbon tetrachloride was shaken and allowed to stand for 2 min. This allowed large particles to settle. c) A 1-ml aliquot was pipetted onto the film, and the solvent was allowed to evaporate. d) The soiled film was polished three times with a clean tissue to distribute the carbon evenly over the surface, then lightly rinsed to remove loose particles. The soiling procedure was the same for experiments involving carbon in the absence of fatty soil except that the first step was omitted.

To obtain a desorption isotherm, a 300-ml aliquot of surfactant solution contained in a 100-mm × 50-mm crystallizing dish was raised beneath the Geiger tube until the soiled window was submerged to a depth of ca. 3 mm. A magnetic stirrer in the dish was then started, and the progress of desorption was followed by observation of the recorder chart.

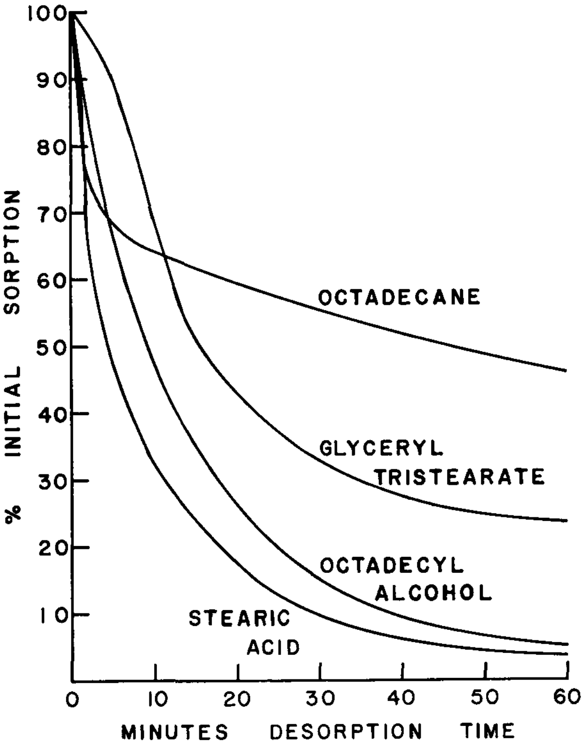

FIG. 1. Effect of soil type on detergency from PET by NPPG at 20C.

Procedure for Fabric

A small fabric sample was mounted on a 1.5-in. diameter stainless steel ring in a manner similar to that used for polymer films. Solutions of radioactive fatty soil were pipetted onto the fabric surface, and the solvent was allowed to evaporate. The fabric-covered ring was then suspended in a 100-mm diameter × 50-mm crystallizing dish with the plane of the fabric surface normal to the bottom of the dish. The dish was filled with a 300-ml aliquot of surfactant solution, and the magnetic stirrer was started. After a measured time-interval the ring was withdrawn from the surfactant solution, the water was allowed to evaporate from the fabric surface, and the radiation from both sides of the fabric was determined with the Geiger counter. The average of the two readings was used to calculate the results.

Experimental Results

Fatty Soil

Effect of Polymer Surface Roughness and Surface Concentration of Soil. Autoradiographs and selected

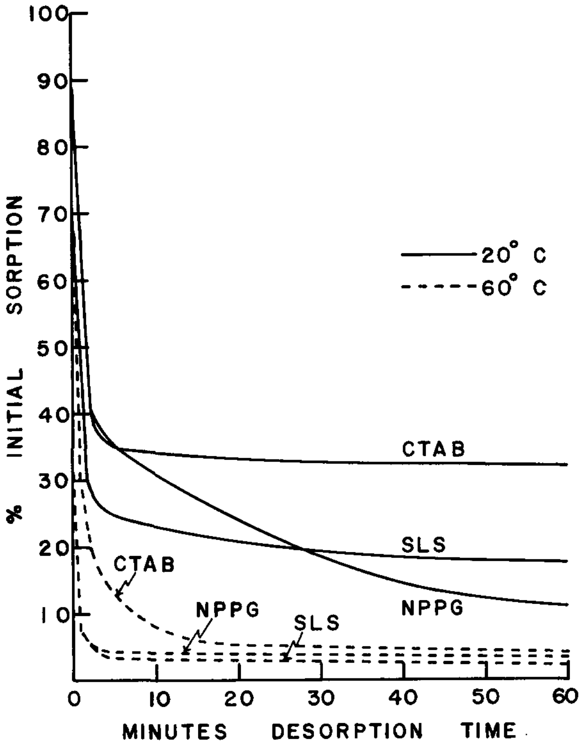

FIG. 2. Detergency of glyceryl tristearate from cellulose by 0.01M detergent solutions.

area-counting experiments showed the distribution of soil on the polished polymer film surfaces to be uniform. Average values for the initial surface population density of each soil on each polymer was approximately the same and equivalent to from 5 to 8 monolayers. Electron micrographs showed that test films were not perfectly smooth, but roughening the films with sandpaper did not affect the relative detergency rate at either 20° or 60° and changing the initial surface concentration of glyceryl tristearate on PET surfaces did not alter the detergency rate. Comparison of data from the different polymer film substrates should therefore be meaningful.

