work of Rao and Daubert (2), who characterized vaccenic acid as the *trans* isomer, and of Honn, Bezman, and Daubert (3), who studied the autoxidation of linseed oil by means of infrared absorption, as well as the studies of Shreve, Heether, Knight, and Swern (4) on the *cis-trans* isomers of unsaturated fatty compounds are among the notable recent contributions to the chemistry of fats and oils.

In fatty-acid chemistry, as in all organic chemistry, infrared spectroscopy has already become an indispensable tool. It is being applied to both theoretical and practical problems and has only begun to demonstrate its real value.

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The Nature of Soil to Be Deterged and Its Bonding to the Surface[1]

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Summary

A SOIL is ordinarily composed in varying amounts of oil, wax, or grease; solid particles of diverse types; and special water-soluble or water-dispersible materials such as sugar, salts, starch, etc. Quantitatively the fatty portion on fabrics may run to a substantial fraction of 1% and contains roughly one-third neutral fat, one-third higher fatty acids, one-third other materials, and undetermined. Airborne dust may contain over 20% of fatty matter, over 30 per cent of other organic matter. Soil is retained on fabrics by mechanical forces, chemical forces, electrostatic attraction, and oil-bonding, which itself operates by means of electrical forces on the molecular scale.

The fundamental equations of wetting are presented. They imply that oily soils will gravitate toward the smallest capillaries in fabrics and thus become increasingly difficult to remove as the soiled fabric ages. Polymerization of unsaturated oils and chemical linkage of conjugated unsaturated bonds to active sites on the fibers are also factors in the setting of soil as fabric ages.

For extremely light soiling, the darkening of the fabric is roughly proportional to the amount of soil. As degree of soiling increases, the amounts of soil needed to give proportional darkening become enormously greater. From the viewpoint of detergency this means that the difference between good and bad results depends on removal of the last traces of soil.

The nature of the soil to be removed and the surface from which it is removed has been stressed necessarily, in recent publications by two of us (12, 16). Thus the removal of siliceous soil from metal and from porcelain constitutes two different problems. Likewise the removal of metal particles held by an oily matrix is a different problem with those two types of surface.

Much work on soaps or more recently on synthetic detergents has called for washing tests with some artificial soil. This has in general dealt with a surface of cotton or woolen fabric and a soil of oily nature pigmented with carbon black. Relatively little work has been carried out to determine quantitatively what soil may be, what causes it to adhere to a surface, and the influence of the nature of the fabric or other substrate. So although a limited amount of quantitative work is included in this series, the discussion which follows is largely qualitative and speculative. For simplicity, the numerous terms in use, such as hydrophyllic, lipophyllic, etc., have been roughly translated as either polar or nonpolar. By polar we mean soluble in or preferentially wet by water and other solvents with high dipole moment. By nonpolar we mean soluble in or preferentially wet by nonpolar liquids and not by water. Nonpolar substances may have appreciable dipole moments although not as great as polar substances.

Qualitative Nature of Soil

Soil on clothing, household textiles, dishes, the floor, or other surfaces is always a mixture. The ingredients will vary according to the use and situation of the surface. Many components have been mentioned by different investigators. Those described as being possible components, according to the condition of use, include the following:

Oily, Waxy, or Greasy Soil. This may contain saponifiable oils, including those of both animal and vegetable origin; unsaponifiable matter such as long chain alcohols and mineral oils. All of these substances are nonpolar, not readily wet by water.

Solid Soil. Solid soil may or may not be coated with a greasy film. It may consist of particles of soot, dust, clay, carbon, sand, and iron rust (5, 10). The electrical charge, while generally negative, may occasionally be positive. Dirt particles may be relatively polar such as sand, or nonpolar such as carbon black. All particles coated with oils, waxes, or grease are nonpolar (14).

Special Types of Soil. These may consist of food residues such as sugar, starch, and salts, readily wet by and usually readily soluble in water; proteins such as eggs, blood, and other albuminous matter, readily wet by and partially soluble in water, except at high temperatures. In addition, various stains are encountered which may be more or less water-soluble or which may require special removal treatment other than the usual detergent process.