Effect of Soil Type. Fig. 1 compares detergency rates of the four test soils from PET at 20°. Relative removal rates for the four sorbed species increased as polarity increased in the order: octadecane < glyceryl tristearate < octadecyl alcohol < stearic acid. Similar experiments were performed on the other substrates with each detergent under study, at both 20° and 60°. With a given polymer-detergent combination, the above order was always maintained except that octadecane sometimes showed anomalous behavior at the higher temperature because of its undesirable volatility.

Effect of Polymer Substrate Type. Fig. 2 to 4 show data for the removal of glyceryl tristearate from the three test substrates by the three detergents, both at 20° and 60°. Removal of this soil was much faster from some substrates than from others, and the behavior depended on the temperature. Thus at 20C PET ~ Nylon << cellulose; at 60° PET < Nylon < cellulose. The rate of removal increased as the hydrophilicity of the substrate increased. A residue of nearly irremovable glyceryl tristearate remained on the cellulose after the 20° experiments, and on the PET after the 60° experiments. Residues of the other soils were also left on PET and cellulose after similar washing treatments.

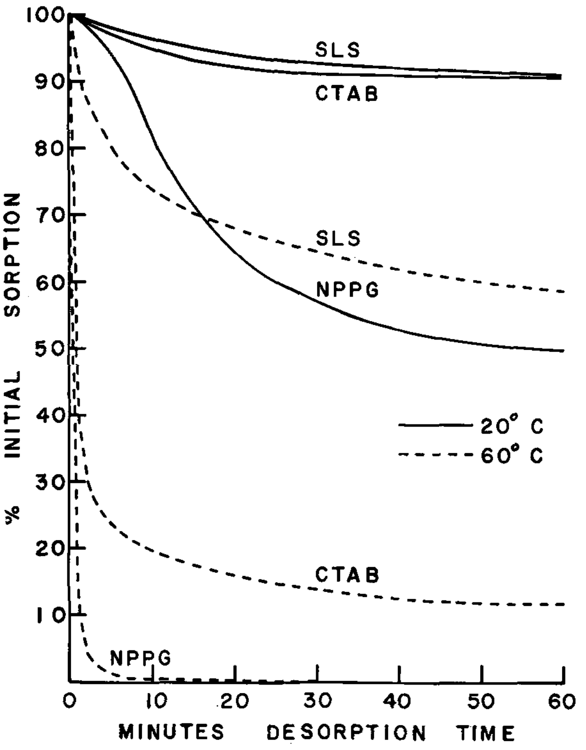

FIG. 3. Detergency of glyceryl tristearate from Nylon by 0.01M detergent solutions.

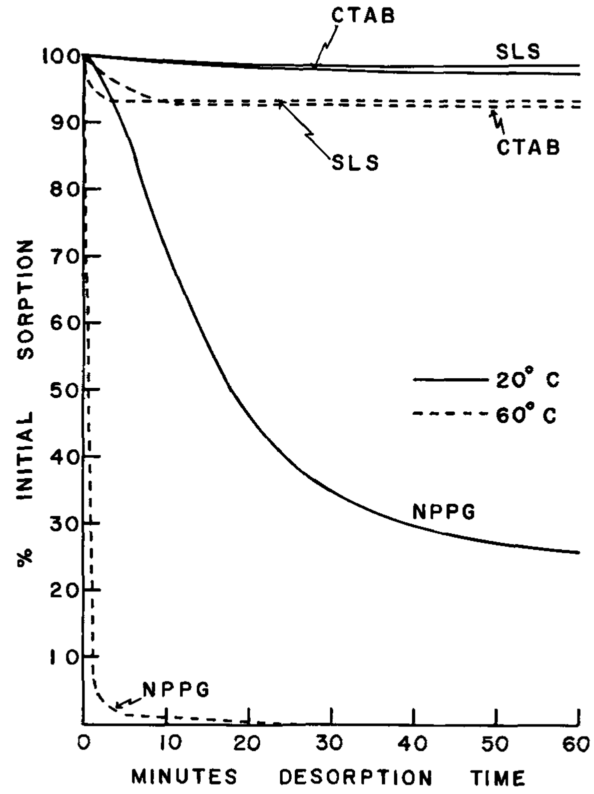

FIG. 4. Detergency of glyceryl tristearate from PET by 0.01M detergent solutions.

Effect of Surfactant. Comparison of the data of Fig. 2 through 4 shows that the 0.01M surfactant solutions varied widely in their ability to remove glyceryl tristearate from the three polymer surfaces and that surfactant effectiveness was dependent on the polymer substrate. For cellulose, the order of increasing efficiency was CTAB < NPPG < SLS; for the other three polymers it was SLS < CTAB << NPPG. Data obtained for the other soils showed that this same order was followed for stearic acid and octadecyl alcohol.

The detergency rate was quite dependent on surfactant concentration. The rate of removal of glyceryl tristearate from PET at 20° increased as NPPG concentration was raised to a maximum near 0.001M surfactant, then fell off at higher concentrations. With the cationic and anionic at all temperatures, and with the nonionic at 60° no maximum in detergency rate was observed. Even with optimum conditions of temperature and concentration however, removal of the more nonpolar soils from the more hydrophobic surfaces was, with the ionic detergents, slow and incomplete.