Perspiration, often an important soil ingredient on clothing, is itself a complex mixture of substances, partly water-soluble, partly insoluble (9). In addi-

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TABLE I

Amount of Oil on Articles Soiled by Domestic Use

Article	Total Weight of Fabric in Grams	Number of Soilings and Extractions	Amount of Oil per Soiling in Percentage
Soft cotton collars—Expt. 1	147	1	1.1
Soft cotton collars—Expt. 2	122	1	1.2
Cotton shirts	1,350	8	0.25
Linen pillowcases	430	7	0.6
Tea towels	420	4	0.5
Woolen socks—Expt. 1	292	1	1.1
Woolen socks—Expt. 2	204	1	0.5
Woolen socks—Expt. 3	475	1	0.8
Mean value			0.75

tion to soluble mineral salts, chief of which is sodium chloride, perspiration contains a high content of sebum. This consists of a mixture of fats, including oleic, palmitic, and stearic glycerides; fatty acids including oleic, palmitic, and stearic, occasionally butyric and caproic acids; together with cholesterol, organic salts, albuminoids, and epidermal debris (2). About 25-30% of the lipid in perspiration is unsaponifiable; less than half of this is cholesterol. The lipid portion of perspiration is nonpolar, not readily wet by plain water. Perspiration may be difficult to remove and may even be classed as a stain.

As a general principle, it has been found that stain removal is most efficient in laundry practice under conditions which give the best general cleaning (11). In other words, a definite tie-up appears to exist between general soil removal and stain removal.

Quantitative Nature of Soil

No attempt has been made to study the complete composition of soil as it actually occurs on garments and household textiles because of its extremely variable nature. Natural soil is not uniformly distributed so that experimental washing tests using it could hardly be standardized. Many standard-soil mixtures have been described in the literature, or used by different investigators, most of which represent an attempt to approximate the content of natural soil.

A study of the fatty portion of soil on domestically soiled fabrics has been reported (2). The articles used were soft cotton collars, cotton shirts, linen pillowcases, tea towels, and woolen socks. The shirts, pillowcases, and tea towels were obtained new and were freed from sizing materials. The shirts were worn by workers doing fairly heavy manual labor and were collected after seven days' use. The pillowcases and tea towels were used in a middle-class home, the pillowcases for 14 days and the tea towels for four days. These materials include the cellulosic fabrics, cotton and linen, and wool fabrics.

After use, the soiled shirts, pillowcases, and tea towels were extracted with carbon tetrachloride to remove the oil. Solvent extraction failed to render the shirts sufficiently clean to meet the approval of the wearers so that after every second or third treatment the extracted shirts were boiled in distilled water solutions of an alkaline salt before reissue.

This brings out the fact that solid particles of dirt adhered to the fabrics of themselves even after all oily coating had been removed. Adhesion of solid soil to fabric is not necessarily due to the oily film which is ordinarily present.

Socks and collars were dried over phosphorus pentoxide, then extracted with sodium-dried methylated ether. Thus if soap deposits were present before these articles were worn, none of the soap would be removed as such or as fatty acid during extraction. Shirts, pillowcases, and towels were given a number of soilings and the oils collected from each were analyzed as a whole. One soiling only was given to the socks and collars. A sufficient number of each was taken to provide the required amount of oil. Table I shows the amount of oil obtained.

The average amount of oil present in the accumulated soil under the conditions selected, varied from 0.25% on the shirts to 1.2% on the soft collars. Analysis of the various oil samples gave the data condensed in Table II. The content of fatty acids is surprisingly high in the oil—17.8 to 39.5—even though that calculates back to quite modest figures in the original cloth. Clothing in contact with the body acquires a complex soil which includes fatty acids below lauric, presumably from perspiration. This is in contrast with such fabrics as tea towels showing only higher acids and esters as derived from usual food fats. The soil derived from the body contains substantial amounts of sterols as well as nonacetylatable unsaponifiables. These unsaponifiables may reasonably be interpreted as closely related to fatty acids on the basis of similar molecular weight —a not-too-firm basis for the statement. These data would be of further value if they could be related to the solid soil, either water-soluble or water-insoluble, with which they were associated.

TABLE II

Composition of Oil Obtained From Domestically Soiled Articles

	Percentage in Total Oil		Molecular Weight Range of Values	Iodine Number Range of Values	Hydroxyl Number Range of Values
	Range of Values	Average Value			
Neutral fat and fatty acids, capric and below	1.0- 6.1	2.7	....	....	....
Neutral fat of acids higher than capric	8.6-60.7	29.2	803-968	33-64	....
Fatty acids higher than capric	17.8-39.5	31.4	255-310	33-64	....
Total unsaponifiable matter	5.8-53.6	31.0	281[1]	24.6, 52[2]	77, 89[3]
Unaccounted for	1.7-14.0	5.7	....	....	....