Effect of Temperature. Fig. 2 through 4 show that desorption of glyceryl tristearate from each of the polymers was always much faster at 60° than at 20°. Tests showed that the rates of removal of the other soils were also faster, at the higher temperature, with each of the detergents. A more detailed investigation was made of the effect of temperature on detergency from PET. It was found that the total amount of stearic acid, octadecyl alcohol, and sometimes glyceryl tristearate, removed from this polymer in a given wash-time, often passed through a maximum as the wash temperature was raised although the initial rate of soil removal always appeared to increase. Examples of the effects of temperature on detergency from PET

TABLE I
Back/Front Activity Ratio After Baking, Divided by Back/Front Activity Ratio Before Baking Soiled Polymer Films at 80° for 15 Minutes

	Polymer		
Soil	Cellulose	Nylon	PET
Glyceryl tristearate	1.0	1.1	1.0
Stearic acid	1.2	1.0	1.2
Octadecyl alcohol	1.2	1.2	1.2
Octadecane	4.7	2.0	1.5

are shown in Fig. 5 through 7. These effects were observed with all three surfactants which were studied.

The fact that the temperature at which maximum soil was removed from the polymer film substrates was not always the highest wash-temperature (this might have been expected with 0.01M NPPG, which has a cloud point of 53°, but not with CTAB or SLS) suggests that, when the fatty soils sorbed on the polymer film surfaces were heated above their melting points by hot surfactant solution, they sometimes diffused away from the polymer surfaces and into the interior of the test films, where they were inaccessible to the surfactants. This hypothesis was substantiated for each of the test films by depositing C-14 labeled soil on the films, then measuring the radiation from both the front and back of the samples. The radiation from the front was always greater than that from the back because the polymer films acted as radiation shields. The films were then baked in an oven at 80°, and radiation from the front and back was measured again. A significant increase in the ratio of back-to-front count rate implied that diffusion during heating had occurred. Some data are collected in Table I. It is significant that diffusion into all the polymer films was indicated and that the extent of diffusion was an inverse function of diffusing molecule polarity and size.

PET film was selected for further study. Diffusion into this polymer was confirmed by three separate types of experiments.

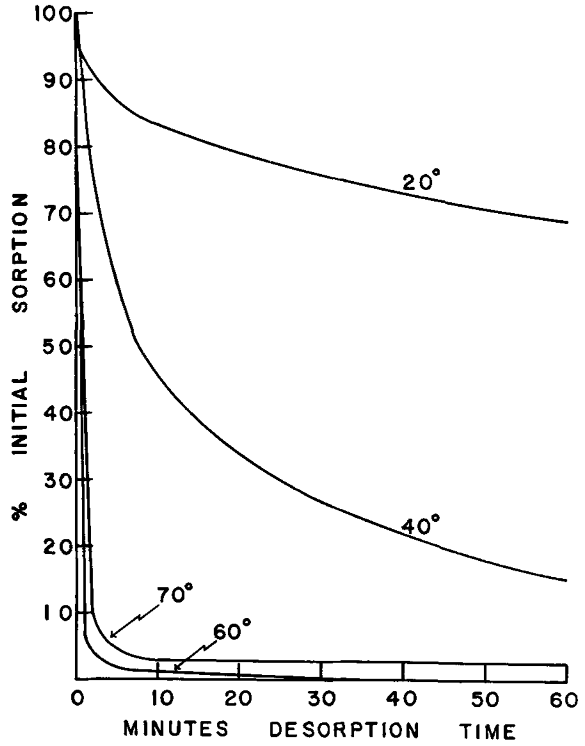

FIG. 5. Effect of temperature on removal of stearic acid from PET by 0.01M SLS.

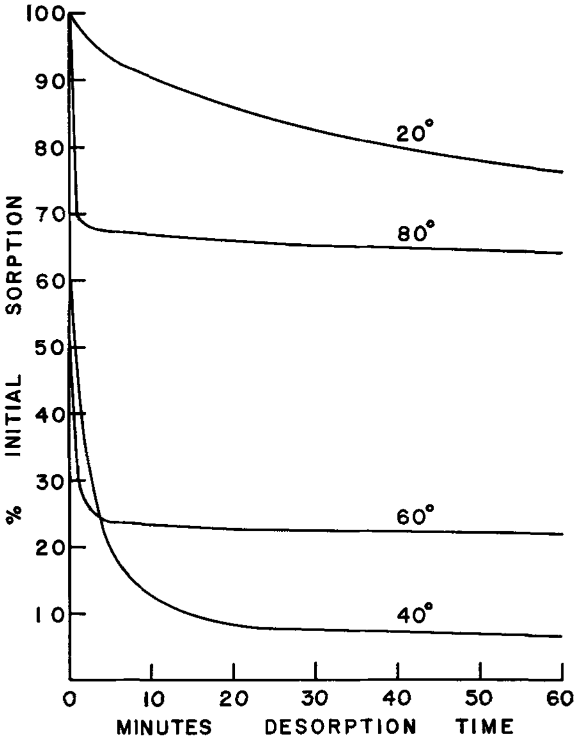

FIG. 6. Effect of temperature on removal of octadecyl alcohol from PET by 0.01M SLS.

It was shown that pre-baking a soiled PET film in an air oven to a temperature above the soil's melting point made a large part of the soil inaccessible to a detergent operating at the soil's optimum wash-temperature. The amount of soil made inaccessible by the oven treatment, which volatilized only a small fraction of the soils in 10 minutes of baking at 80°, could be varied from 0% to 100% by varying the baking time.