[1] Woolen socks only.
[2] Shirts and woolen socks only.
[3] Collars and shirts only.

Air-borne dirt, which usually would be only a modest part of that on soiled garments but a larger percentage of that on some household textiles, can be studied in terms of that collected in glass filters of air-conditioning systems and ventilating systems, or of air compressors (7). In one type the filter is washed with water, in another it is not. Data are available from a water-washed filter from a unit servicing a rubber cementing room in a rubber factory operated under very severe conditions of use to provide highly humidified air at an elevated temperature. The unwashed filter reported was from the inlet dust of a compressed air unit in the power house of a chemical plant. Both are shown in Table III.

The general nature of such materials follows:

a) The oils extracted with ethyl ether may consist of saponifiable oils, mineral oils, and waxes, nonsaponifiable fatty matter, such as sterols, and true waxes. In some places a large part of this fraction consists of incompletely burned hydrocarbons.

TABLE III

Data on Composition of Air-Borne Dirt

Dirt Fraction	On Water-washed Filter in %	On Dry Filter in %
1. Oils extracted with ethyl ether	1.3	22.1
2. Material soluble in hot water	6.3	14.2
3. Additional material soluble in hot dilute hydrochloric acid	33.3	11.2
4. Loss on ignition of oil-free, acid-insoluble residue	15.4	32.8
5. Acid-insoluble inorganic residue	43.7	19.7
Total organic matter (1 + 4)	16.7	54.9

b) Material dissolved out by cold water may consist of sugars, salts, soluble hydroxides, etc. That soluble in hot water but not in cold may consist of difficultly-soluble salts, oxides, and hydroxides.

c) Additional material soluble in hot dilute hydrochloric acid may consist of carbonates, phosphates, some metal oxides such as magnesium or lead oxide, and other basic compounds.

d) Loss on ignition of the residue should be largely from free carbon and carbon compounds. Examples are soot, coal dust, lint from textiles, and dust from wood. Moisture in terms of water or hydration of inorganic compounds would also be included here.

e) The final inorganic residue may consist of siliceous dust from sand, pumice, quartz, granite, and silicates.

Water-washed dirt can also contain some hard-water scale deposited from the water on evaporation. The differences between soils from different localities can be more significant, for example, the contrast between a textile mill and a theatre. A further study of dust from dry filters taken from selected spots could be very informative. In terms of dust which might accumulate on clothing the nature of the dust on the dry filter, collected from the atmosphere, is much more significant than from the water-washed filter.

Forces Holding Soil to Fabric

Several forces operate to make soil cling to fabric. These include mechanical, chemical, and electrical forces. Of these the least important in general soiling is chemical attraction in a narrow sense.

A broad distinction can be drawn between direct attachment of solid soil to the base and attachment by means of a film of oil which wets both soil and base. The physico-chemical principles governing the second case are known much better than those governing the first because technics for studying attractive forces between liquids and solids are far more convenient and reliable than those used in studying attractive forces between solids. This does not mean that the nature of the attractive forces, on a molecular scale, is different, although it sometimes is.

Greying of fabrics by soil redeposited during washing is familiar. Such soil is much more difficult to remove than ordinary soils which have been applied directly. It seems reasonable to hypothesize that this is soil which has, during the washing process, achieved direct contact with and adhered to the fiber. This could occur by contact between a soil particle and fiber, both of which have been stripped temporarily of protecting oil layers by solubilization. It might also occur as a kinetic effect, whereby soil particles, under the influence of agitation and Brownian motion, pierce the protective oil layers and sorbed layers occasionally, and contact the fiber surfaces.

The ability of carboxymethylcellulose to prevent redeposition of soil may be ascribed to its sorption as a protective layer at the fiber surfaces. This appears more logical than ascribing it to an emulsifying or stabilizing effect on suspended soil. Unpublished data in our files show that 5% of carboxymethylcellulose in a synthetic detergent does not measurably increase the ability of the detergent to emulsify and suspend a standard oiled umber soil and yet is highly effective in preventing soil redeposition.

Forces Controlling Direct Cloth-Soil Adhesion

Mechanical Forces. Loosely held dirt should be the easiest to remove. It can be visualized as penetrating the interyarn capillary system of the fabric. The amount which can penetrate in this way will depend on the closeness of the weave, the type of weave, and the nature of the fabric in terms of its resilience. A closely woven fabric will hold less dirt mechanically than one having an open weave; a smoothly woven fabric will hold less dirt than one having a rough or knobby weave; a relatively non-resilient fiber such as cotton will entrap less dirt than a resilient fiber, such as protein.