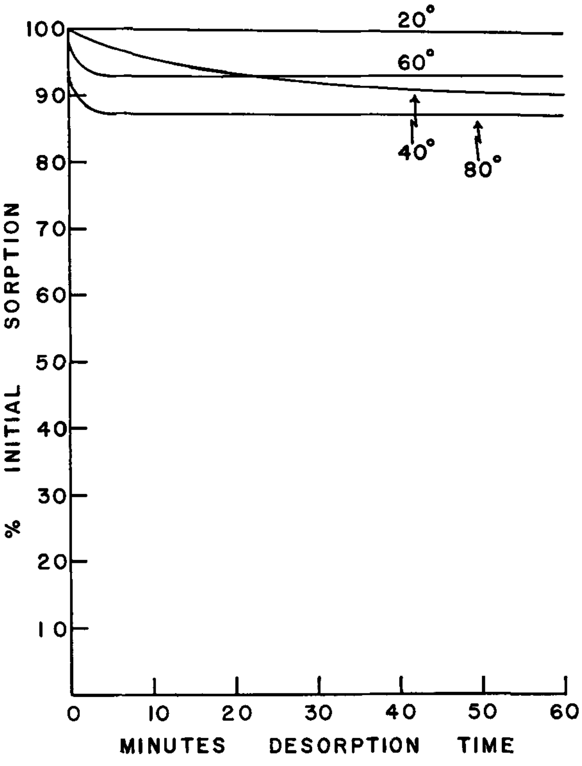

FIG. 7. Effect of temperature on removal of glyceryl tristearate from PET by 0.01M SLS.

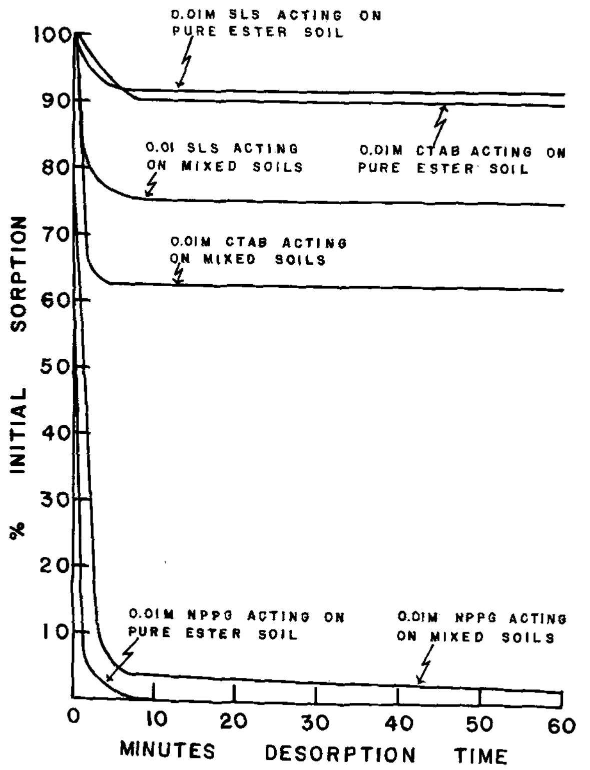

FIG. 8. Effect of other soil constituents on detergency of glyceryl tristearate from PET by 0.01M surfactant solutions at 60C.

It was shown that either pre-baking or washing at a high temperature made the soil which remained on (in) the polymer completely irremovable by light mechanical polishing of the soiled film surface. Much of the soil which had not been subjected to heating could be polished off.

It was shown that both the acid and the alcohol, when sorbed on the polymer surface, acted as efficient lubricants for the PET. It was then shown that acid or alcohol remaining on the PET after baking and high-temperature washing had no lubricating action whatsoever.

Each of these experiments confirms that diffusion had occurred. Thus, if the soils were present, as indicated by the Geiger counter, but could not be washed off or rubbed off, or act as boundary lubricants, they could not have been on the polymer surface and must therefore have diffused to the interior of the PET. The fact that the relatively large molecule, glyceryl tristearate, did not behave in as extreme a fashion as stearic acid and octadecyl alcohol is additional evidence that diffusion took place.

Effect of Agitation. The wash solutions were normally stirred with a magnetic stirring bar at 1,400 rpm. However a number of experiments were run to show the effect of agitation on soil removal. Stirring was found to be more important for the removal of liquid soils than solid soils, and the effect was larger on hydrophobic than on hydrophilic substrates.

Detergency of Multicomponent Fatty Soils. Comparison of the data of Fig. 8 and 9 shows that, at 60°, the presence of other fatty soil constituents increased the rate of removal of glyceryl tristearate and decreased the rate of removal of stearic acid from PET by CTAB and SLS. When the detergent was NPPG, the apparent effect of the other soil components was less than the uncertainty in the data. The beneficial influence of small amounts of polar soil in the removal of nonpolar oily soils from difficultly wettable polymers is well known (3). The polar soil constituents increase the solubility of the detergents in the soil films. This, and the reduced melting and penetration temperatures of the soil mixtures, aid complex formation and rolling up. Soil removal by nonionic detergents, which are relatively soluble even in nonpolar oily soil, is not as greatly affected by the presence of more polar oily soils.

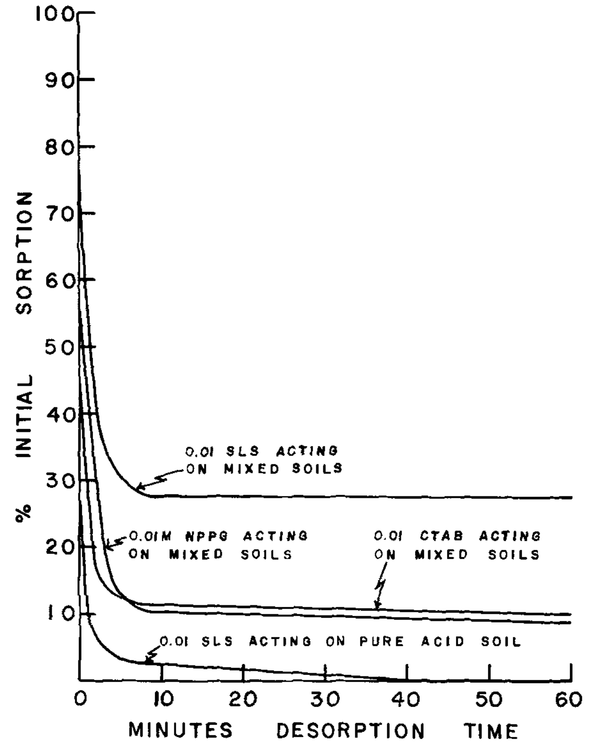

FIG. 9. Effect of other soil constituents on detergency of stearic acid from PET by 0.01M detergent solutions at 60C.

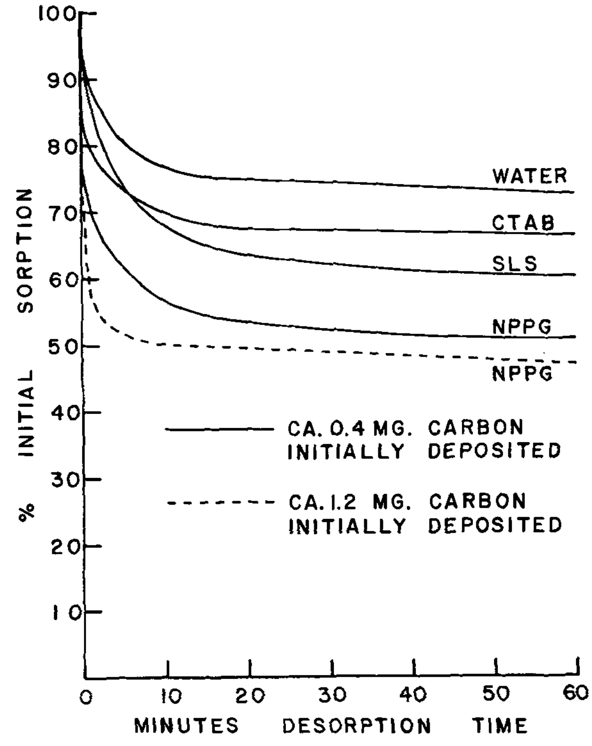

FIG. 10. Removal of hydrophobic amorphous carbon from PET film by 0.01M surfactant solutions at 60C.

TABLE II

Comparison of Removal of Fatty Soil from Polyester Film and Fabric

	% Initial Soil Remaining After 15-Minute Wash at 60C			
	0.01M SLS		0.01M NPPG	
Soil	Film	Fabric	Film	Fabric
Glyceryl tristerate	97	92	10	0
Stearic acid	18	1	6	8
Soil mixture 1[a]	54	75	5	3
Soil mixture 2[b]	32	27	6	7

[a] Labeled component was glyceryl tristearate.

[b] Labeled component was stearic acid.

The order of decreasing efficiency of the detergents for constituents of fatty soil mixtures was the same as for the pure materials: NPPG > CTAB > SLS. Exceptions to this order either were isotherms which were so close together that the difference between them could have been experimental error or were isotherms for removal of stearic acid which showed a unique susceptibility to detergency by CTAB. Experiments with Nylon indicated that soil mixtures, like monocomponent soils, were removed relatively rapidly from the more polar polyamide substrate.

Correspondence of Soil Removal Data Obtained with Films and Fabrics. The data of Table II show that, qualitatively, the results obtained by using fabric confirm what had previously been observed with film. The nonionic surfactant solution was superior to the anionic surfactant solution for removing soil from polyester. Polar stearic acid was easier to remove than less polar glyceryl tristearate. The other components of Soil Mixture 1 aided in removal of glyceryl tristearate by 0.01M SLS, and other components of Soil Mixture 2 hindered in the removal of stearic acid by 0.01M SLS.

Particulate Carbon Soils

Effect of Amount of Carbon on the Surface, Polymer Substrate Type, and Surfactant Type. Isotherms for the removal of hydrophobic carbon by 0.01M NPPG at 60° when ca. 0.4 mg of carbon was deposited on a PET film 3 in. in diameter and when ca. 1.2 mg was deposited on the same size of sample are shown in Fig. 10. These show that intentionally changing the initial concentration of particulate soil did not markedly change either the rate or extent of removal. Thus slight variations in the amount of initial carbon which was deposited should not alter the percentage of soil removed.