Since this soil is held only mechanically, much of it can be removed by mechanical force in terms of agitation and the pounding action of the water in the laundry wheel or household washing machine. Such mechanical removal is a significant part of the cleansing process, corrected for in laboratory detergent evaluation by a control run with plain water. In a typical run in 15-grain water with 0.3% coconut-tallow soap the cleansing in terms of brightness recovery was 40% mechanical and 60% due to the soap.

Chemical Forces. Some soil is attached to the fibers by ionic or by hydrogen bonding. Such soil should be the most difficult to remove because of the strong forces which have to be broken down. This soil is typified by many classes of stains not completely removed by ordinary cleaning methods, but requiring special chemical agents for their removal or for changing the color of the stain to that of a colorless compound. For example, iron stains are removed by treatment with a reducing agent such as oxalic acid, to give a soluble, colorless ferrous compound.

Electrical Forces. Although natural soil ordinarily contains fatty or greasy matter, practical trials have shown that it is not necessary for solid dirt to be surrounded by oily layers in order to adhere to clothing. The particles have the power to adhere. For example, adhesion of lamp black or iron oxide to textile fabric can be much more difficult to overcome than that of fatty substances (10). Undoubtedly electrostatic force constitutes one of the important factors in the direct adhesion of soil to fabrics.

The nature of the charge on a substance can be established by cataphoresis. Cellulose and cellulosic materials are negatively charged (17). Silk and wool are essentially protein materials, the former made up of fibroins, the latter of keratin. The lower isoelectric range for silk fibroins is pH 2.1-5.1, for wool 3.4-4.8 (19). Above pH 5.1 silk would migrate to the anode since it is negatively charged; similarly above pH 4.8 wool is negatively charged. Under the conditions of household and laundry washing all of the fabrics, cellulosic, silk, and wool, are negatively charged. This is because ordinary washing solutions are either alkaline or approximately neutral.

When synthetic detergents are used for washing, this is sometimes carried out in the neutral range, sometimes in an alkaline medium. Soap solution is necessarily alkaline due to hydrolysis. In dilute solution pure tallow soap gives a pH of about 10.2. When built with alkaline salts, the pH is usually brought up to at least 10.7. This alkalinity will affect the soil in the wash liquid and the fabric. The further the solution departs from the isoelectric point, the greater is the negative charge which the proteins carry.

The soil present on textiles is chiefly negatively charged (4). Cataphoretic experiments show that carbon in plain water is uncharged; but in alkaline solution it migrated to the cathode and is positively charged (16). Finely divided particles of iron oxide are also positively charged (4). This suggests that soil containing carbon and iron rust is positively charged under some conditions and therefore can be attracted to the fabric carrying a negative charge.

A simpler method than cataphoresis is available for the study of colloidal systems. Filter paper, like other forms of cellulose, is negatively charged. Because of this charge it may be employed to distinguish qualitatively between positively and negatively charged colloidal systems. A strip of filter paper is dipped into the test solution. If the hydrosol is positive, a little will be sucked up before sorption of the particles takes place, after which only the dispersion medium rises in the strip of paper. On the other hand, a negative hydrosol is sucked up by the paper without separation of the phases. Addition of a protective colloid to the positive hydrosol will permit this also to be sucked up unaltered (10).

The application of electrostatic forces is illustrated by the sorption of soap on fabrics. When different types of fabric were immersed for 48 hours in 0.5% solution of potassium olive-oil soap, varying amounts of the latter were sorbed as shown in Table IV (18).

TABLE IV

Per Cent by Weight of Soap Sorbed in Terms of Fatty Acids

	Fatty acid sorbed by the cloth in weight %
Wool serge	3.6
Spun silk yarn	1.8
Cotton cambric	0.4

The figures represent the percentage of soap sorbed by weight on the cloth; the soap was recovered as fatty acid. The much larger proportion of soap sorbed by wool is probably due to both the large surface area of the wool fibers and the greater intensity of the negative charge on the fabric. When the same sample of wool material had been drained and rinsed in cold water, it still had 0.8% of soap sorbed on the cloth.

In a study by the British Research Association for the Woolen and Worsted Industries of the sorption of neutral sodium oleate, the wool was immersed for two hours in different concentrations of the soap solution with agitation from time to time (3). The amount of oleic acid sorbed per 100 grams of wool decreased sharply to a minimum at 0.04-0.06 *N* in terms of the original normality of the soap solution, then increased gradually. This minimum is so close to the concentration of oleate solution exhibiting minimum conductivity as to suggest that the amount of oleic acid sorbed by the wool is governed by the aggregation of the soap molecules. When they are crystalloid and therefore small, they can diffuse into the wool fibers; when they are highly aggregated and therefore large, they can diffuse into the wool only with difficulty.

In contrast to the sorption of the oleic-acid radical of the soap molecule, more sodium hydroxide or sodium ions are sorbed from the concentrated solutions than from the more dilute solutions of the soap. For example, 1.2 molecules of sodium hydroxide per molecule of oleic acid are sorbed from 0.005 *N* solution while 13.6 molecules of sodium hydroxide per molecule of oleic acid are sorbed from 0.165 *N* solution. These results show that wool sorbs almost equal numbers of sodium and oleate ions from dilute solutions of sodium oleate but that it can sorb only sodium ions freely from concentrated solutions. In dilute solutions one can picture the sodium oleate molecule as being sorbed with the sodium attached to the fiber and the oleate end sticking out into the solution. In more concentrated solutions the sodium ions would still be strongly attracted to the fiber, but the large micellar structure of the colloidal system would prevent its strong attachment to the layer of sodium ions.

In a recent summary of published work on the sorption of detergents by textile fibers (6) Harris concludes that cotton is relatively inactive as sorbent for anionic and nonionic agents from water solution, presumably because of its lack of chemically reactive groups. On the other hand, it sorbs cationic agents strongly. Wool, being more reactive, sorbs surface-active agents much more strongly; the degree depends on such factors as pH, temperature, concentration, and the specific surface-active agent. Nonionic agents do not seem to be sorbed as strongly as anionic agents.

Degree of Polarity of Fabric and Soil. A factor in sorption and retention of soil by fabric is the nonpolar nature of the fabric and of soil. Ordinarily fabrics are somewhat nonpolar, in part because of innumerable tiny air pockets. The number of these would vary with the weave and with the nature of the fiber. Since oil is strongly nonpolar, this may account for the light coating of oil present on used fabrics. The two nonpolar substances are compatible. Oil may be expected to penetrate into the inter-fiber capillary system formed by the closely grouped individual fibrils. The average radius of the pores in the inter-fiber capillaries is much smaller than in the inter-yarn system of fabrics.

In considering the sorption of soil on fabrics and the later wetting of the fabric in the initial phase of the detergent process, it is necessary to consider displacement of air from the capillary spaces. This surface wetting may be slow, particularly if the fibers are appreciably nonpolar. The soiled capillaries will generally be nonpolar and will have appreciable contact angles against water. The inter-fiber capillaries offer the greatest resistance to complete penetration; it is within these fine capillaries that the ingrained and most difficultly removed dirt resides. The ease of penetration is probably related to the resilience of the fibrils. Protein is highly resilient. This may be due in part to the disulfide linkages of keratin, which are easily split to form sulfide groups. Cellulose, on the other hand, is much less resilient because of the hydrogen bonding between the carbon chains. Owing to the uneven degree of soiling, some areas will be penetrated by water or a detergent solution more rapidly than others. Also it is possible for air-locks to be formed within the fabric, which can only be displaced by a mechanical squeezing action.

Soil Adhesion by Oil Bonding

To a large extent the adhesion of soil to fabric is simply the adhesion of oil to fabric. This is true because much soil is simply oily matter or, where it is solid particles, is attached to the fabric by oil films and can be removed by breaking those oil films. Natural oils would always contain some mildly surface-active materials, such as fatty acids, higher alcohols, etc. Sorption of such material at the fiber-oil and soil-oil interfaces can be expected. Thus the soil particle would not actually contact the fiber, just as two lubricated metal surfaces do not actually contact each other.

The mechanism of adhesion of oil thus merits special consideration. However much of the obstinate greying of fabrics which have been washed repeatedly is probably due to direct soil-fabric bonds. Such soil is extremely difficult to remove. The oily films which attach ordinary soil to fabric are probably highly desirable since they are broken by proper washing methods, and the solid soil is then removed by a type of flotation process, in which oil takes the place of air bubbles. Removal of soil in this way is properly called emulsification. It requires only the breaking of oil-oil linkages. An extremely thin film of oil remains coating the fibers, but all solid particles can be removed along with their oily coatings. For all practical purposes the fabric is then clean.