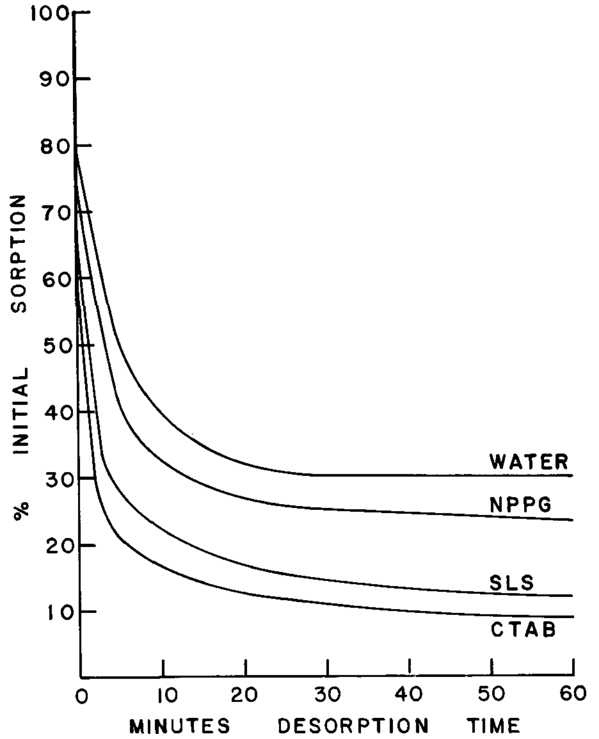

FIG. 11. Removal of hydrophobic amorphous carbon from cellulose film by 0.01M surfactant solutions at 60C.

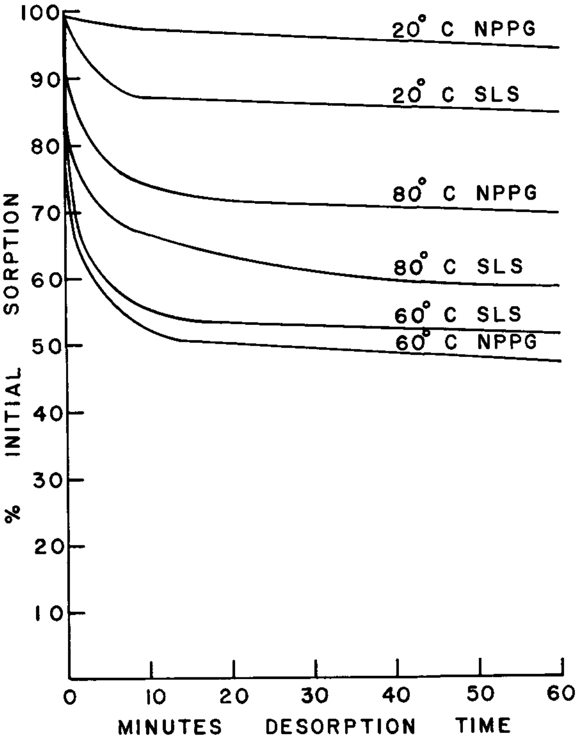

FIG. 12. Removal of hydrophobic amorphous carbon from PET film by 0.01M surfactant solutions.

Comparison of isotherms for the removal of hy-

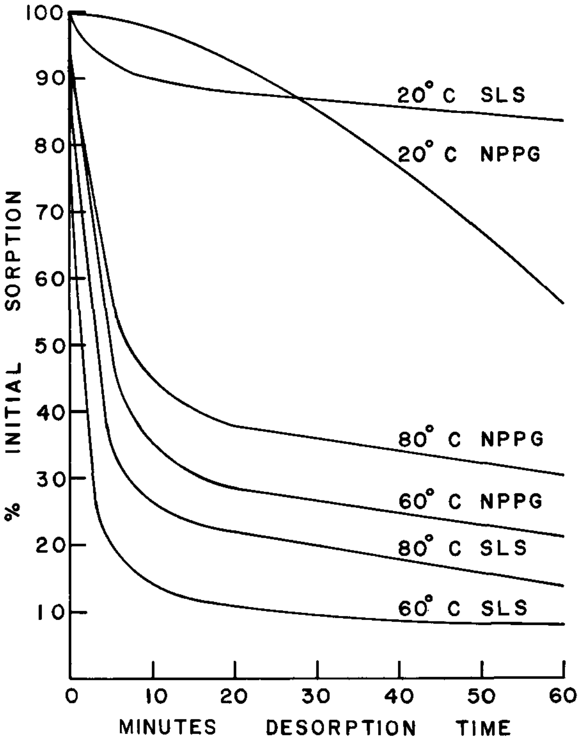

FIG. 13. Removal of hydrophobic amorphous carbon from PET film soiled with fatty mixture (30% glyceryl tristearate, 30% stearic acid, 20% octadecyl alcohol, and 20% octadecane) and carbon by 0.01M surfactant solutions.

drophobic particulate carbon from cellulose film in Fig. 11 with those for PET in Fig. 10 demonstrates that this soil was significantly easier to remove from the cellulose film.

The isotherms in Figs. 10 and 11 indicate no great difference between the rates of removal of hydrophobic carbon from either cellulose or PET film by the various surfactant solutions.

Effect of Temperature. The isotherms in Fig. 12 establish that both 0.01M NPPG and 0.01M SLS were more effective at 60° and 80° for removing hydrophobic particulate carbon from PET film than at 20°. For both surfactants there was an unexpected decrease in carbon desorption in going from 60 to 80°.