The work required for removing oil in this way is measured by the interfacial tension of the oil against the detergent solution. Thus the effect of the detergent in lowering tension at that interface can be very important. The viscosity of the oil is also important. Thermodynamically, no more work is needed to create one square centimeter of oil-water interface with a viscous oil than with a mobile one, provided both show the same interfacial tensions. In fact, however, the viscous oil is removed more slowly.

An alternative method of soil-removal is by displacement of oil films. The detergent wets the fiber preferentially, and oil with its solid particles is simply stripped off. One of the fundamental problems of detergent chemistry is establishing the roles of these two methods of soil removal under various conditions.

Two of the authors (13) have demonstrated by a new method for measurement of preferential wetting that a detergent need not increase the tendency of water to displace oil from fiber surfaces. Indeed, under some circumstances, synthetic detergents and soaps can decrease the rate at which oils are displaced from fiber surfaces. Molecularly dehydrated phosphates are very effective in accelerating displacement of oil by water. If to a solution of such a phosphate a suitable synthetic detergent is added, the rate of displacement decreases markedly, yet detergency is improved. This does not mean that complete displacement of oil is not a useful mechanism in detergency, but simply that it is not the only mechanism. Splitting of oil-oil bonds is important, and the synthetic detergent favors this by lowering interfacial tension radically. Deflocculation and stabilization of loosened soil particles so that they are not likely to reattach themselves to the fibers is also of great importance, especially during the rinsing operation.

Adhesion of oil to fabric can be due to physical and chemical mechanisms which, regardless of their details, may be lumped together for thermodynamic treatment. Wetting tendency can be expressed as a mathematical function of surface tension and contact angle. It is important to note that there are three different types of wetting expressible by three different functions, thus

Adhesional wetting	$W_a = S_1(\cos\theta + 1)$
Capillary wetting	$W_c = S_1\cos\theta$
Spreading wetting	$W_s = S_1(\cos\theta - 1)$,

where S_1 = the surface tension of the liquid and θ = the contact angle of the liquid on the solid surface. These formulas apply when θ has a finite value. However, when θ becomes zero, cos θ must be replaced by K which can be equal to or greater than 1.

Adhesional wetting is a measure of the tendency of a liquid to adhere to a solid surface and resist displacement. Capillary wetting measures the tendency of a liquid to penetrate into capillary spaces in a solid. Spreading wetting measures tendency of a liquid to spread out as a thin film over a solid surface.

Adhesional wetting becomes zero when θ becomes 180°. In practice no such case has been encountered; hence all liquids show positive adhesional wetting for all solids. It follows that once oil has come in contact with a fiber surface, it will adhere, and a definite amount of work must be done to remove it. That work can be physical, or chemical, or both.

Capillary wetting is positive when θ is less than 90° and negative when θ is greater than 90°. The test is simple. A piece of fabric is dipped in the liquid. If θ is less than 90°, liquid will rise through the cloth by capillary action, else it will not. Ordinary oils on ordinary fabrics show contact angles under 90°, and hence the oils will penetrate into the capillary spaces among and perhaps even within the fibers.

The rate of penetration of a liquid into a capillary system depends not only on wetting tendency $S_1\cos\theta$, but also on the viscosity of the liquid and the diameter of the capillaries. The rate is

$$\frac{dl}{dt} = \frac{r \cdot S_1\cos\theta}{4\eta l}$$

where r = radius of capillary
l = length of liquid column already in capillary
t = time
η = viscosity
S_1 = surface tension of the liquid
θ = contact angle of the liquid on the capillary surface.

Assume a capillary of radius 0.001 cm., with a column of liquid 0.01 cm. long already present in the capillary. Suppose the liquid to have a viscosity of 1 poise, contact angle of zero, and surface tension of 40 dynes/cm. Then the rate of penetration would be $\frac{(0.001)(40)(1)}{4(1)(0.01)} = 0.1$ cm./sec. Suppose however that the oil is very viscous, 1,000 poises, and that the radius of the capillary is of colloidal dimensions, say 0.000001 cm. Now the rate of penetration will be only 0.0000001 cm. per second or about 1 centimeter in 116 days. Thus capillaries between fibers will probably be filled in seconds or minutes while submicroscopic capillaries may require weeks or months, particularly if the oil is of high viscosity.

Naturally the same applies to soil removal. When preferential wetting conditions are favorable, oil held at the fiber surface or in large capillaries may be removed readily while oil trapped in small capillaries would require a much longer time. This is undoubtedly one mechanism of soil retention. It may be called capillary entrapment. The soil is removable in theory, but the time requirement is outside of practical limits. The longer the fabric has remained in contact with oil or oily soil, the greater will be the penetration into fine capillaries, and the more difficult will be removal of that oil.