Effect of the Presence of Fatty Soil. Comparison of isotherms for the removal of hydrophobic particulate carbon, deposited on fat-soiled films in Figs. 13 and 14, with those obtained in the absence of fat in Figs. 10 and 11 shows that for both films at 60°, 0.01M SLS and NPPG removed the carbon which was deposited on fat more effectively than when no fat was present. Removal of carbon from fat-soiled cellulose was so complete at 20° that no significant improvement at 60 and 80° was detected; however carbon removal from fat-soiled PET film was significantly better at 60 and 80° than at 20°. The anionic surfactant appeared to be slightly superior to the nonionic for removing hydrophobic carbon in the presence of fat except for the removal from PET film at 20C after 40 min of desorption time (Fig. 13).

Effect of Wettability of the Particulate Soil. Hydrophobic C-14 labeled carbon was made hydrophilic by treatment with wet air containing 1.5% ozone at 90°. The isotherms in Fig. 15 reveal that hydrophilic carbon was easier to remove from PET film than hydrophobic carbon in the presence of fat. It was also found that hydrophilic carbon was easier to remove from PET film than hydrophobic carbon in the absence of fat.

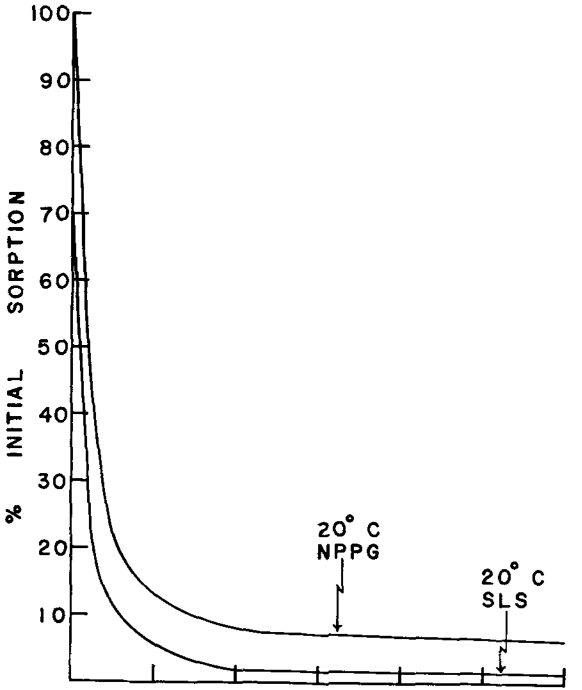

FIG. 14. Removal of hydrophobic amorphous carbon from cellulose film soiled with fatty mixture (30% glyceryl tristearate, 30% stearic acid, 20% octadecyl alcohol, and 20% octadecane) and carbon by 0.01M surfactant solutions.

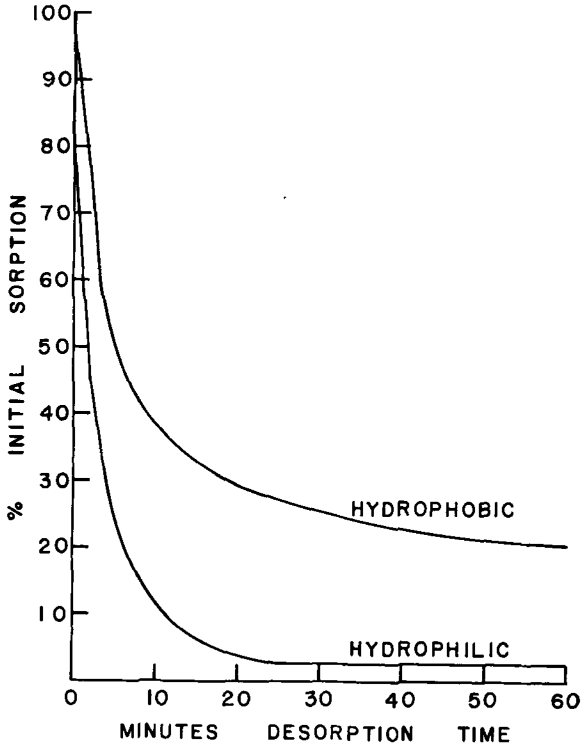

FIG. 15. Removal of hydrophobic and hydrophilic carbon from PET film soiled with fatty mixture (30% glyceryl tristearate, 30% stearic acid, 20% octadecyl alcohol, and 20% octadecane) and carbon by 0.01M NPPG at 60C.

Discussion

It was shown by Adam in 1937 (4) that displacement of liquid oil films from solid surfaces by aqueous detergent solutions occurs through a process of "rolling up." Adam also showed that the contact angles (Θ_o), exhibited by oil drops at the three-phase interface, increased with increasing detergent concentration, as predicted by Young's equation (5). At $\Theta_o \sim 180°$, the oil spontaneously separated from the solid and was solubilized by the detergent solution. Harker (6) demonstrated that rolling up was more difficult to achieve from hydrophobic than from hydrophilic surfaces and that, for a given oil-polymer-detergent solution system, cos Θ_o approached -1 as the water wettability of the substrate increased. The contact angles in Table III show that this is consistent with the order of increasing rates PET < Nylon < cellulose obtained at 60° in this study.

Rolling up was not the only kinetically important means of soil removal. Considerable glyceryl tristearate was deterged, by NPPG, from even the most difficultly wettable substrates at 20°. Even faster room-temperature removal of octadecyl alcohol and stearic acid was effected by this detergent, and significant quantities of these more polar soils were also deterged by CTAB and SLS. Stevenson (3,7) and Lawrence (8,9) have shown by direct observation that detergent-water solutions "penetrate" fatty soils, which have some polar character at temperatures well below the melting points of the soils, to form highly viscous liquid-crystalline membranes at the oil-water interface. The soil is subsequently desorbed either

TABLE III
Water Contact Angles on Polymer Surfaces

Polymer	Θ_o
Cellulose	32
Nylon	70
PET	79

through mechanical break-up of the membranes or through solubilization of soil molecules into detergent micelles. Both Lawrence (9) and Scott (10) have shown by microscopic observation that the myelinic figures characteristic of penetration detergency are formed on the surface of crystals of long-chain acids and alcohols exposed to detergent solutions similar to those used in this work. The kinetic importance of penetration for desorption of these soils in experiments can therefore be regarded as confirmed.

It is pointed out by Stevenson (7) that the penetrating and solubilizing power of nonionic detergents is significantly greater than that of their ionic counterparts. This results from the uncharged nature of the nonionics, which makes them appreciably soluble in oil as well as in water. Stevenson believes (11) that nonionic detergents may actually penetrate a sorbed oil film to such an extent that the oil is made water-soluble; the detergent acts as co-solvent. Thus the relatively high, solid fatty soil-removing ability of NPPG seems plausible.

Another way in which solid fatty soils may be removed is through the penetration of detergent solution into cracks and crevices in the soil films, with subsequent dislodgment of "chips," or microcrystalline aggregates, of solid (10). That soil was actually removed in this way was implied by the retention of radioactive material by a fine membrane after used wash-water had been passed through it. Further indication that the chip dislodgment mechanism operated, and an explanation for the easy detergency of all solid fatty soils from cellulose, were obtained by comparing the amount of soil retained on the filter after passage of wash water for different substrates. These data indicate that much more soil was retained on the filter after passage of cellulose wash-water than after passage of PET wash-water. This was because the cellulose was a relatively hydrophilic material which sorbed, on contact, nearly 100% of its weight of water and swelled considerably in the process. The swelling was an aid to mechanical dislodgment of solid fatty soil from this polymer's surface. However some soil was carried into the cellulose with the sorbing water, and this imbibed material was removed only slowly by the detergent solution.

The energy, W, that must be provided isothermally and reversibly to remove a particle of carbon from a polymer surface into suspension in a detergent solution is given by:

$$W = \gamma_{CS} + \gamma_{PS} - \gamma_{CP} \qquad (12)$$

in which free energies at the carbon-solution, polymer-solution, and carbon-polymer interfaces are represented by γ_{CS}, γ_{PS}, γ_{CP}, respectively. The contact angle Θ of a drop of solution, resting on a polymer surface in air measured in the liquid phase, is related to the surface energy values as follows:

$$\cos \Theta = \frac{\gamma_{PA} - \gamma_{PS}}{\gamma_{SA}}$$

where free energy values at the polymer-air and solution-air interfaces are represented by γ_{PA} and γ_{SA}. When γ_{PS} decreases, cos Θ increases. Since Θ decreases, the wettability of the polymer increases.

In the equation for the work to remove the carbon particle, a low value for γ_{PS} favors easy removal of the carbon. Thus it is not surprising that particulate carbon was easier to remove from cellulose film (water contact angle 32°) than from PET film (water contact angle 79°). A low value for γ_{CS} also decreases the value of W so the easier the particle is to wet by the solution, the easier it should be to remove. The observation that hydrophilic carbon was easier to remove than hydrophobic is consistent with the statement.

The fact that more carbon particles were removed at 60° and 80° than at 20° may be explained by assuming that the particles serve as nucleation points for bubble formation from dissolved gases. These bubbles then pull the particles off the surface. This concept has been substantiated by experiments with cotton soiled with vacuum-cleaner dust. Brown (13) found that the removal of this soil by detergent solution was much less below 100° than when the liquor was boiling. He also found that, when the detergent baths were evacuated, detergency was virtually the same at all temperatures between 40° and 100° so long as the liquor was boiling under reduced pressure.

The easier removal at 60° than at 80° was unexpected. The solution was brought to the operating temperature prior to immersion of the film. At 80° more of the dissolved gases were probably removed from the solution than at 60°, thus less dissolved gas was available to assist removal at the higher temperature.

Both hydrophobic and hydrophilic carbon were more difficult to remove from PET film by any of the surfactant solutions than fatty soil similar in composition to human sebum. Thus it is not surprising that the presence of fatty soil aided the removal of particulate carbon. When the more easily removed fatty soil desorbed, it carried the carbon on the surface off with it. The presence of fatty soil would be expected to retard the removal of a particulate soil only if the particulate soil were easier to remove than the fat. In this case the fat would act as a glue and hold the particulate soil to the surface.

The effects of different detergent types, concentrations, wash temperatures, etc., as defined in the polymer film detergency studies, should extrapolate to the cleaning of fabrics in a home or commercial laundry. Such was indicated by a linear correlation coefficient for fatty soil-removal data which were obtained from polyester fabric and a film of 0.95. This was highly significant at the 99.5% confidence level. Proper interpretation of fabric detergency data, of course, also requires consideration of the effects of fiber geometry, fabric construction, optical whiteners, detergent builders, and soil redeposition on fabric whiteness. Fiber surface roughness also plays a part; the crenulated surfaces of cotton fibers are known to be "traps" for both particulate soil and optical whiteners.

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