Two of the authors have shown in a recent paper (12) that a minor percentage of fatty acid can increase radically the preferential wetting of steel by mineral oil. The mechanism is oriented sorption of the fatty acid by the solid surface, whereby the surface being wet becomes, in effect, a layer of outward-pointing hydrocarbon chains. Cation-active agents have a similar effect on glass and cellulose surfaces. The fundamental mechanisms of such phenomena are based on the tendency of polar-nonpolar molecules to sorb in an oriented manner and thus alter surface characteristics. Such sorption is undoubtedly due to electrical forces rather than Van Der Waal's forces. It follows that a very small percentage of a suitable third substance can serve to attach soil to fabric much more firmly.

Although the amount of oil present may be small, so that the large capillaries are not completely filled, the oil will nevertheless pass slowly into the finest capillaries. This is due to the fact that the capillary attractive force is $2S_1\cos\theta/r$ so that the attractive force is greatest in the smallest capillaries. Of course, only the finest particles of solid soil could accompany the oil into submicroscopic capillaries.

There is abundant evidence in the literature that soil becomes set and thus more difficult to wash out as the soiled cloth ages. This is particularly true when the oily fraction of the soil is highly unsaturated. Setting of soil in this way is favored by the presence of moisture and by high temperature.

One explanation appears to be polymerization of the unsaturated oils, whereby the oils become more viscous or even solid. The oily coating, with its entrapped particles of solid soil, would thus lock into inter- or intra-fibrular pores and cracks. A second mechanism is chemical linkage of the unsaturated bonds in the oil to active groups in the fiber. In that connection it should be noted that conjugated double bonds are very effective in linking dye molecules to fibers. A third factor, which unquestionably accounts for some part of the effect, is the tendency of liquids with positive capillary wetting to move into the smallest capillaries, as discussed earlier.

Soil Removal and Its Measurement

The relative importance of these mechanisms is a question of considerable practical importance. Thus if entrapment in crevices is a major factor, smoothing out the fibers should reduce soil retention. That this factor is of some importance is indicated by the relative ease of removing soil from the smooth fibers of regenerated cellulose, rayon, as distinguished from the irregular, curled fibers of natural cotton. On the other hand, the chemical addition theory suggests the possibility of altering the fiber by chemical or physical treatment to eliminate reactive surface groups and thus aiding removal of subsequently attached soil. One advantage would be reduced cost of laundering. Another, and probably a greater one, would be increased lifetime of the fabric because of the less vigorous washing and bleaching which would be required.

Appreciable amounts of foreign matter may be present in fabrics without constituting a soil. Indeed starch and other sizings are added to improve the feel and appearance of many types of cloth. Insofar as dry, solid soils are concerned, they are objectionable only if they are present in excessive amounts or if they differ markedly from the fabric in color. The extreme and also the most common example of that is black soil on white cotton and linen fabrics. The amount of soiling, from a practical point of view, is the extent to which the fabric is darkened. If, due to the small amount of soil present, or to the lightness in color of the soil, no darkening is visible, the fabric will usually be called clean.

It is common to report washing test results in terms of the per cent brightness regain on a standard soiled cloth. This is defined as

$$P = \frac{W - S}{C - S} \times 100$$

where W = reflectance of washed cloth
S = reflectance of soiled cloth before washing
C = reflectance of clean, unsoiled cloth.

The objection may be raised that this percentage is not the percentage of soil removed. It could not be unless there were a linear relation between amount of soil and reflectance. Nevertheless, for many purposes, P is a very useful concept since it indicates the result of washing in terms of the practical result, whitening of the fabric.

Attempts have been made in the literature to derive a mathematical relationship between amount of soil and reflectance (1, 20). While the data presented are of very considerable interest, the relations proposed are not considered valid. The authors of the present paper have derived a mathematical relationship based on both published data and unpublished work done at our laboratories. This will be published in the near future. However certain data calculated are presented in Table V. Suppose a piece of clean white cloth to have a reflectance of 84%, which is about normal. Let us further assume that one unit of soil applied to this fabric lowers its reflectance to 83. Table V shows the amounts of soil required to

TABLE V

Soil Units as Related to Reflectance

Reflectance	Lowering in Reflectance	Soil Required
%	%	*units*
84	0	0
83	1	1
82	2	2.83
79	5	11.7
74	10	40.6
64	20	170
44	40	1,200
24	60	6,820
14	70	20,600

achieve still lower reflectances, ranging from 82 to 14. Thus it will be seen that for very light soiling, 1 or 2 percentage units, the drop in reflectance is roughly proportional to the amount of soil, but that as soiling becomes heavier, more and more soil is required per unit of brightness loss. If a standard soiled cloth has a reflectance of 24%—and this is not unusually low—and its reflectance is raised to 64% after washing, its percentage brightness increase is $\frac{64-24}{84-24}.100$ or 67%. However the per cent soil removal is 100 — 170/6820 or 97.5%. So the difference between good washing performance and poor performance often depends on the effectiveness with which the last stubborn traces of soil are removed.

Conclusions

A great deal remains to be done in the way of studying the soils which are encountered commonly and in determining the methods by which they attach to fabric fibers and other bases. Such studies are fundamental to the development of a true science of detergency. At present it would be incorrect to say that detergency is on a scientific basis in the same sense as, say oil refining or soap manufacture.

There is a considerable amount of basic knowledge as to the general mechanisms by which soils are attached and by which they can be detached. Unfortunately there has been very little study of the ways in which these mechanisms operate, of which ones predominate, and of the specific factors involved in the attachment of individual representative soil types to particular fabric types. Such studies would be of the greatest possible value in developing a true science of detergency.

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ABSTRACTS . . . . Don Whyte, Editor

• Oils and Fats

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CRYSTAL STRUCTURE OF SILVER SALTS OF FATTY ACIDS. V. Vand, A. Aitken, and R. K. Campbell (Lever Bros. & Unilever Ltd., Port Sunlight, Cheshire). *Acta Cryst. 2,* 398-403(1949). Seven silver salts of even-numbered *n*-fatty acids were investigated by X-rays at 20 and 78°. Their unit cells which were determined from powder photographs proved to be triclinic with 2 molecules of silversalt per unit cell. Changes of the unit-cell dimensions with temperatures have been observed. A packing of the molecules in the unit cell was suggested.

AMIDES OF SATURATED ALIPHATIC ACIDS. AN X-RAY DIFFRACTION STUDY. D. H. Wurz and N. E. Sharples. *Anal. Chem. 21,* 1446-8(1949). X-ray diffraction data for the amides of the saturated aliphatic acids (C_1 to C_{14}) are presented. Isostructuralism among the even members and also among the odd members of the series above C_8 is shown.

STUDY ON THE EVOLUTION OF THE PEROXIDES FORMED DURING THE OXIDATION OF FATS. M. Loury and M. T. Mellier. *Oleagineux 4,* 665-8(1949). The methyl esters of the liquid fractions of palm oil absorbed more than twice as much oxygen from an atmosphere of pure oxygen than from air. The changes in peroxide value on autoxidation at 40, 80, and 105° are tabulated and plotted.

RELATIONS BETWEEN THE OXIDATION OF UNSATURATED GLYCERIDES AND THEIR ABSORPTION IN THE ULTRAVIOLET. A. Chevallier, S. Manuel, and C. Burg. *Arch. sci. physiol. 2,* 329-59, 358-60(1948). A 1% solution of guinea-pig subcutaneous fat (I) in petroleum ether has a relatively level absorption spectrum from 3000 to 2600 Å. and a steadily rising optical density down to 2300 Å. The absorption at 2400 Å. increases linearly with time of exposure to light, but if oxygen is excluded, the absorption change is negligible. This effect is not shown by the unsaponifiable matter of the fat. Triolein (II) kept in the dark shows a rise in absorption for 48 hours, then a descent until 96 hours elapses, followed by a leveling off. (The possibility of contamination with esters of linoleic acid was not excluded.) The onset of the rise can be delayed 96 hours by restricting the access of the II to air. This effect is less manifest with lightly oxidized II. Oxidation of II produces a product with a strong ultraviolet absorption, and this in turn decomposes into a product with less absorption. (*Chem. Abs. 43,* 9091-2.)

PATENTS

PURIFICATION OF OLEIC ACID. C. G. Goebel (Emery Inds., Inc.). *U. S. 2,482,760.* Oleic acid containing polyunsaturated acids is refined by subjecting it to polymerizing conditions and then distilling pure oleic acid from the polymerized polyunsaturated acids.

FATTY ACIDS AND GLYCERINE FROM FATS. W. M. Leaders (Swift & Co.). *U. S. 2,489,713.* A process for the manufacture of fatty acids and glycerine from fats comprises splitting the fat in the presence of water into a mixture of glycerine and fatty acids of